Controlled Polymerization of Alkyl Vinyl Ethers via 'Covalent' Propagating Species

by

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(ABSTRACT)

The study of the polymerization of alkyl vinyl ethers initiated by HI/I_2 catalyst is directed into two areas: the kinetics of the polymerization and the strategy of amine functionalized prepolymer synthesis.

The polymerization reactions show living behavior in nonpolar solvents at low temperatures. The observed rate of polymerization under reaction conditions is linearly dependent on the initial concentration of hydrogen iodide and iodine, respectively. However, the monomer concentration does not influence the rate of polymerization(apparent zero order). Two possible reaction schemes are proposed from the observed rate equation and attempts are made to distinguish them by using UV/visible spectroscopy and carbon-13 NMR spectroscopy. In both schemes a reversible interaction between a monomer and an iodine molecule is postulated as a necessary elemental reaction to fit the observed expression for the rate of polymerization. From spectroscopic analysis results, the interaction between the iodide compound(chain end) and the iodine molecule seems to be very weak compared to the interaction between the monomer and the iodine molecule.

A synthetic strategy for amine functionalized prepolymer synthesis has been developed via a series of model reactions. Incorporation of a styrenic monomer at the propagating chain end of living poly(alkyl vinyl ethers) provides a convenient intermediate synthesis of a relatively stable amine functionalized prepolymer. Proper selection

of substituents at the styrenic monomer optimizes the cross addition reaction and amination reactions. Linear alkylamines with lower carbon numbers are used in the amination reaction in order to promote the nucleophilic substitution reaction and to minimize possible elimination reactions. A series of amine functionalized oligomers are synthesized by employing the synthetic strategy in combination with the previous kinetic result of the homopolymerization. For oligomers, incorporation of a few units of ethyl vinyl ethers at the chain end facilitates the cross addition reaction. Synthesized amines are characterized by various spectroscopic methods. Then, titrated molecular weights show good agreement with their theoretical molecular weights in several cases.

Dedication

TO MY PARENTS

AND TO MY WIFE

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Chapter I

Introduction

Ionic polymerization includes important branches of polymerization processes such as anionic and cationic polymerizations. Many polarizable monomers are prime candidates for ionic polymerization. Polymerizations initiated by coordination compounds and solid metals or metal oxides are usually also ionic in nature. These are termed stereospecific or coordination polymerizations and have great importance in the commercial utilization of less polarizable monomers such as ethylene or propylene.

Compared to radical polymerization a smaller number of carbon-carbon double bond containing monomers undergo ionic polymerization. But ionic polymerizations are indispensable in the polymerization of monomers which cannot be polymerized by other means, including many monomers with carbon-carbon double bonds and almost all cyclic monomers.

Many ionic polymerizations are not well understood. The nature of the active chain end is often not clear because many side reactions accompany these polymerizations. The use of heterogeneous inorganic initiators also clouds the understanding. Extreme

sensitivity to the presence of small concentrations of impurities and other adventitious materials is another of the characteristics which make understanding and practical application difficult.

For many anionic polymerizations and some cationic polymerizations, side reactions such as termination or transfer steps are not involved in polymerizations if the polymerization systems are clean and impurity free. Thus a polymerization reaction can be dealt with by initiation and propagation steps only. These polymerizations are referred to as "living" polymerizations[1]. The initial charge ratio of monomer to initiator controls molecular weight and molecular weight distribution well in living polymerization provided the rate of initiation is much faster than that of propagation. Living ionic polymerization can be referred to as, or included in, 'controlled' polymerization which generally means polymerization in which the structure of the polymer can be controlled. One of the biggest advantages of ionic polymerization lies in the presence of this living polymerization.

When a living polymerization is initiated by a functional initiator or terminated by a compound with a functional group, the formed polymer becomes a functionally-terminated prepolymer, very important in the structural design of polymer molecules[2-3]. For example, the functional group in the prepolymer can be reacted further with monomers to generate graft copolymers or can be converted into block copolymers by reaction with other living polymers or prepolymers. In the preparation of functionally-terminated prepolymers living polymerization has played a great role. The preparation of a well-defined functionally-terminated prepolymer depends largely on ionic living polymerizations.

Ionic polymerizations have many very similar characteristics in their propagation reactions. Both anionic and cationic polymerizations depend on the formation and propagation of ionic species, negative in one case and positive in the other. For both

cases, gegenions(counterions) are present in the polymerization system in order to meet the requirement of electroneutrality. Thus the propagating species for a polymerization system ranges from the extreme of a completely covalent species to one of a completely free or highly solvated ion, depending on the degree of dissociation between the active chain end and the the gegenion[4]. Intermediate species include the tightly bound or contact ion pair, and the solvent-separated or loose ion pair. The above propagating species for a given polymerization system can exist in equilibrium, and the direction of the equilibrium can be shifted by the reaction medium, temperature, and gegenion. The nature of the solvent has an especially large effect in ionic polymerizations by altering the identities and relative concentrations of propagating species present.

Since free ions are generally more reactive than ion pairs in a polymerization reaction[5], the degree of dissociation of an active chain end and its equilibrium are very important to the rate of polymerization. This can be related further to the possibility of side reactions. When a polymerization proceeds via free ionic species, some polymerization parameters such as solvent polarity and reaction temperature have to be regulated in order to make the systems living. In other words, a polymerization system could become a living system if the nature of the propagating species is altered to reduce its reactivity.

Many polymerization systems in anionic polymerization undergo living anionic polymerization due to the enhanced stability of the carbanion relative to carbocationic intermediates. However, for some polymerization systems fully dissociated carbanionic intermediates are too reactive to yield living polymerizations. In order to direct a polymerization reaction toward living polymerization, therefore, the polarity of the solvent and its reaction temperature are usually decreased.

But this methodology of polymerization via ionic intermediates has certain limitations for some monomers containing side groups vulnerable to the attacks of

carbanions[6]. With these monomers the formation of living polymerization has been only partly successful with conventional ionic propagating species. To circumvent this problem a slightly different type of polymerization method in which polymerization proceeds via a 'non-ionic' intermediate has to be applied. A good example is the polymerization of methacrylate monomers via group transfer polymerization[7] where the polymerization occurs via a 'covalent' intermediate.

Some cationic polymerizations of heterocyclic monomers have been known as living systems, but the cationic living polymerizations of monomers with carbon-carbon double bond are very rare due to the high reactivity of the carbocationic species toward side reactions. Chain transfer reactions are usually predominant in carbocationic polymerization[8] so that control of molecular weight and molecular weight distribution is extremely difficult. Various attempts to overcome this problem have been made.

One example is the initiator transfer polymerization[9] in which the chain transfer reaction is utilized in the preparation of telechelic polymers. This polymerization is different from living polymerization strictly defined, but it gives hope for carbocationic polymerization controllability because the molecular weight and functionality can be controlled reasonably well.

Major efforts, however, have been made by utilizing less reactive propagating species. A good example is the polymerization via a 'covalent' propagating species, where a mixed catalyst system is applied. Examples of the mixed catalyst system includes hydrogen iodide/iodine[10], esters/Lewis acids[11-12], and esters/titanium tetrachloride[13]. Polymerizations with these catalyst systems have been proven successful in the achievement of living polymerizations. These polymerization achievements result largely from the idea of pseudocationic polymerization[14] proposed two decades ago from the polymerization of styrene initiated by perchloric acid. Though pseudocationic

polymerization is not living, the idea of covalent propagating species is the common bases of the recent trend of polymerization where mixed catalyst systems are applied.

Besides this approach utilizing covalent propagating species, another approach utilizing less reactive propagating species by modification of the nature of the active chain end with a second component of solvent containing ethers[15] has been tried. But all these approaches are so new that more development and investigation is needed in order to expand the horizon of living carbocationic polymerization research.

Alkyl vinyl ethers are highly reactive monomers toward cationic polymerization. During polymerization the oxygen atom adjacent to the carbocation stabilizes the carbocationic intermediates via resonance. Due to the high reactivity of alkyl vinyl ethers compared to that of styrenic or other monomers they have often been used as major monomeric species in many kinetic investigations of cationic polymerization.

Recently polymerization of alkyl vinyl ethers has been initiated with mixed catalyst systems, and it has been found that living polymerizations occur. Polymerization by the hydrogen iodide/iodine initiation system[10] is especially interesting and has given great impetus to the development of cationic living polymerization.

The following review of the literature lays the foundation for the work discussed in this dissertation. It reviews controlled ionic polymerization in general and emphasizes polymerization via covalent propagating species, especially in cationic polymerization. First, the polymerization of alkyl vinyl ethers by a hydrogen iodide/iodine initiation system is studied via kinetic investigation in order to get more information on this relatively new, relatively unknown and controversial polymerization system. Then, various attempt to apply this polymerization in the preparation of functionally-terminated prepolymers will be presented. Living poly(oxazoline) synthesis and utilization in the preparation of block copolymers will be presented. Finally, various characterization

techniques for the confirmation of structures of starting materials and polymers will be presented throughout this research.

Chapter II

Review of Literature

A. Controlled Ionic Polymerization

1. Introduction

There are two major types of polymerization methods used to convert small mole-
cules into polymers. One is addition polymerization and the other is condensation
polymerization. Recent usage defines addition polymerization as chain growth or chain
reaction polymerization, and condensation polymerization as step growth or step re-
action polymerization. The major distinction between these two methods is a result of
differences in the kinetics of polymerization reactions.

In a chain growth polymerization, a vinyl or alkene monomer is transformed into
a long chain macromolecule via a chain reaction process. This process involves the ad-

dition of a monomer to an activated or initiated form of the monomer and involves a change in the bonding from an sp^2 to an sp^3 type bond. This process of chain polymerization is usually not spontaneous but rather must be catalyzed or initiated. For most monomer systems of this type, one can discern at least three individual steps in the overall process of polymerization: an initiation step; a propagation or growth step; and a termination step. The details of these three individual events are highly dependent on the exact mechanism of polymerization. The active intermediates produced may be categorized as either radicals, anions, cations, or coordinated species, depending especially on the electronic nature of the *transition state* of the polymerization.

It is often possible to avoid the termination step for some of these mechanistic processes. These systems are termed "living" polymerization[1] systems. In a living system, only the initiation and propagation steps are important. This in turn, permits prediction of number average molecular weight on the basis of the initial ratio of the monomer concentration to the initiator concentration. When the initiation reaction is much faster than the propagation reaction, the polymers produced may have a very narrow molecular weight distribution[16], as opposed to the much broader Gaussian type random distributions observed especially in step growth reactions.

Living polymerizations are often described as 'controlled' polymerizations because molecular weights, molecular weight distributions, etc. are predictable. Also 'controlled' polymerization is often used when the nature of the propagating species is regulated through reaction parameter changes in a polymerization.

Living polymerization has even been reported for several cases in radical polymerization[17-20] and many times in ionic or coordination polymerization[21]. Thus living polymerization has become very important because precise molecular structural design is quite feasible. Anionic polymerization is the earliest and perhaps most representative example of a living polymerization. Accordingly, this polymerization has be-

come a novel polymerization route to produce block copolymers. For monomers which can be polymerized anionically, many possible combinations of block copolymers have been reported.

However, there is a restricted number of available monomers which can undergo anionic polymerization. Scheme 1 shows a general criterion for the types of chain polymerization of a double bond[22]. Sometimes coordination polymerization is also included in the ionic polymerization category. The number of available monomers means that synthesizable polymeric materials are limited. Therefore, researchers are extending the concept of controlled polymerization to other monomers in order to meet the need for new materials. One good example is in the field of cationic polymerization where highly reactive carbocationic intermediates are not easily suited to controlled polymerization[23].

The traditional concept of 'free' carbocationic propagation has been modified by many workers by introducing several concepts such as inifer[9], dissociation suppression[24], transfer suppression[25], covalent bond activation[26], pseudocationic polymerization[14,27], etc. Essentially, the principal effort has been to alter the reactivity of a carbocationic propagating chain end.

By reducing the reactivity of a carbocationic intermediate, the reaction rate becomes slower and the nature of the intermediate(or propagating chain end) approaches that of a 'covalent' -like bond. Similarly, the reactivity of anionic and coordination intermediates can also be modified in order to better control the polymerization. Reactivity modification in anionic polymerization is usually attained by the proper selection of reaction media, temperature, and counterionic group. Thus, the nature of the bond in the propagating species can be shifted toward a more covalent-like nature in anionic or cationic polymerization, as shown in Scheme 2. The more covalent-like nature means that the orbital changes to a more 'filled-like' structure which more closely satisfies the

$$CH_2=C \overset{\displaystyle R}{\underset{\displaystyle R}{\Huge<}}$$
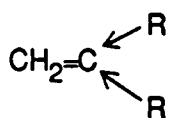
Inductive
or
Resonance

Cationic polymerization

$$CH_2=C \overset{\displaystyle R}{\underset{\displaystyle R}{\Huge<}}$$
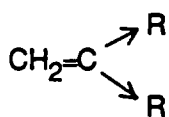
Inductive
or
Resonance

Anionic polymerization

Intermediate

Free radical polymerization

- Electron density at the double bond may determine whether a particular monomer polymerizes via anionic, cationic or free radical mechanism.

- Some monomers can polymerize via two or more routes.

Scheme 1. Types of chain polymerization[22].

$$C^- \, Y^+ \quad \longrightarrow \quad C\text{-}Y \quad \longleftarrow \quad C^+ \, Y^-$$

Anionic	Covalent	Carbocationic
sp^3	sp^3	sp^2
Octet structure	Octet structure	Non-octet structure
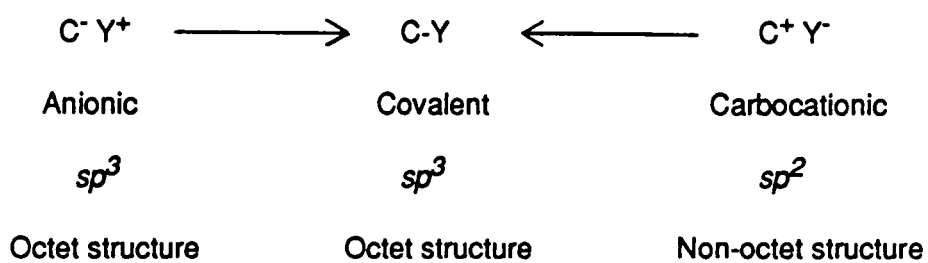
C : Propagating chain end - carbon.

Y : Counter group.

Scheme 2. Possible extremes in the nature of propagating chain end.

octet rule than, for example, the isolated carbocation does. Consequently, the stability changes as well as the reactivity.

In order to change the nature of the propagating chain end in an ionic polymerization, the easiest parameters to change are the reaction media and the temperature. Of course there are certain limits to the range of modification possible. On the other hand, a small change in the structure of a counter group may lead to a large difference in the nature of the propagating chain end and resultant polymerization behavior. Use of this method of modification is a recent trend in ionic polymerization researches as seen in group transfer polymerization[7], pseudocationic polymerization[14,27], HI/I_2 initiated polymerization[10,26], etc.

2. General Applicability of Ionic Polymerization

Ionic polymerization includes the typical elementary reaction steps of initiation, propagation, termination, and chain transfer - as in other chain polymerizations[28]. The above four steps are similar for both anionic and cationic polymerization but differences exist in each step, especially in the initiation and chain transfer steps. In this review, anionic polymerizations and cationic polymerizations are discussed separately and compared in each elementary reaction step.

a) Initiation Reaction

The fundamental process involved in any initiation reaction is the generation of an active site by the attack of an anion or cation on a monomer, which is capable of propagating the kinetic chain through further monomer addition steps.

1) **Anionic Polymerization:** Anionic initiators, broadly speaking, include all electron donors of varying base strengths. These include covalent or ionic metal amides such as sodium amide, lithium dialkylamides, alkoxides, hydroxides, cyanides, phosphines, amines, organometallic compounds such as n-butyl lithium and phenyl magnesium bromide, and alkali metals or alkali metal complexes. The required initiator type for a particular polymerization depends on the ease with which an anion can be formed from the monomer, which acts as an electron acceptor in anionic polymerizations.

Very strong nucleophiles such as the amide ion or alkyl carbanions[29] are required to polymerize hydrocarbon monomers, such as styrene and 1,3-butadiene which have relatively weak electron-withdrawing substituents. A nucleophile of medium strength such as 1,1-diphenylethyl lithium[30] can polymerize monomers within a relatively broad reactivity range. Weaker nucleophiles such as enolate or alkoxide ions can polymerize monomers, such as acrylonitrile and methyl methacrylate which have strong electron-withdrawing substituents. A monomer, such as methyl α-cyanoacrylate, with two such substituents can be polymerized with very mild nucleophiles such as Br^-, CN^-, amines, phosphines, and even with water[31].

The general relationship between the reactivity of an alkali metal initiator and that of a monomer has been qualitatively investigated[32] for specified monomers. The anionically polymerizable monomers may be classified into five reactivity groups(Table 1), wherein polymeric anions of those in the lower numbered group can initiate the polymerization of monomers in their own or higher numbered group, but not conversely. In that case then, styrene(group 1), methyl methacrylate(group 2), and acrylonitrile(group 4) can be chosen as probe monomers to examine initiator reactivity. Initiators are therefore divided(Table 2) into three categories according to their ability to initiate all three monomers(group 1), the last two(group 2), or only acrylonitrile(group

3). However this relationship excludes polymerization where the use of coordinating additives leads to the unusual reactivity of an initiator[34].

Two principal anionic processes[1,36] are nucleophilic attack on the monomer and electron transfer. The process of nucleophilic attack is the addition of a negatively charged entity to the monomer and involves mainly alkali metal alkyls, metal alkoxides, metal amides, and Grinard reagents. The general initiation process is:

$$Z\text{-}B \ + \ CH_2 = \underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}} \quad \rightarrow \quad B\text{-}CH_2\text{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}^- \ ^+Z \tag{1}$$
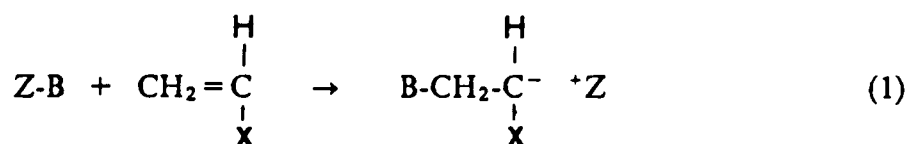
where the nucleophilic part of the initiator is denoted B and the gegenion is formed from the metal Z. X is pendant group. The group of electron transfer initiators includes alkali metals and complexes of these metals with aromatic hydrocarbons. The general reaction is:

$$Z \ + \ CH_2 = \underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}} \quad \rightarrow \quad \cdot CH_2\text{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}^- \ ^+Z \tag{2}$$
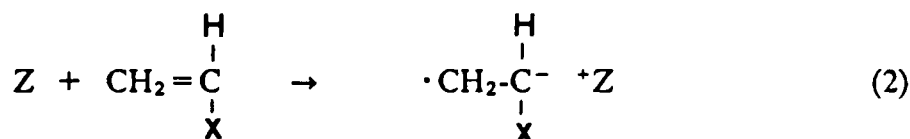
The formed radical-anion dimerizes to form a dicarbanion.

$$2 \ \cdot CH_2\text{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}^- \quad \rightarrow \quad ^-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\text{-}CH_2CH_2\text{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}^- \tag{3}$$
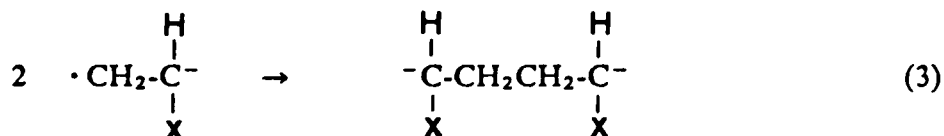
2) Cationic Polymerization: Cationic initiators are usually protonic acids, Lewis acids, and organic cationic salts. Unlike the anionic process, the actual initiation process is often preceded by a reversible reaction or series of reversible reactions between the ini-

Table 1. Relative Reactivities of Monomers[a]

Group	Monomers
1	Styrene, 2-methylstyrene, butadiene, isoprene, o- and p-halostyrene[b], 2- and 4-vinylpyridine, 1,2-dihydronaphthalene, tetraethylvinyl germanium, triethylvinyl tin
2	Acrylates, methacrylates
3	Ethylene oxide, ethylene sulfide, propylene sulfide, dimethyl ketone, formaldehyde
4	Acrylonitrile, methacrylonitrile, mono- and di-isocyanates, carbodiimides, N-substituted maleimides
5	Nitroethylene, nitropropene, cyanogen, vinylidene cyanide

[a] Data from [33].
[b] It has been subsequently reported that the p-bromostyrene does not polymerize styrene[35], possibly due to major side reactions.

Table 2. Relative Reactivities of Alkali Metal Initiators[a]

Group	Initiators
1	Metal, organometallic compound Monometal and dimetal adducts of aromatic hydrocarbons Dimetal adducts of aromatic carbonyl compounds, azomethines nitriles
2	Monometal adducts of aromatic carbonyl compounds, azomethines and nitriles Dimetal adducts of aromatic azo, azoxy and nitroso compounds
3	Monometal adducts of aromatic azo, azoxy and nitroso compounds Metal alkoxide

[a] Data from [32].

tiator and other species. The preinitiation reaction sequence may be quite complex and attainment of the equilibria involved is often slower than subsequent initiation or propagation reactions.

The general reaction between an olefin and a protonic acid HA can be written as:

$$H^+A^- + CH_2=\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}} \rightarrow CH_3\text{-}\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}}{}^+ \quad {}^-A \qquad (4)$$
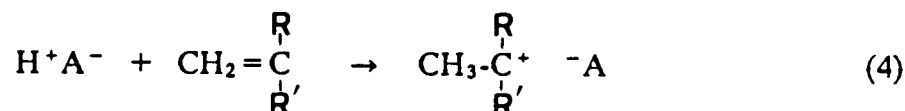
Acids such as H_2SO_4, $HClO_4$, and H_3PO_4 are better initiators than hydrogen halides because their anions are larger and less nucleophilic. If the anion A is a strong nucleophile, then it will react with the carbocation to form a nonpropagating covalent compound.

Initiation by proton addition is usually accomplished by interaction of a Lewis acid(*cocatalyst*) with a second compound(*catalyst*) that can donate a proton or carbenium ion to the monomer(*the old term 'cocatalyst' is now called 'catalyst,' and also 'catalyst' is called 'cocatalyst,' but still, old terminology is often used*). Lewis acids include halides and alkyl halides of Group III metals and of transition metals in which the *d* orbitals are incomplete. Compounds like BF_3, $SnCl_4$, $AlCl_3$, AlR_2Cl, $SbCl_5$, etc. are good examples. Typical catalysts are water, protonic acids, and alkyl halides.

The initiation process can be generalized as:

$$ZX_n + BA \overset{K}{\longrightarrow} [ZX_nB]^- A^+ \qquad (5)$$

$$[ZX_nB]^-A^+ + CH_2=\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}} \overset{k_i}{\longrightarrow} ACH_2\text{-}\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}}{}^+[ZX_nB]^- \qquad (6)$$
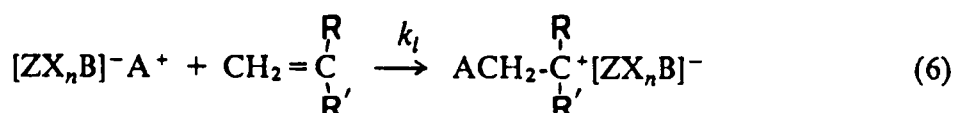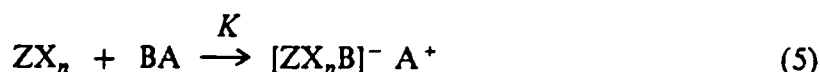
where ZX_n is a Lewis acid, BA is an ionizable cocatalyst. Z here is a metal, and X is generally a halogen or an organic entity. The activity of a catalyst - cocatalyst complex is dependent on its ability to donate a proton or cation to the monomer which, in turn, depends on the catalyst, cocatalyst, and monomer. The extent of formation of the catalyst - cocatalyst complex(i.e., the value of K in equation 5) and its rate of addition to monomer(i.e., the value of k_i in equation 6) generally increases with increasing acidity of the Lewis acid. Thus, the general order of activity of aluminum catalysts becomes: $AlCl_3$ > $AlRCl_2$ > AlR_2Cl > AlR_3[37]. The activity of the complex also increases with increasing acidity of the initiator, for example, hydrogen chloride > acetic acid > nitroethane > phenol > water > > methanol > acetone in the polymerization of isobutylene with $SnCl_4$[38].

Some organic cation salts can be isolated as crystalline solids. Examples of such initiators are hexachloroantimonate($SnCl_6^-$) salts of triphenyl methyl($(C_6H_5)_3C^+$) and cycloheptatrienyl($C_7H_7^+$) carbenium ions[39] (*According to recent conventions, the term 'carbenium' ion is used for trivalent trigonal sp^2 hybridized species, and 'carbonium' is used for pentavalent positively charged carbon ions[40]. Both species are called 'carbocation.' But still, the use of the new terminology is not widespread, and in many cases, 'carbonium' means 'carbocation.'*). The stability of carbenium ions is enhanced if the electron-deficient carbon is conjugated with olefin or aromatic groups, or with atoms with unshared electron pairs(O, N, S). These initiators are very similar to the catalyst-cocatalyst complex in equation 5, thus their initiation processes are fairly straightforward compared to the complicated equilibria that can exist in other systems. This simplifies the study of the kinetics of the propagation and other processes involved in cationic polymerization. Since these cations are stable, their use is limited to the initiation of more reactive monomers like N-vinyl carbazole and alkyl vinyl ethers[41].

b) Propagation

Monomers are consumed during the propagation reaction and the site of the reactive center changes, but the number of active centers does not change. The propagation reaction is probably the most fundamental of all the elementary reactions which comprise a polymerization process since it is the repetitive act which produces polymeric species. The rate of propagation is influenced by equilibria between various degrees of association of the active center and its gegenion. This will be reviewed in the next section.

The propagation reaction in anionic polymerizations, though complex, is better understood because chain transfer or termination reactions can often be minimized. Only initiation and propagation reactions are involved for many anionic polymerizations.

In contrast, cationic polymerizations usually display complex chain transfer reactions in their propagation reactions. The propagation reaction can be complicated by the occurrence of intramolecular rearrangement due to hydride($H:^-$) ion or carbanion($R:^-$) shifts in some cases. Such polymerizations are often referred to as isomerization -polymerizations[42]. The extent of rearrangement during cationic polymerization depends on the relative stabilities of the propagating and rearranged carbenium ions and on the relative rates of propagation and rearrangement.

c) Chain Transfer and Termination

Chain transfer reactions interrupt the growth of a polymer chain by terminating one chain and generating a new active center capable of adding more monomers. When

the chain transfer reaction occurs without generating a new active center, it essentially becomes a termination reaction. This distinction is ambiguous in many cases and depends upon the reactivity of the newly formed ionic species(or active center).

The newly formed ionic species cannot initiate polymerization in many anionic polymerizations. But the newly formed ionic species are active enough to reinitiate polymerization in many cationic polymerizations. This chain transfer reaction makes most cationic polymerizations more complicated.

1) Anionic Polymerization: As discussed earlier, many anionic polymerizations are rigorously clean systems and do not have termination or chain transfer reactions. Such systems are referred to as living systems. In these cases, termination occurs by impurities or deliberately added transfer agents such as water, methanol, carbon dioxide, and ethylene oxide. Newly formed ionic species(e.g. hydroxide ion) are usually not sufficiently nucleophilic to re-initiate polymerization, and the kinetic chain is broken as in equation 7. This method may be used to make functionally terminated prepolymers.

$$\sim CH_2\text{-}\overset{\overset{\displaystyle H}{|}}{\underset{\phi}{C}}:^- \quad + \quad HOR \quad \rightarrow \quad \sim CH_2\text{-}\underset{\phi}{CH} \quad + \quad RO^- \tag{7}$$
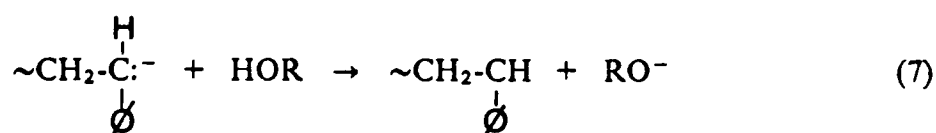
In the absence of terminating agents, the concentration of carbanion centers in a solution of living styrene decreases very slowly over a long period of time(day or weeks) by β-hydride elimination[43]. A propagating carbanion sodium salt will generate an unsaturated end group and a sodium hydride as indicated in equation 8. Sodium hydride is more than sufficiently reactive to reinitiate polymerization. However, termination of the kinetic chain occurs when the allylic hydrogen of the unsaturated end group in the

above equation is abstracted by a propagating carbanion to yield an unreactive 1,3-diphenylallyl anion.

$$\sim CH_2\text{-}\underset{\underset{\phi}{|}}{\overset{\overset{H}{|}}{C}}\text{:}^-Na^+ \quad \rightarrow \quad \sim CH_2CH\text{-}\underset{\phi}{\underset{|}{CH}}=\underset{\phi}{\underset{|}{CH}} \quad + \quad H\text{:}^-Na^+ \qquad (8)$$
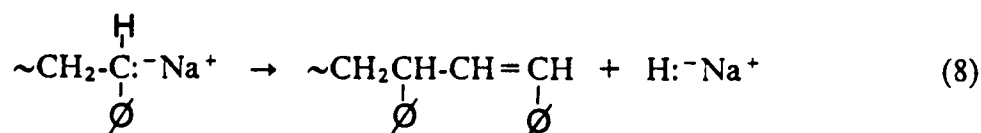
Anionic polymerizations of polar monomers, such as methyl methacrylate[MMA], methyl vinyl ketone, and acrylonitrile, are much more complicated than those of non-polar monomers. These monomers contain substituents that are reactive toward nucleophiles. In MMA, three different major side reactions are observed[6,36,44]. One example is the attack of an alkyl lithium initiator on the carbonyl of the monomer, converting the active alkyl lithium to a less active alkoxide initiator. This problem can be avoided to a large extent by using a less reactive initiator, for example, 1,1-diphenylhexyl lithium[30]. Lower reaction temperatures and more polar solvents favor normal propagation relative to the carbonyl side reaction. Polymerizations in vinyl ketones and acrylonitrile are also complicated by addition reactions of initiators and propagating nucleophiles to the ketone[6,45] or nitrile[46] groups.

2) Cationic Polymerization: Most reactions which terminate the growth of a propagating chain do not terminate the kinetic chain because a new propagating species is formed in the process. They are thus kinetically indistinguishable from propagation, but slight traces of impurities can still exert significant effects because of the high reactivity of the propagating species. In a wide variety of possible transfer reactions, some are general and apply to any monomer susceptible to attack from electrophilic reagents, while others are specific to certain monomers only.

Chain transfer to monomer is one of the most common chain-breaking reactions for many monomers. It usually involves transfer of a proton to a monomer molecule with the formation of terminal unsaturation in the polymer molecule.

$$\sim CH_2\text{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{}^+X^- \;+\; CH_2 = \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \;\rightarrow\; \sim CH = \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \;+\; CH_3\text{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{}^+X^- \qquad (9)$$
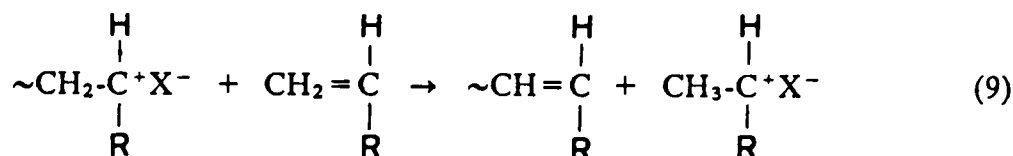
Another type of chain transfer to a monomer is a hydride ion abstraction from the monomer by the propagating species. This is a less likely mode of transfer compared to a proton transfer to a monomer due to the stability of carbenium ions.

Chain-breaking can also take place by spontaneous regeneration of protonic catalyst species.

$$\sim CH_2\text{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{}^+X^- \;\rightarrow\; \sim CH = \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} \;+\; M^+X^- \qquad (10)$$
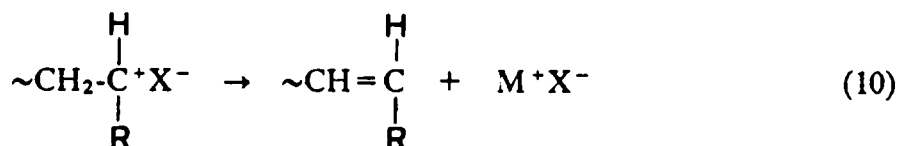
The ejected proton is a powerful electrophile and can readily add to another monomer molecule, initiating a new polymer chain. This type of termination is also referred to as a chain transfer to a gegenion.

Chain breaking by the combination of a propagating carbonium ion with a gegenion occurs, for example,

$$\sim CH_2\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^+ (BCl_3OH)^- \;\rightarrow\; \sim CH_2\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}Cl \;+\; BCl_2OH \qquad (11)$$
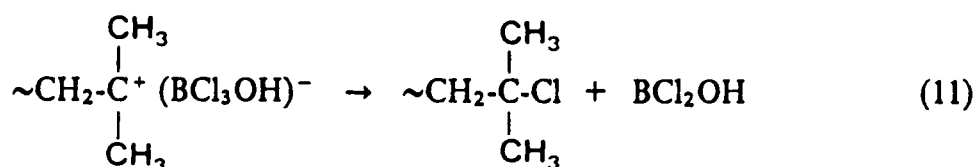
This combination differs from other modes of transfer in that a kinetic chain is usually terminated by the decrease of the initiator-coinitiator complex concentration. For example, termination in BCl_3 initiated polymerizations of isobutylene and styrene occurs almost exclusively by combination with chloride[47]. For BF_3 initiated polymerization, chain transfer to monomer is the major mode of termination with a minor contribution by combination with OH. The differences are explained by the order of bond strengths: B-F > B-O > B-Cl[48]. A similar reaction is envisaged in the polymerization of isobutylene by aluminum chloride catalysts[49], or in the polymerization of vinyl ethers by $SbCl_6^-$ salts[50]. When aluminum alkyls-alkyl halides, initiator-coinitiator systems are used, termination occurs by combination[37a-b,51], either by alkylation or hydridation, whenever the aluminum alkyls have β-hydrogens.

One or more other transfer reactions besides the chain-breaking reactions mentioned above may be important in any specific polymerization system. Backbiting reactions, which occur in the polymerization of styrene and most other aromatic monomers with the formation of a terminal indanyl structure[41a-b,52] and chain transfer to polymer in the polymerization of α-olefins such as propylene[53], are good examples. Various transfer agents such as solvents, impurities, or compounds deliberately added to the system, can also terminate the growing polymer chain by chain transfer.

3. Nature of the Active Intermediate

a) Free Ions and Ion Pairs

Ionic polymerizations involve successive insertions of monomers between a macromolecular ion(*macroion*) and a more or less tightly attached gegenion of an opposite charge. Electroneutrality demands that macroion and gegenion form an organic salt which may exist in several forms in the reaction medium. Depending on the distance between the charged particles, which in turn is determined by the intrinsic properties of the ions and experimental conditions, a continuous spectrum of ionicities exists("Winstein spectrum")[6,8,54]. If we represent the organic ionic species as M^+X^-, then several forms must be considered:

$$MX \ \rightleftharpoons \ M^+X^- \ \rightleftharpoons \ M^+/X^- \ \rightleftharpoons \ M^+//X^- \rightleftharpoons \ M^+ + X^- \quad (12)$$

covalent	contact	solvent	solvated	free
bonding	(tight)	separated	(loose)	ions
	ion pair	ion pair	ion pair	
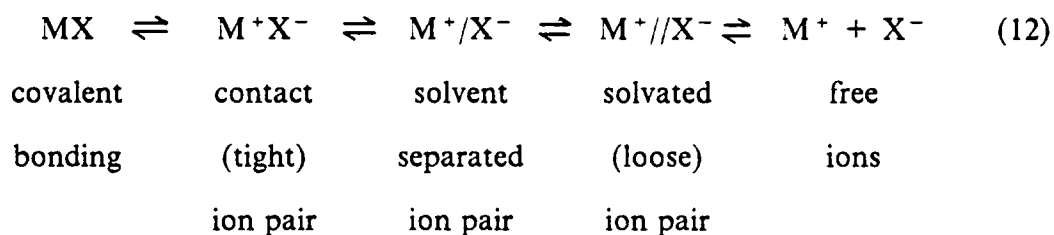
The form actually important in a given polymerization will depend on the natures of species M and X, the solvating ability of the medium, and the temperature. In general, greater separation of the the macroion and its gegenion leads to higher propagation rates. Steric control of the polymer microstructure is greater, however, when the macroion and the gegenion are associated. It is not unusual to find two of the above forms coexisting in significant quantities in a given polymerization. In general, more polar media favor loose ion pairs or free ions. Free ions will not coexist in hydrocarbon media where other equilibria may occur. Multiple ion clusters have been postulated to

occur in anionic polymerizations[55], particularly in hydrocarbon solvents. However the cationic polymerization literature lacks studies along these lines.

In polymerization reactions in solvents with a medium polarity, the concentration of contact ion pairs is often neglected because the concentration and reactivity of intimate ion pairs are negligible compared to those of solvated ion pairs. The equilibrium which exists between associated ions and free ions as in equation 13 has been studied much in the field of anionic polymerizations because the active species are stable, or *living*. Significant advances have been made in defining $k_p^{\pm}$ (rate constant of ion pair propagation), k_p^{-} (rate constant of free ion propagation), and dissociation constant Kd.

$$
\begin{array}{ccc}
& Kd & \\
M^{+}X^{-} & \rightleftharpoons & M^{+} \ + \ X^{-} \qquad (13) \\
k_p^{\pm} \Big\downarrow \text{monomer} & & \text{monomer} \Big\downarrow \ k_p^{+} \text{ or } k_p^{-} \\
\text{Polymer} & & \text{Polymer}
\end{array}
$$
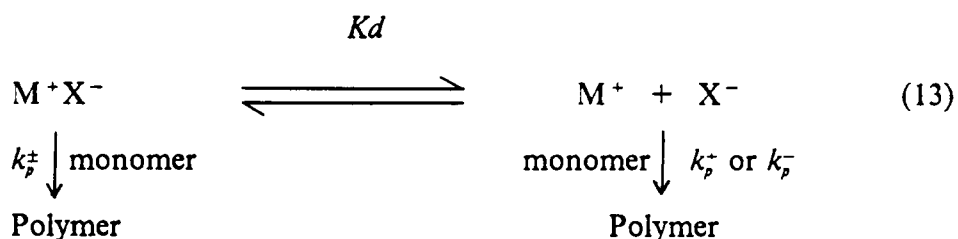
Only the Kd has been determined[56] by conductivity measurements in cationic polymerizations. The relatively high reactivity of the propagating species makes the determination of k_p^{+} and $k_p^{\pm}$ difficult in most cationic polymerizations.

b) Reactivity

The reactivity of ionic polymerization is generally dependent on charge separation of the propagating species, and is measured as the rate constant of propagation. The observed k_p (usually the apparent rate constant, k_p^{app}) in the above simplified reactions is composed of contributions from ion pairs and free ions, for example, in a cationic polymerization

$$k_p^{app} = \alpha k_p^+ + (1-\alpha)k_p^{\pm} \qquad (14)$$

where α is the degree of dissociation of ion pairs into free solvated ions and the k_p values are defined as in equation 13[57].

In solvent like CH_2Cl_2(dielectric constant 9.1) the k_p^+ values for cationic olefin polymerizations are of the order of $10^3 \sim 10^5$ l/mol.s. These values are similar to the k_p^- for anionic polymerizations with free ions. Typical k_p^- values in anionic polymerization are of the order of $10^4 \sim 10^5$ l/mol.s, and $k_p^{\pm}$ are $\sim 10^2$ l/mol.s. But the comparison is not strictly valid because the anionic reactions are carried out in solvents with relatively lower dielectric constants. In media of low polarity, however, the k_p^+ values could increase to the order of $10^6 \sim 10^9$ l/mol.s.

Carbenium ions are more reactive than carbanions under similar conditions due mainly to unfilled bonding orbital considerations. A carbenium ion has vacant bonding orbitals while the orbitals in the propagating carbanion and monomer are already filled. The formation of an anionic transition state requires the use of the antibonding orbitals of the monomer[28b].

c) Effect of Reaction Medium

The type of solvent suitable for ionic polymerization is limited to nonpolar solvents or aprotic polar solvents. Any tendency of the medium to interact with the initiator would jeopardize the chance of obtaining a reasonable concentration of active species. Even with formally acceptable solvents, care must be taken to ensure that no specific chemical interaction occurs, especially in cationic polymerization.

The reaction medium can affect polymerization by altering the relative concentrations of free ions and ion pairs and the type of ion pair present. If the dielectric constant of the medium is taken as a measure of its ability to solvate and thus stabilize ionic or polarized species, solvents can be classified broadly into three categories: nonpolar solvents(ε = 2~6), solvents of modest polarity(ε = 7~15), and polar solvents(ε > 15). Large increases in the rate and degree of polymerization are generally observed as one increases the dielectric constant[23,38,47,58]. The dielectric constant is only a general indication of the solvating power of a solvent. Specific solvation effects and polarizability are sometimes more important.

Although many solvent effects are well recognized and have been investigated in great detail, no quantitative theory is available to guide researchers in this area. Only qualitative or at best semiquantitative theories are available starting with the Born equation[59].

$$\Delta G = \frac{-z^2 e^2}{8\pi\varepsilon_0 a} \left[\frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_2}\right] \tag{15}$$

In this equation the change in free energy ΔG is determined by the radius a and charge z of the ion transferred from the gas phase(ε_1 = 1) into a solvent with a dielectric constant ε_2. Thus the energy of solvation of an ion increases with increasing ε_2 and is inversely proportional to a.

This equation is not accurate, however, because bulk dielectric constants are not valid in the immediate neighborhood of an ion. Correction of this equation has been tried by using an effective radius of the ion[60], but still it is extremely difficult to define what is meant by polarity of a solvent, because of the multiplicity of special effects that may operate and thus complicate or even completely obviate predictions derived from the above equation. Examples of special effects include distortion of the dielectric

continuum by placing a charged particle in it, mixed solvent and nonsolvent(monomer), solvent shell saturation, solvent shell reconstruction due to charged entities, solvent polarizability, geometry effects, aggregation effects, non-uniform charge distribution, and preferential solvation.

In anionic polymerization, the rate of polymerization is affected drastically by changing the polarity of the solvent. One example is the polymerization of styrene by sodium naphthalene($3x10^{-3}$ M) at 25°C[61] as in Table 3. The apparent propagation rate constant is increased by two and three orders of magnitude in tetrahydrofuran(THF) and 1,2-dimethoxyethane, respectively, compared to the rate constants in benzene or dioxane. The higher reaction rate in 1,2-dimethoxyethane compared to that in THF is due to a specific solvation effect of the ether group. The increased rate observed with increasing solvating power of the reaction medium is mainly due to the increased fraction of free ions relative to ion pairs.

Solvent polarity also affects the rate of cationic polymerization greatly. One example is the polymerization of p-methoxystyrene by iodine[62] at 30°C as in Table 4. The apparent propagation rate constant increases by more than two orders of magnitude, going from the low dielectric constant, $CCl_4(\varepsilon = 2.2$) to the higher dielectric constant $CH_2Cl_2(\varepsilon = 9.1$).

In general, polar solvents speed polymerization by changing the nature of the ion pair from the intimate ion pair to the solvent-separated ion pair and by increasing free ion concentration. But both k_p^+(or k_p^-) and $k_p^\pm$ decrease with increasing solvent polarity[23]. The transition state theory of chemical reactions suggests that this is because the initial state(monomer plus ion or ion pairs) is more polar than the activated complex in which the monomer is associated with the macroion and the charge is dispersed over a larger volume. A comparison of reported k_p^+ values for cationic

Table 3. Effects of Solvent on Anionic Polymerization of Styrene[a]

Sovent	Dielectric constant(ε)	k_p^{app} (liter/mole.sec)
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxyethane	5.5	3,800

[a] Data from [61].

Table 4.   Effects of Solvent on Cationic Polymerization of p-Methoxystyrene[a]

Sovent	Dielectric constant(ε)	k_p^{app} (liter/mole.sec)
CCl_4	2.1	0.12
CH_2Cl_2/CCl_4, 1/1	-	0.31
CH_2Cl_2/CCl_4, 3/1	-	1.8
CH_2Cl_2	9.1	17

[a]   Data from [62].

polymerizations of isobutyl vinyl ether[23] and styrene[63] in different solvents indicates a decrease in k_p^+ with increasing solvent polarity.

d) Effect of Gegenion

Whenever ions are the chain carriers in a polymerization there will be an equal amount of gegenions(counterions), except in initiating systems involving electron ejection from the monomer and formation of bare ions[64-66]. The identity of the gegenion is expected to exert an influence on ionic polymerizations involving ion-pair propagating species. The larger and less tightly bound the gegenion, the greater is the predicted reactivity of the ion pair toward propagation. Gegenion solvation plays a great role in the rate of polymerization by promoting more solvent separated ions. The effect of a gegenion on the reactivity of ion pairs is well-established due to the good stability of active centers and simplicity of gegenions especially in anionic polymerization. Table 5 shows the value of Kd(dissociation constant) and the propagation rate constant for free ions and ion pairs in styrene polymerization in THF and dioxane at 25°C. with various alkali metal gegenions[67].

In dioxane, solvation is apparently not important, since conductivity measurements show that there is no detectable dissociation of ion pairs to free ions. The solvation of contact ion pairs to solvent separated ion pairs is also very weak. Hence, the ion pair with the highest reactivity is that with the weakest bond between the carbanion center and the gegenion. As the size of gegenion increases, the bond strength decreases. In THF, however, the reactivity of the carbanion decreases as the size of the gegenion increases. The smaller Li^+ is solvated to the greatest extent and the larger Cs^+ is the least solvated.

Table 5. Effect of Gegenion on Anionic Polymerization of Styrene[a]

Gegenion	Dioxane	THF		
	$k_p^{\pm}$	$k_p^{\pm}$	$K_d \times 10^7$	k_p^-
Li^+	0.94	160	2.2	6.5×10^4
Na^+	3.4	80	1.5	6.5×10^4
K^+	19.8	60-80	0.8	6.5×10^4
Rb^+	21.5	50-80	0.1	6.5×10^4
Cs^+	24.5	22	0.02	6.5×10^4

[a] Data from [67].

In equilibria of ion pairs and ions increasing solvation promotes the formation of free ions as well as solvent-separated ion pairs. The fraction of ion pairs that are of the more solvent-separated type increases with the increasing solvation of the gegenion. Because solvent-separated ion pairs are much more reactive than contact ion pairs, the highest values of $k_p^{\pm}$ in THF relative to dioxane are a consequence of the presence of a higher fraction of the more reactive solvent-separated ion pairs. Also, the dissociation constant for the ion pair decreases in going from Li^+ to Ce^+ as the gegenion. The decrease in Kd has a very significant effect on overall polymerization since there is a very significant change in the concentration of the highly reactive free ions. Thus, the free ion concentration for polystyryl cesium is less than 10 % of that of polystyryl lithium.

In cationic polymerization, gegenions, i.e. anions such as Cl^-, Br^-, and CCl_3COO^-, are obtained in polymerizations initiated by Brønsted acids or large coordinately bonded conjugate bases of Lewis acids such as BF_3OH^-, $SnCl_6^-$, and $AlBr_4^-$. In some cases, gegenions may be present, as solvated free electrons in high-energy induced carbocationic polymerizations, or as ill-defined entities embedded in solids in heterophase cationic processes. The larger and less tightly bound the gegenion, the greater should be the reactivity of the ion pair toward propagation. But little experimental verification has been attained due to the complexity of carbocationic polymerization and the variety of gegenions.

The nucleophilicity of a gegenion determines its ability to recombine with the carbocation. For gegenions derived from Brønsted acids, nucleophilicity is the measure of the covalent nature of the propagating chain ends. Highly nucleophilic anions such as Cl^- and CH_3COO^- have a great tendency to form covalent bonds with carbocations and, therefore, except under very special circumstances where extremely basic monomers or very polar media are involved, the life time of the ionic active centers is very limited. Accordingly, the reactivity or rate of polymerization is very low. Efforts to quantify

nucleophilicities of various gegenions have been made in aqueous media[68], but similar nucleophilicity scales have not been devised for gegenions in nonaqueous media or for Friedel-Crafts acids.

Though an absolute scale of nucleophilicities of gegenions does not exist, workers in this field generally agree that the nucleophilicity of gegenions derived from Friedel-Crafts acids is low. A scale, however, is valuable in helping to determine the outcome of cationic polymerizations with regard to yields, conversions, and product molecular weights. Experimental results make it possible to obtain information on gegenion nucleophilicities of Friedel-Crafts acids[69-71]. Thus, molecular weights of polyisobutylenes obtained under carefully comparable conditions change as indicated in Table 6.

Counterion nucleophilicity is determined not by its actual size but *effective* size, that is, the area over which charge delocalization occurs[70]. In the latter series of experiments the number and nature of alkyl groups were constant and only the identity of halogen was changed. This and other data are interpreted to mean that the molecular weight of polyisobutylene is determined by the nucleophilicity of gegenion, which in turn, is determined by charge delocalization over electronegative groups. For gegenions with an equal number of similar alkyl groups, nucleophilicity is determined only by the nature of halogens; that is, nucleophilicity decreases as $R_3AlCl^- > R_3AlBr^- > R_3AlI^-$. However, the acidity sequence of Lewis acids is different, for example, $BF_3 < BCl_3 < BBr_3 < BI_3$[71-74], $AlCl_3 < AlBr_3 < AlI_3$[75], or $Me_3Al < Me_2AlCl < MeAlCl_2 < AlCl_3$. The unexpected acidity sequence of Boron based Lewis acids has been investigated by many workers. Some investigators[72,76-77] conclude that the vacant $2p$ orbital of boron in boron halides is partially occupied by back-donation by nonbonding electrons resulting in contributions by double bonded structures:

Table 6. Relative Nucleophilicity of Gegenion from Friedel-Crafts Acid[a]

Mn (nucleophilicity) ↑		Mn ↑	
	$Me_2AlCl_2^-$		$Et_2AlCl_2^-$
	$Me_2AlClBr^-$		$Et_2AlClBr^-$
	$Et_2AlCl_2^-$		$Et_2AlBr_2^-$
	$Et_2AlClBr^-$		Et_2AlClI^-
	$MeAlCl_2OH^-$		$\cong Et_2AlBrI^-$
	Et_3AlBr^-		$Et_2AlI_2^-$
	Et_3AlCl^-		

[a] Data from [70].

$$\begin{array}{ccc} |\overset{\_}{F}{}^{+} & & |\overline{Cl}\,|\;\delta^{+} \\ \| & & | \\ B^{-} & & B\quad\delta^{-} \\ \diagup\;\diagdown & & \diagup\;\diagdown \\ F\quad\;F & & Cl\quad Cl \end{array}$$
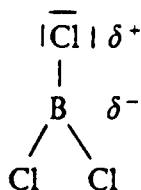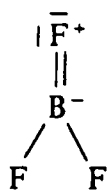
On the other hand, the nucleophilicity of a gegenion is linked to Drago's equation[78-82]. The equation was developed by Drago et al. in order to estimate semiquantitatively the enthalpy ΔH of the reaction A + B $\to$ AB. The equation

$$-\Delta H \;=\; E_A E_B \;+\; C_A C_B \tag{16}$$

contains four empirical constants, E_A, C_A, E_B, and C_B, characteristics of acids and bases(subscripts A and B respectively). Table 7 shows E_A and C_A values reported for various acids, and E_B and C_B data for different bases.

One example of the application of this equation is(ΔH in kcal/mole):

$$BF_3 + F^- \to BF_4{}^-$$
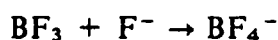
$-\Delta H$ = 55.47 using 7.96 and 3.08, 45.86 using 9.88 and 1.62
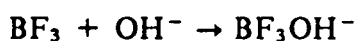
$$BF_3 + OH^- \to BF_3OH^-$$

$-\Delta H$ = 59.54 using 7.96 and 3.08, 48.97 using 9.88 and 1.62

$$SbCl_5 + Cl^- \to SbCl_6{}^-$$
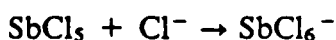
$-\Delta H$ = 67.78

Thus the relative stability sequence for the three gegenions for which data are available is $SbCl_6{}^- > BF_3OH^- > BF_4{}^-$.

Table 7. Drago's Empirical Constants for the Calculation of ΔH of Friedel-Crafts Acid-Base Reactions[a]

Acid

	$SbCl_5$	BF_3[b]	Iodine	ICl	IBr	I+	CH_3^+	Et+
E_A	7.38	7.96	1	5.10	2.41	68.72	62.1	51.49
		9.88						
C_A	5.13	3.08	1	0.830	1.56	4.57	7.30	7.05
		1.62						

	n-Pr+	Ph+
E_A	48.93	57.08
C_A	7.08	7.77

Base

	F-	Cl-	Br-	I-	Me-	Et-	OH-	Ph-
E_B	2.94	2.47	2.47	2.46	3.24	3.29	3.10	2.80
C_B	10.38	9.66	8.59	7.50	12.07	11.66	11.32	12.86

[a] Data from [78].
[b] The two E_A and C_A values have been obtained by applying two different assumptions in the calculation.

e) Effect of Temperature

The effect of temperature is related to the kinetics and thermodynamics of a polymerization. Frequently, the activation energy of the side reactions in a polymerization is higher than that of propagation or initiation. In these instances, a lower temperature gives cleaner systems, but the extent of the decrease of the temperature depends upon the effect it has on the main reaction. The best operating temperature, therefore, depends on the values of the activation energies of possible alternative steps.

In general, the effect of temperature on ionic polymerizations can be described by the Arrhenius equation:

$$k = Ae^{-Ea/RT} \tag{17}$$

where k is the rate constant of reaction, A is the pre-exponential factor, Ea is the activation energy, and R is the gas constant. For a living polymerization, the activation energy for the rate of polymerization(E_{Rp}) becomes that of the rate of propagation(E_p). For a polymerization of slow initiation and an appreciable extent of termination, the activation energy E_{Rp} is the combination of those of initiation, termination ,and propagation.

For a particular process by a particular ion in a Winstein spectrum, activation energy has a positive sign. However, this overall reasoning based on kinetics must be accompanied by its thermodynamic counterpart, i.e., the effect of temperature upon the equilibria among the active species formed.

From the equilibria as in equation 13, the dissociation constant can be represented[83] as

$$Kd = \exp(-z^2/a\varepsilon kT) \qquad (18)$$

where z is the charge of the ions, a is the sum of the van der Waals ionic radii, and k is Boltzmann's constant. It is well known that the dielectric constant(ε) of a medium increases, as the temperature, T, decreases. Thus, free ions are favored by cooling. In a poor solvent(nonpolar solvent) ion pairs are tightly bound and there is a negligible fraction of solvent-separated ion pairs at all temperatures. Where ion pairs exist almost as solvent separated ion pairs, i.e. within a good solvent(polar solvent), the Winstein spectrum does not change much with temperature. In both cases, the rates of polymerization increase as the temperature increases. Thus, for a solvent with intermediate polarity, a decrease in temperature increases the dielectric constant enough that it may itself considered a polar solvent, in turn affecting the Winstein spectrum. For example, the dielectric constant of CH_2Cl_2 is 9.1 at 25°C, but becomes 13.4 at -60°C, and 17.0 at -100°C[84]. A good illustration of this is the polymerization of styrene in THF[85].

4. Ionic Polymerization via 'Covalent' Propagating Species

In an equilibrium of free ions and ion pairs, as in the Winstein spectrum[4], covalent bonding is usually considered as an inactive species. However, it has been shown that for certain systems, these covalent species can propagate the growth of a polymer chain. While there is no doubt about the fact that propagating covalent species are less active than their ionic counterparts, their importance can be overwhelming if the specific conditions under which a polymerization is carried out is highly unfavorable to the presence of the latter, and if one achieves the highly desirable living polymerization.

a) Pseudocationic Polymerization

The existence of active ester molecules in the cationic polymerization of styrene was recognized in 1964 by Gandini and Plesch[87]. Plesch also proposed the concept of pseudocationic polymerization. Before their papers were presented, Pepper et al.[88-90] reported on polymerization of styrene by sulfuric acid and perchloric acid using polar solvents, but they interpreted their observations in terms of conventional carbocationic polymerization schemes though they had difficulties in explaining the unusually high activation energy of propagation(Ea = 8.5 kcal/mole). This idea of pseudocationic polymerization was not easily accepted and a widespread controversy over its validity has continued until today.

Evidence of pseudocationic polymerization appears most established in the perchloric acid initiated polymerization of styrene, at 30 to 20°C, in methylene chloride. By using spectrophotometry and conductivity measurements coupled with kinetic studies[14,27,86,91] ions are shown to be absent during propagation and to be formed only when the concentration of styrene is less than four times of that of the acid.

Polymerization proceeds through three successive stages. There is a rapid, but short-lived reaction involving ions in stage 1 followed by a much slower reaction stage 2 in which ions cannot be detected by conductivity or spectroscopy. In stage 3 there is a reaction involving the rapid and simultaneous increase in conductivity and rate of polymerization. Apparently, free ions are formed in stage 1, but these are insufficiently stable. Ion combination yields the covalent ester, which is stabilized in solution by the monomer. At high conversion, there is insufficient monomer to stabilize the ester. As a result, ionization occurs, leading to the rapid reaction in stage 3. The reaction in stage 2 is attributed to a pseudocationic mechanism in which propagation involves monomer insertion into the C-O bond of a perchlorate ester[92] as in equation 19.

Pseudocationic polymerization has been proposed in many systems as in Table 8[8]. The most compelling evidence for the existence of a covalent propagating species is the absence of any effect of added water on the rate of polymerization in stage 2 though stage 1 and 3 are suppressed.

$$\sim CH_2\text{-}CH \overset{\phi}{\underset{}{|}} O\text{-}ClO_2 \quad \rightarrow \quad \sim CH_2\text{-}\overset{\phi}{\underset{|}{C}}H\text{-}CH_2\text{-}\overset{\phi}{\underset{|}{C}}HOClO_3 \qquad (19)$$
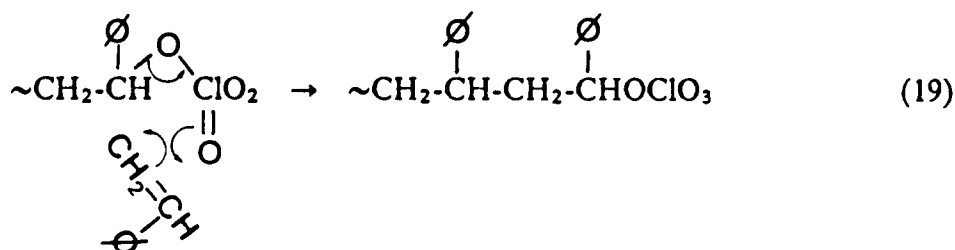
More recent evidence lies in the observation of a bimodal molecular weight distribution(MWD) by GPC in this polymerization[96]. A bimodal MWD consists of a mixture of two MWDs of sufficiently different molecular weights that one can observe each MWD separately. The higher MWD portion was assigned due to propagation by free ions or ion pairs and the lower MWD portion to propagation by the covalent ester. A bimodal MWD indicates the presence of the covalent ester species simultaneously with free ions. Hence, these two types of species is expected to interconvert at a much slower rate, allowing sufficient life times for each to give rise to a different molecular weight distribution.

Bimodal molecular weight distributions have been observed in a number of other polymerizations: styrene initiated by CF_3SO_3H, CH_3COClO_4, and CF_3CO_2H ; p-methoxystyrene and p-methylstyrene initiated by iodine; p-chlorostyrene by CF_3SO_3H and CH_3COClO_4[63,97-100]. The polymer of higher molecular weight distribution in these systems appears to be due to propagation by free ions as evidenced by its suppression when a common ion salt is added, for example, $(n\text{-}C_4H_9)_4N^+ClO_4^-$ in polymerization initiated by $CH_3CO^+ClO_4^-$. Another interpretation of the result of the

Table 8.   Systems That Proceed by Pseudocationic Polymerization[a]

Monomer	Initiator	Solvent	Reference
Styrene	$HClO_4$	CH_2Cl_2	86
	$HClO_4$	$(CH_2Cl)_2$	14
	$HClO_4$	$EtNO_2$	91
	$HClO_4$	$EtNO_2 + (CH_2Cl)_2$	91
	H_2OSnCl_4	CH_2Cl_2	14
	CF_3COOH	CH_2Cl_2	14
	$C_6H_5CH(CH_3)ClO_4$	CH_2Cl_2	14
p-Methoxystyrene	CF_3COOH	CH_2Cl_2	91
Acenaphthylene	$HClO_4$	CH_2Cl_2	91
N-Vinylcarbazole	$HClO_4$	CH_2Cl_2	91
	H_2SO_4	CH_2Cl_2	91
1,1-Di-p-methoxyphenyl-ethylene	CCl_3COOH	C_6H_6	34, 93
1,1-Diphenylethylene	$HClSbCl_3$	C_6H_6	95

[a] Data from [8].

addition of salt is that water adsorbed on the salt reacts with the free ion present which suppresses $k_p^\pm$ and propagation occurs exclusively through the covalent ester[63a].

Recently, the idea of pseudocationic polymerization has been reinvestigated and challenged again by several workers. The molecular weight distribution of polystyrene formed at 50°C in 1,2-dichloroethane(DCE) or mixtures of DCE and benzene by trifluoroacetic acid, is found to be bimodal. Increasing the solvent polarity facilitates the formation of the high polymers[101]. However, when the styryl ester(1-phenylethyl trifluoroacetate) is used as an initiator no polymerization is observed under the same conditions. This observation certainly complicates the theory of pseudocationic polymerization. To clarify this observation more experiments were performed by Plesch using high vacuum dilatometry[102]. These are summarized as follows:

- When Trifluoroacetic acid(TFA) is not dried at all, but where the $[H_2O]$ is still substantially less than $[TFA]$, the reaction rate becomes

$$-d[St]/dt \ = \ k_4[St][TFA]^3 \tag{20}$$

where St = styrene.

- The product of the polymerizations with undried TFA contains an appreciable amount of oligostyrene of DP(degree of polymerization) about 3.

- When TFA is partly dried(with calcium sulfate) the reaction rate becomes

$$-d[St]/dt \ = \ k[St][TPA]^x \tag{21}$$

where x is unknown.

- When TFA is dried(with phosphorous pentoxide) the rate of polymerization becomes

$$-d[St]/dt = k_5[St]^2[TFA]_0^3 \qquad (22)$$

where $[TFA]_0$ is the initial concentration of TFA.

- The product formed in the dry systems contains very little oligomer.

- At the end of the polymerizations the reaction mixture contains poly-(and oligo-) styryl trifluoroacetates and a conducting species; the latter is formed rapidly from the start when the TFA is wet, but only near complete conversion when the system is well dried. It is most probably the free TFA which is present when the polymerization is completed.

- Polymerizations reach completion even with the lowest $[TFA]$ for both wet and dry systems. However, the irreproducible results indicate that there may be a threshold $[TFA]$(for any given $[M]_0$) below which polymerizations do not reach completion.

- The ester, 1-phenylethyl trifluoroacetates(PET) alone does not initiate polymerization of styrene.

- The presence of PET in a polymerization mixture reduces the rate of polymerization.

- The presence of PET produces a distinctly bimodal molecular weight distribution.

Finally, GPC traces change to bimodal from monomodal when the TFA becomes wet or mixed with PET, as in Figure 1[102]. Recently, Matyjaszewski and Sigwalt[103] reported that the polymerization of styrene by CF_3SO_3H, which was assumed previously to proceed via a pseudocationic mechanism, could be explained more satisfactorily by a more classical ionic mechanism. They also pointed out the different behavior of perchloric acid and triflic acid, previously considered to be similar in the polymerization of styrene. Upon the addition of N-*tert*-butylaziridine to the polymerization system of styrene initiated by triflic acid, a mixture of homo polystyrene and homo

poly(N-*tert*-butylaziridine) was obtained. This observation is different from the one observed in $HClO_4$ system in which block copolymer was obtained[104].

The idea of pseudocationic polymerization has, therefore, not been strictly proved. However, the concept that chain carriers can be covalent species instead of being ionic remains. Certainly this concept sheds some new light upon cationic polymerization known for a long time to be difficult to convert to controlled polymerization.

b) Group Transfer Polymerization(GTP)

Group transfer polymerization is a new polymerization process discovered by scientists at E. I. du Pont de Nemours & Company in 1983[7,11,105-109]. This polymerization makes it possible for the derivatives of acrylic and methacrylic acid to be polymerized with controlled molecular weights using silicon containing initiators in the presence of catalysts. Interestingly, GTP combines the important advantages of living polymerization, such as controls of molecular weight and molecular weight distribution, facile preparation of block and functionalized polymers[105,110-111], with the additional advantage that the polymerization can be carried out at ambient temperature or above. In contrast, anionic polymerization of methacrylates creates living polymers only at low temperatures[112] with the exception of *tert*-butyl methacrylate.

$$
\begin{array}{ccc}
CH_3 \diagup \diagdown O & 1)\ (CH_3)_3SiH & CH_3 \diagdown \diagup OSi(CH_3)_3 \\
\diagup\diagdown & \longrightarrow & \diagup\diagdown \\
CH_2 \diagdown \diagup OCH_3 & 2)\ (Ph)_3RhCl & CH_3 \diagup \diagdown OCH_3
\end{array}
\qquad (23)
$$

$$\underset{\sim}{1}$$
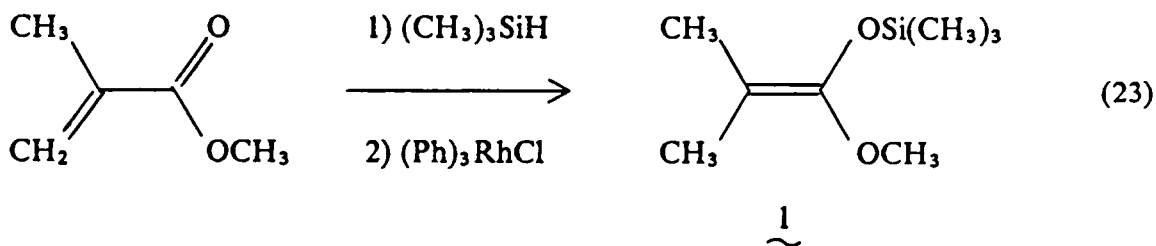
The components of a GTP include an initiator, catalyst, monomer, and a solvent such as acetonitrile, THF, chlorinated aliphatics, or toluene. The initiator in GTP is a
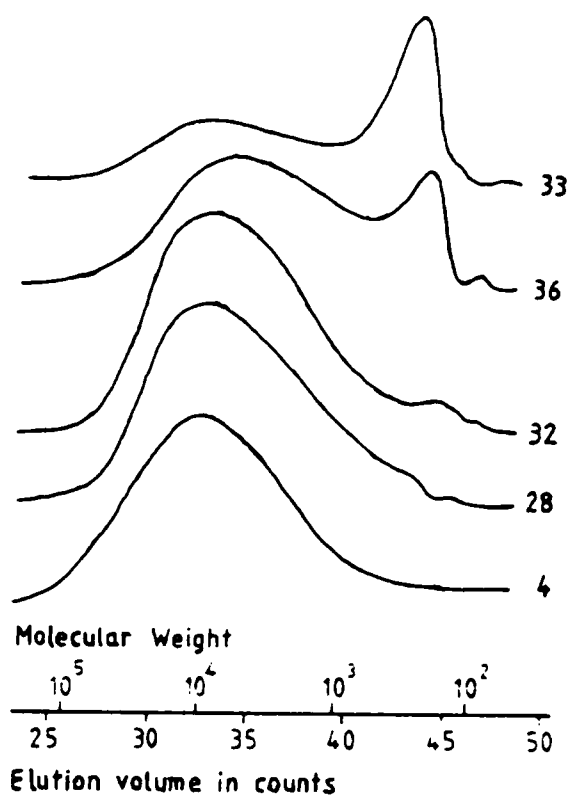
Figure 1. GPC chromatograms of polystyrenes prepared with different TFA: No 28; drying with P₂O₅, No 4 and 32; CaSO₄, No 36; no drying, No 33; CaSO₄(PET present)[102].

usually silyl ketene acetal, e.g., trimethylsilyl dimethylketene methyl acetal as in $\underline{1}$, which could be generated by the reaction as in equation 23. Besides this initiator, compounds which can rearrange themselves into ketene acetals such as α-silyl esters(equation 24), or compounds which can generate ketene acetals, for example, trimethylsilyl cyanide or trimethylsilyl methyl sulfide, act as initiators(equation 25)[113-114].

$$(CH_3)_3SiCH_2CO_2CH_2CH_3 \; \rightleftharpoons \; CH_2 = \overset{\displaystyle \overset{OCH_2CH_3}{|}}{C}OSi(CH_3)_3 \tag{24}$$

$$(CH_3)_3SiCN \; + \; CH_2 = \underset{\underset{CH_3}{|}}{C}\text{-}CO_2CH_3 \; \rightarrow \; NC\text{-}CH_2\text{-}C = \overset{\overset{OCH_3}{\diagup}}{\underset{\diagdown}{C}}{OSi(CH_3)_3} \tag{25}$$
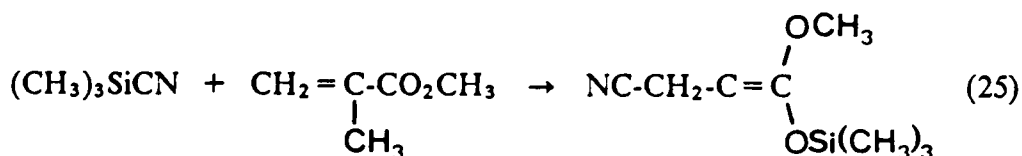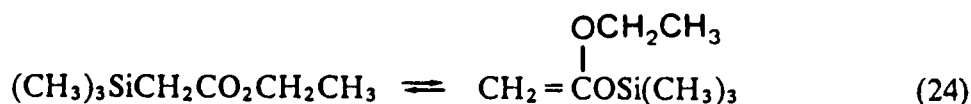
These initiators alone cannot initiate the polymerization of MMA, but given the presence of a catalyst, polymerization takes place as in Scheme 3[7,115-116]. In the proposed mechanism the trimethylsilyl group is transferred to the carbonyl oxygen of the incoming monomer repetitionary, hence the name is "group transfer." In a broad sense the transfer of the trimethylsilyl group is equivalent to the participation of an initiator fragment in a polymerization as in the case of a gegenion in an ionic polymerization. But the GTP differs since the participation of the trimethylsilyl group is not straightforward.

In GTP the catalyst has a wide variety of choices. Nucleophilic catalysts such as soluble fluorides, bifluorides, azides, and cyanides are thought to activate the initiator[7]. The amount needed is small - as low as 0.1% based on the initiator. In contrast, electrophilic catalysts or Lewis acids such as zinc halides, alkylaluminum chlorides, and alkylaluminum oxides are thought to operate by activating the monomer[117]. The

R = CH$_3$
Nu$^{\ominus}$ = nucleophilic catalyst
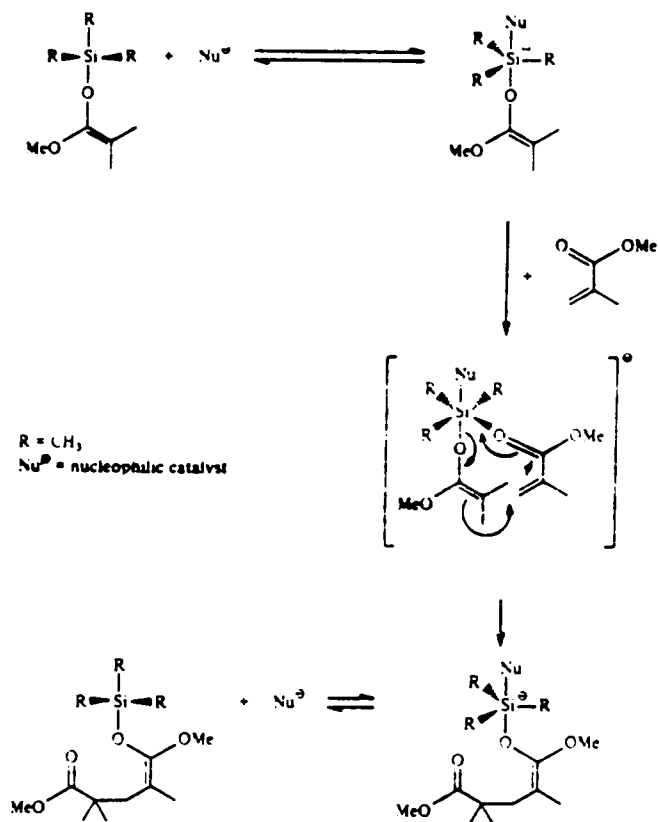
Scheme 3. Proposed mechanism of GTP[7].
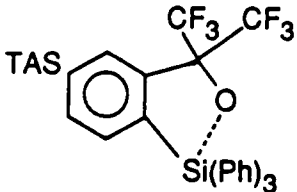
amount needed is large - as much as 10% based on the monomer. Recently nucleophilic catalysts based on quartenary ammonium acid salts which include carboxylate, phenolate, sulfinate, phosphinate, sulfonamidate, and perfluoroalkoxide were also found to have catalytic activity[118]. Table 9 shows the listing of some catalysts which were used in GTP.

Though the properties of GTP allow one to control the molecular weight accurately up to the range of 20K(K = 1000), obtaining a high molecular weight polymer is more difficult since the amount of initiator needed is so low that it begins to match interfering impurity levels. Thus the monomer purity requires an anionic grade attainable by purification from the mixture of alkylaluminum-momoner complex[30c]. Using very pure monomers, solvents, catalysts, and initiators, it is possible to make polymers in the range of molecular weights of 100K to 200K[113].

Another branch of GTP, referred as aldol-GTP, developed as a result of the reaction of aldehydes with silyl vinyl ethers[120-121]. Aldehydes are known to react with silyl vinyl ethers to give silylated crossed-aldol products[122]. Since a new aldehyde group is formed in aldol condensation of silyl vinyl ethers, continued addition of the silyl vinyl ether should give a polymer. The reaction scheme is represented in equation 26.
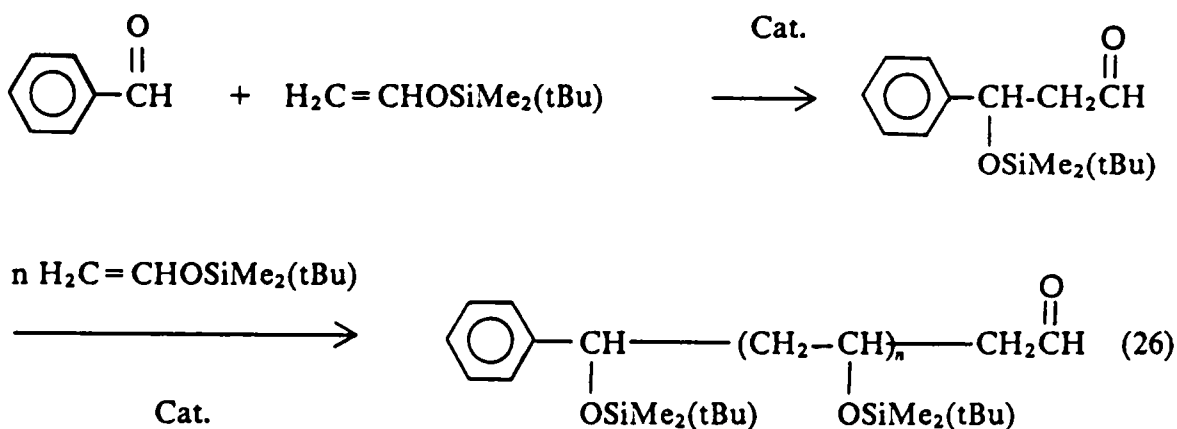
Table 9. Catalysts Used in GTP

Catalyst	Reference
Electrophilic	117

ZnI_2, $ZnBr_2$, $ZnCl_2$, iBu_2AlCl, $(iBu_2Al)_2O$, Et_2AlCl

Nucleophilic

Based on $(Me_2N)_3S^+ \equiv TAS^+$	3

$TASHF_2$, $TASCN$, $TASF_2SiMe_3$

Based on quarternary ammonium salt

Et_4NCN, Bu_4NF	119
Bu_4NOAc, $Bu_4NOOCPh$, Bu_4NOPh, $Bu_4NOOC(Ph-NO_2)$,	118
$Bu_4NO(Ph-F)$, $Bu_4NOOC(Ph-CN)$, $Bu_4NO(Ph-OCH_3)$,	
$Bu_4NOOC(Ph-Cl)$	
$Bu_4NO_3S(Ph-Me)$	118
Quarternary ammonium salts + Acids(1/1)	118

The products are stable and neutral living polymers whose hydrolytic stability depends on the bulkiness of the silyl group. By using *tert*-butyl dimethyl silyl ethers which are more stable than the corresponding trimethyl silyl ethers, the molecular weight of the polymer is well controlled over a wide temperature range(-80 to +70°C).

Lewis acids, such as zinc halides and diisobutylaluminum chloride, or titanium tetrachloride, act as catalysts. Good results were obtained using zinc halides in dichloromethane. In contrast to the Lewis acid catalyzed GTP of methacrylates, where catalyst levels of about $10\sim20\%$ are needed relative to the monomer for quantitative conversion, a much smaller amount of catalyst is needed in the aldol-GTP. This usually ranges from 10^{-4} to 10^{-2} mole% relative to the monomer. These living polymers can themselves be hydrolyzed to make poly(vinyl alcohol). They are also used in the production of Reformatsky products, i.e. as a result of the reaction of the terminal aldehyde with another ketenyl silyl ether. The combination of living PMMA in GTP with living poly(t-butyl dimethyl silyl vinyl ether), thus creates block copolymers. After hydrolysis, these become PMMA-poly(vinyl alcohol) block copolymers.

c) Living Cationic Polymerization

1) Polymerization by the HI/I₂ Initiation System: Although the catalytic effect of hydrogen-iodide/iodine has been recognized since the 1960's[123], a synthesis of living polymers by this initiation system had not been reported until recently. Japanese workers[10,26,124] were the first to experiment living polymerization with this initiation system. When this initiation system was added to isobutyl vinyl ether in a nonpolar solvent, polymerization showed living behaviors. These included the possibility of sequential addition polymerization, narrow molecular weight distribution, and the linear relationship of molecular weight versus conversion. Interestingly, hydrogen iodide can-

not initiate polymerization by itself, but requires iodine to initiate it these conditions. In the polymerization, the hydrogen iodide makes adduct, 2, quantitatively[125] with an alkyl vinyl ether, as in equation 27. This adduct acts as an initiator in the polymerization though it cannot initiate the polymerization under this condition:

$$HI + CH_2 = CH\text{-}OR \rightarrow CH_3\text{-}CHI\text{-}OR \qquad (27)$$
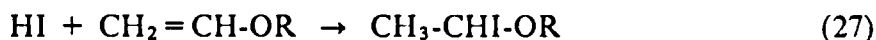
Polymerization is initiated by further addition of iodine.

The above process was elaborately studied using isobutyl vinyl ether(IBVE) and the following polymerization scheme(Scheme 4) is proposed based on the following observations[26].

- Prior to the polymerization, HI is added quantitatively to yield adduct, 2.

- HI or 2 can barely polymerize IBVE.

- Addition of iodine to an apparently quiescent mixture of IBVE and HI, however, induces polymerization without an induction period and yields monodisperse polymers.

- The -CHI terminal groups are observable throughout the process.

- The molecular weight of the living polymer produced by HI/I_2 initiator is dependent only on the HI concentration and is independent of the iodine concentration.

For this mechanism, Higashimura et al. assumed from a UV spectroscopic study and alcoholysis experiment with methanol that the added iodine in part forms a diiodo compound as in equation 28.

$$CH_2 = CHOR + I_2 \rightarrow ICH_2\text{-}CHI\text{-}OR \qquad (28)$$
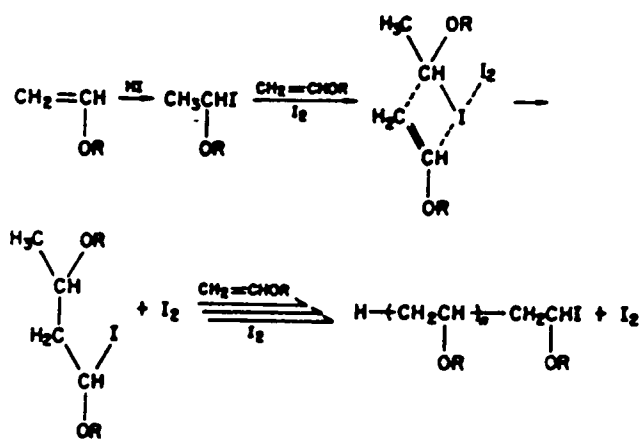
Scheme 4. Proposed polymerization mechanism of alkyl vinyl ethers by HI/I_2[26].

The compound remains intact throughout the polymerization, and the remainder of the iodine stays free at a constant concentration in the polymerization mixture. During polymerization the role of iodine is often thought to be equivalent to that of Lewis acid. The carbon-iodine bond is activated by iodine, thus making the monomer insertion into the activated carbon-iodine bond possible.

The amount of iodine used was usually a 1/1 ratio to the initial HI concentration at the initial stage of the development of this polymerization technique, because the formation of triiodide ion was thought to be the major gegenion formation reaction[124a]. Later, it was possible to reduce the amount of iodine in a solvent with medium-polarity[126], and a linear relationship between the rate of polymerization and the initial concentration of the iodine was reported[127].

This polymerization system can be applied to the monomers which have a high reactivity toward cationic polymerization. Examples include alkyl and aryl vinyl ethers, p-methoxystyrene, alkyl propenyl ethers, and 5-methyl-2,3-dihydrofuran[128]. Much more reactive monomers such as N-vinyl carbazole are not included. The reactivity of a monomer toward a specific catalyst in cationic polymerization was visualized recently in terms of the stability of growing carbocation, derived from a monomer, and the nucleophilicity of the counteranion, derived from an initiator[24]. The relationship is shown in Figure 2. In this Figure, the carbocations need not be free ions, but may have a covalent nature depending on the polymerization condition.

This living polymerization certainly utilizes the nature of the covalent active center, such as low reactivity, longer lifetime, and low chance of side reactions.

2) Polymerization by the Ester/Lewis Acid Initiation System: The complexes of esters of carboxylic acids and Lewis acids have been known for a long time[129]. In some cases, for example in the case of ester-BCl_3 complexes, the chemical behavior was studied
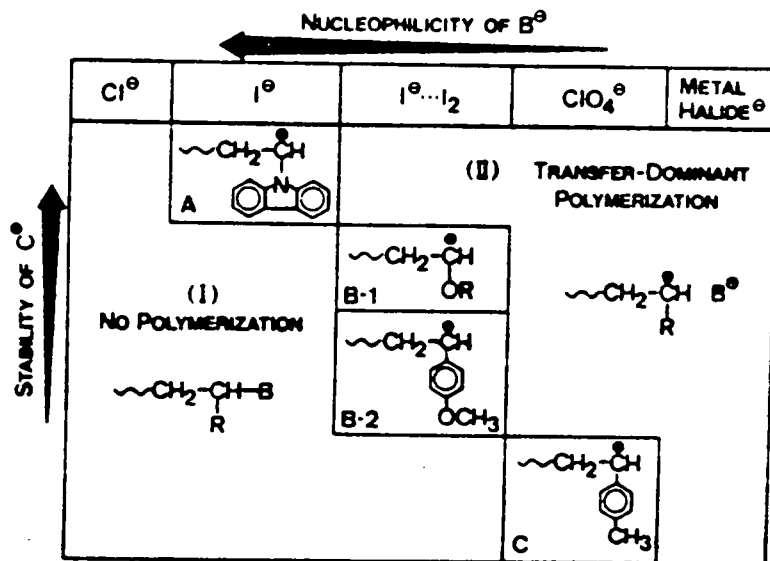
Figure 2. Scope of living cationic polymerization of vinyl monomers: Boxes A, B-1, B-2, and C indicate the monomer/initiator combinations for living polymerization[24].

earlier[130]. The application of these compounds to cationic polymerization was, however, not attempted until 1986[11-12,131].

When the polymerization of IBVE was initiated by the $EtAlCl_2$/ acetate complex, the molecular weight, MWD, and rate of polymerization became quite different from those initiated only by $EtAlCl_2$.

- Polymerization was retarded so much that the half life of the monomer consumption became quite longer than that of the polymerization initiated by $EtAlCl_2$ alone[12], as follows

$EtAlCl_2$(0.2 hr) < $EtAlCl_2$/ethyl benzoate(6.5hrs) < $EtAlCl_2$/ethyl acetate(27 hrs)

- The molecular weight and molecular weight distribution decreased as the polymerization rate decreased. With $EtAlCl_2/CH_3COOEt$ catalyst, narrow molecular weight distribution was obtained(1.12-1.15) in toluene solution and the polymerization was living at the even higher temperature, 25°C.

During polymerization fairly large amount of ethyl acetate(100% to the monomer) was used and the molecular weight increased as the polymerization temperature increased, i.e., not all the $EtAlCl_2$ molecules generated polymer chains. The initiation efficiency was rather low, so although this polymerization system is living it needs more study.

Another example of the application of the complex to polymerization is isobutylene polymerization initiated by BCl_3/t-butyl acetate[11]. The polymerization system consists of isobutylene, t-butyl acetate, BCl_3, and chlorinated solvents. At low temperatures, the molecular weight of the polymer formed was linearly proportional to the conversion, though the molecular weight distribution was rather broad(1.3~2.0). But carefully controlled experiments gave a narrow molecular weight distribution(1.17~1.3). Interestingly, the effect of moisture was not important in the polymerization, which was

similar to the case of pseudocationic polymerization, but quite different from that in the usual cationic polymerization. The polymerization of isobutyl vinyl ether by acetate/EtAlCl₂ was also different, since the molecular weight of the polymer was determined by the initial ratio of monomer/t-butyl acetate. The acetate initiation efficiency was rather low(24~51% for t-Bu). When the acetate was changed from t-butyl acetate to 2,4,4-trimethylpentane-2-acetate or cumyl acetate, the initiation efficiency became close to 1, but deviation still occurred due to the rather broad molecular weight distribution of the resultant polymer. Possibly imperfect mixing is also important here. Polymerization is thought to take place as in Scheme 5[11].

When considering the fact that metal halides(MX_n) by themselves lead to uncontrollable and transfer-dominant cationic polymerization except under special conditions[132], the success of living polymerization as a result of the use of Lewis acid/acetate complexes, as in the above two examples, is a quite remarkable step towards a better understanding of the cationic polymerization.

3) Polymerization by the Cumyl Ether/TiCl₄: Quite recently the polymerization of isobutylene was advanced one step further by using $CH_3OC(CH_3)_2$-p-C_6H_4-$C(CH_3)_2OCH_3$/ TiCl₄ initiating system in CH_3Cl/ n-C_6H_{14} (40/60 v/v) at -80°C[13]. In this polymerization the initiation efficiency of dicumyl methyl ether was almost quantitative when the addition sequence of the reagents followed the pattern of dicumyl ether - monomer - TiCl₄. The molecular weight distributions of the resultant polymers were quite narrow(1.05~1.17). Therefore, the undesirable indanyl end groups, which form in the initiation process of the polymerization even at -80°C, could be eliminated by selecting proper addition sequence of reagents. The indanyl formation and polymerization can be visualized as in Scheme 6. Interestingly, the rate of polymerization showed zeroth order dependence on the
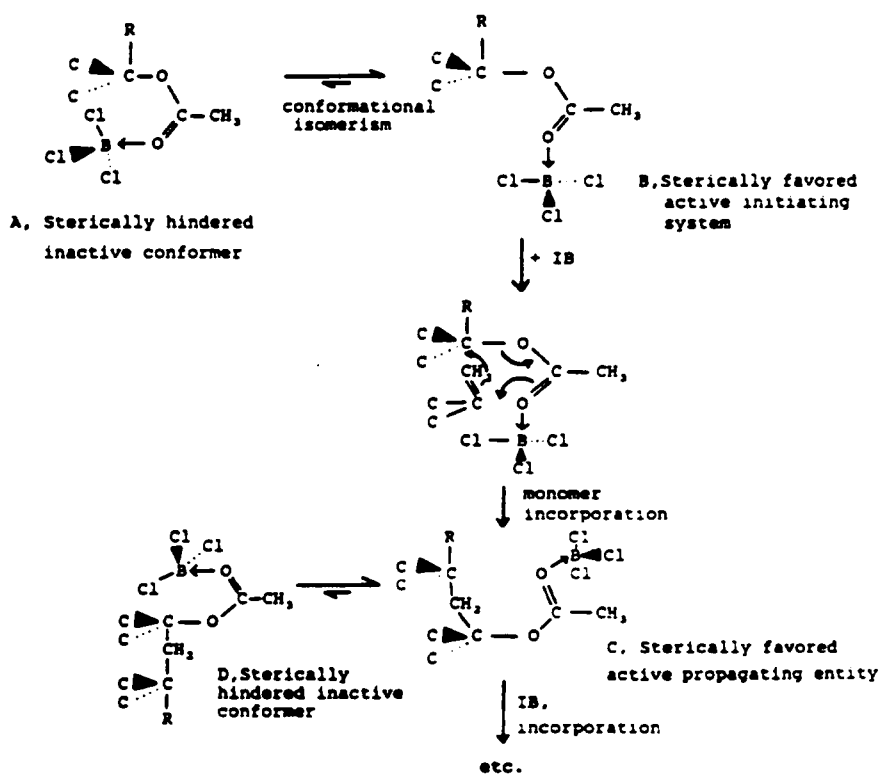
Scheme 5. Proposed mechanism of living polymerization of isobutylene by acetate/BCl₃[11].
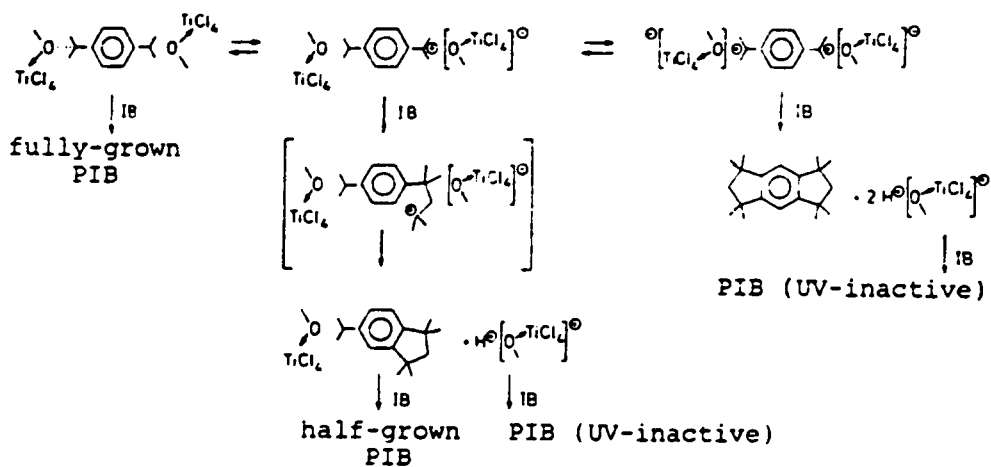
Scheme 6. Polymerization of isobutylene and indanyl formation with dicumyl ether/TiCl₄ initiation system[13].

monomer concentration as in the polymerization of alkyl vinyl ether initiated by HI/I_2 catalyst[127].

5. Controlled Cationic Polymerization via 'Ionic' Propagating Species

a) Introduction

Cationic polymerization is clearly different from anionic polymerization and is usually a transfer dominant polymerization process. However, in some cases, the polymerizations proceed without any noticeable side reactions and thus can be considered as *controlled* polymerizations. The living cationic polymerizations as mentioned in the previous section would be one example of controlled cationic polymerization.

The active intermediate must meet certain requirements to qualify as a controlled polymerization since cations(especially carbocations) are inherently unstable and reactive species. When polymerization proceeds via solvent separated or free ion pairs in the Winstein spectrum, it is very difficult to meet these requirements. Clearly, a less reactive cation is needed in order to minimize possible side reactions and maintain chain end integrity. The monomers which can generate stable cationic species thus can generate a *controlled* polymerization. Many heterocyclic monomers which can produce a relatively stable cation, such as an oxonium ion, sulfonium ion, or immonium ion are attractive in this regard. However, for a monomer which has a carbon-carbon double bond, the stability of the carbocation is the most important factor in determining the controllability.

Carbocation stability is determined by microstructure and by the nature of atoms in the vicinity of the carbocationic center. Electronic and steric effects are of particular

importance. Charge dispersion by conjugation with aromatic rings or heteroatoms with unshared electrons are important in the determination of the carbocation stability. When a monomer is being polymerized, this stability may be roughly related to the ease of initiation or the basicity of the monomer.

Monomers which have carbon-carbon double bond and are polymerizable by cationic mechanism, can be classified into four main categories[97]: (i) aliphatic monoolefins, (ii) aliphatic dienes, (iii) aromatic olefins and (iv) monomers in which the vinyl group is attached to an electron donating atom. Within each category, the ease of initiation for the most representative monomers follows approximately the order given below:

(i) isobutene> 2-butene> cyclohexene> propene> 1-butene

(ii) cyclopentadiene> pinenes> isoprene> butadiene> chloroprene

(iii) p-methoxystyrene> 1,1-diphenylethylene> α-methylstyrene> indene> styrene> p-chlorostyrene

(iv) n-vinylcarbazole> vinyl ethers $\cong$ vinyl sulfides> chlorovinyl ethers

For the four categories, the qualitative order of basicity is (iv) > (iii) > (ii) > (i). The approximate ranking of the carbocation is the same order. These criteria are only shown to indicate broad tendencies. Factors such as the nature of the catalyst used, the type of gegenion and the physical conditions prevailing, are of course also important in determining specific results.

The quantitative carbocation stability expressed in thermodynamic or kinetic terms is elusive, and polymer scientists have to contend with relative stability scales derived by comparisons of large numbers of various cationic reactions. Several methods have been proposed for the estimation of relative carbocation stabilities. One example is to

use the enthalpy required to dissociate an alkyl halide RX into R^+ and X^- as in equation 29.

$$RX \xrightarrow{\Delta H_1} R\cdot + X\cdot \xrightarrow{\Delta H_2} R^+ + e + X\cdot \xrightarrow{\Delta H_3} R^+ + X^- \qquad (29)$$

$$\Delta Hg$$
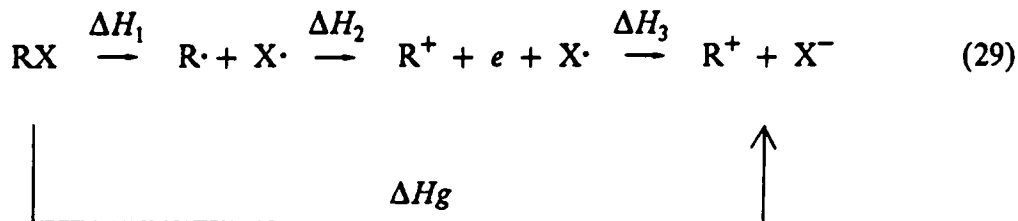
where ΔH_1, ΔH_2, and ΔH_3 are the enthalpy changes due to homolytic bond cleavage, ionization potential, and electron affinity respectively, and

$$\Delta Hg = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Table 10 shows representative enthalpies of carbocation formation calculated in this manner from some alkyl bromides[133].

Another method of determining carbocation stability is to compare ionization potentials of the parent radicals(ΔH_2 in the above equation) as shown in Table 11[134].

Carbocation stability is also estimated by solvolysis rates of the S_{N} reaction[134], by comparison of carbocation formation enthalpies from the corresponding alcohols[135-136], or by quantum mechanical calculations[137].

Controlled cationic polymerization of various monomers has become of great interest recently. Nevertheless, the controlled cationic polymerization via a very reactive carbocation such as styrene has not been reported yet.

This review contains several examples of controlled cationic polymerizations. For all cases the reactivity of the active cationic chain end is not high due to the charge dispersion for a carbocation and due to the existence of stabilizing electrons for a heteroatom. This review also includes an example of controlled polymerization via modification of the reactivity of a carbocation by a second component of solvents[15].

Table 10. Enthalpies of Carbocation Formation from Alkyl and Aryl Bromides[a]

Carbocation	ΔHg (kcal/mole)
Methyl	214
Allyl	152
Benzyl	147
p-Cl-Benzyl	151
o-Me-Benzyl	142
m-Me-Benzyl	145
p-NO$_2$-Benzyl	139
m-NO$_2$-Benzyl	164
m-CN-Benzyl	164
p-CN-Benzyl	161

[a] Data from [133].

Table 11. Ionization Potentials of Parent Radicals Derived from Electron Impact Studies[a]

Radical	Ionization potential(kcal/mole)
CH_3	229.4 ± 0.7
CH_3CH_2	202.5 ± 1.2
$CH_3CH_2CH_2$	200.4 ± 1.2
$(CH_3)_2CH$	182.2 ± 1.2
$(CH_3)_3C$	171.8 ± 1.2
$C_6H_5CH_2$	178.9 ± 1.8
$p\text{-}CN\text{-}C_6H_5CH_2$	197.9 ± 2.3
$p\text{-}MeO\text{-}C_6H_5CH_2$	157.7 ± 2.3
$(C_6H_5)_2CH$	168.8 ± 2.3
$CH_2=CH$	217.9 ± 1.2
$CH_2=CHCH_2$	188.2 ± 0.7
$CH_3CH=CHCH_2$	177.8 ± 1.2
$HC\equiv C\,CH_2$	190.2 ± 1.8

[a] Data from [134].

b) Living Polymerization of THF

Synthesis of high polymers by cationic ring-opening polymerization of heterocycles is hampered by chain transfer which may occur[138] by:

- Back biting or end-to-end closure(intramolecular chain transfer)
- Scrambling by intermolecular chain transfer
- Proton transfer(formation of double bonds at the chain end)

All these polymerizations proceed to a large or smaller extent in the cationic polymerization of any heterocyclic monomer. In the polymerization of THF, however, these reactions are not a serious problem, and the rate can be reduced. Macrocyclization, for example, is not a serious problem because a THF monomer has higher basicity than the polymeric units or the macrocycles of thermodynamically unfavorable sizes. Macrocyclization can also be reduced by carrying out the reaction in bulk rather than dilute solution. The last two side reactions, on the other hand, can be reduced by proper selection of an initiator.

The polymerization of THF is only mildly exothermic, and thus shows a propagation-depropagation equilibrium. The equilibrium monomer concentration $[M]_e$ at which the rate of polymerization becomes zero is reviewed below[139]:

$$RM^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M^* \tag{30}$$

$$\ln([M]_e) = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R} = \frac{\Delta G_p}{RT} \tag{31}$$

For bulk polymerization $[M]_e$ can have only one unique value at a given temperature as in equation 31[140]. The plot of $\ln[M]_e$ versus $1/T$ is a straight line with slope $\Delta H/R$. At 25°C the experimentally determined ΔH_p = -18.8 kJ/mole, ΔS_p = -75.3 J/mole, and ΔG_p = - 3.35 kJ/mole[141-143]. Therefore, the composition of the polymer at equilibrium increases as the temperature decreases[142-143]. At 25°C, equilibrium monomer concentration is 3.1 mole/l. $[M]_e$ depends on the nature and volume fraction of the solvent when solvent is added and the corresponding parameters include the interaction with solvent, thus $[M]_e$ depends on $[M]_0$. The stronger the solvent-monomer interaction, the higher $[M]_e$ for a given $[M]_0$[144]. The explanation given for this phenomenon involves the higher nucleophilicity of the THF relative to that of the polymer segments. The stronger interaction between the THF and the solvent is not fully compensated for by the comparatively weaker solvent-polymer interaction. The stronger the interaction, the higher $[M]_e$ for a given $[M]_0$. Thus, $[M]_e$ increases in the following order; CCl_4 < C_6H_6 < CH_2Cl_2 < CH_3NO_2(Figure 3).

The reaction is carried out in the bulk, at constant temperature, with a known amount of initiator. The polymerization time required to reach a given conversion X, or a given molecular weight(Mn) can be calculated by knowing the rate constant of propagation k_p and the equilibrium monomer concentration $[M]_e$ at the polymerization temperature from the well-known expressions.

$$\ln\left(\frac{[M]_0 - [M]_e}{[M] - [M]_e}\right) = k_p[M^*]t \tag{32}$$

$$X = 1 - \frac{[M]}{[M]_0} \tag{33}$$

$$DP_n = \frac{[M]_0 - [M]}{[M^*]} \tag{34}$$
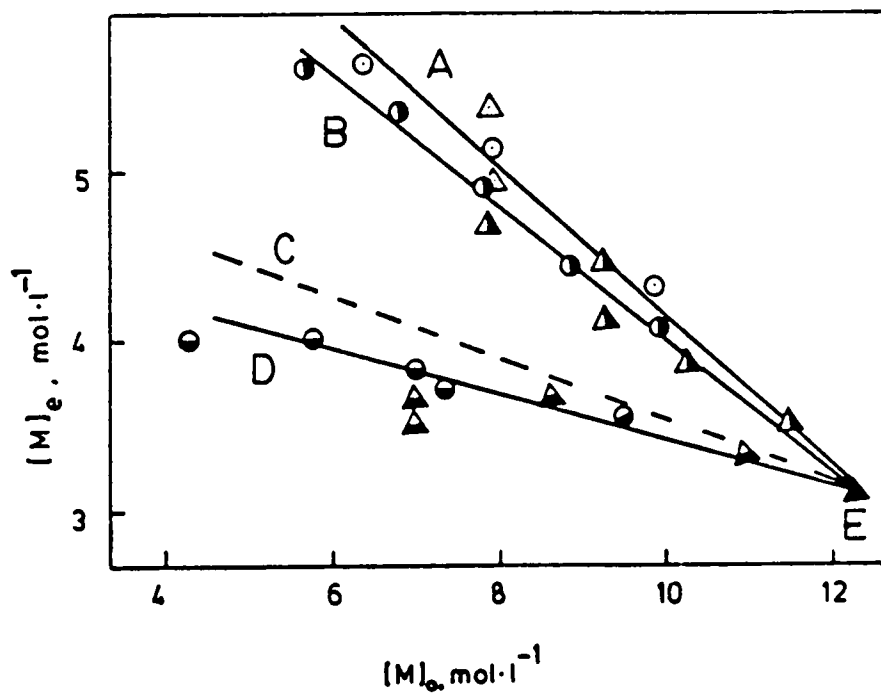
Figure 3. Dependence of the equilibrium monomer concentration [M]e on the initial THF concentration [M]o: At 25°C[144]; A) CH_3NO_2, B) CH_2Cl_2, C) C_6H_6, D) CCl_4, E) neat THF.

where [M*] is the concentration of active sites which is equal to the initiator concentration provided initiation is fast and quantitative, and DP_n is the degree of polymerization. Polymerization is usually stopped at low conversion, e.g., less than 20% in order to synthesize poly(THF) with a narrow molecular weight distribution[145-147].

Various initiators lead to the living polymerization of THF. Ionic initiators such as $Et_3O^+BF_4^-$, $Et_3O^+AsF_6^-$, $Et_3O^+PF_6^-$, and $Et_3O^+SbF_6^-$, have faster initiation rates and the propagating species in the polymerization is exclusively the oxonium ion[148]. In contrast, superacid esters have slower initiation rates and the propagating species is an ionic species which is in equilibrium with covalent esters[149-150]. Table 12 shows kinetic data of the initiation of the THF polymerization with three superacid esters, which are compared with the corresponding data with a typical ionic initiator, $Et_3O^+BF_4^-$. The rate constant of superacid esters are much smaller than that of $Et_3O^+BF_4^-$. In addition, the initiation processes with superacid esters are characterized by lower activation enthalpy($\Delta H_i^{\neq}$) (favorable) and more negative entropy($\Delta S_i^{\neq}$). This tendency has often been observed in various dipole-dipole S_{N2} reactions producing ionic species, e.g., in the Menschutkin reaction[151].

$$R_3N \ + \ RX \ \rightarrow \ R_4N^+X^-$$

In polymerization initiated with ionic initiators, macroion pairs coexist with free macroions. Interestingly, the reactivities of the both species were reported to be of equal scale[144] though earlier findings reported *normal* scale[152-153]. The influence of the anion structure on the rate constant of propagation was reported and the ionic propagating rate constant apparently does not depend on the anion structure[148,154]. When polymerization is initiated with superacid esters, on the other hand, macroion pairs coexist with macroester with equilibrium as in equation 35[155-157].

	Initiators			
	FSO_3Et	$ClSO_3Et$	CF_3SO_3Et	$Et_3O^+BF_4^-$
$k_i \times 10^5$ at 0 °C	0.33	0.38	0.80	6.1 [b]
$\Delta H_i^{\neq}$ (Kcal/mol)	13.5	12.8	10.5	16.4
$\Delta S_i^{\neq}$ (e.u.)	-34	-37	-44	-16

[a] Data from [150].
[b] At 2.5 ° C.

$$-(CH_2)_4\text{-}O\text{-}(CH_2)_4\text{-}OSO_2CF_3 \quad \underset{k_{tt}^{\pm}}{\overset{k_{tt}^{\pm}}{\rightleftharpoons}} \quad -(CH_2)_4\text{-}^+O \qquad (35)$$
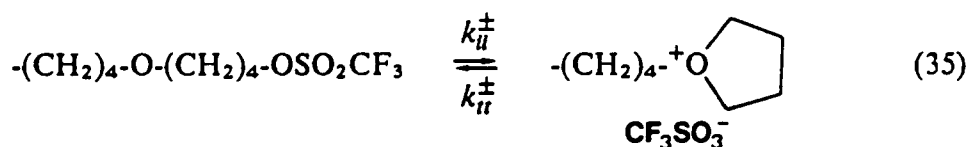
$$CF_3SO_3^-$$

The rate constant of collapse of an ion-pair with $CF_3SO_3^-$ anion is close to the rate constant of monomer addition to the growing cation. The ratio of rate constants, $k_{tt}^{\pm}/k_{tt}^{\pm}$, depends on solvent polarity and the total concentration of the active species due to the formation of higher aggregates of macroion pairs[158]. The reactivity of macroester is much lower than that of the macroion pair, approximately 10^{-2} times depending on the polarity of the medium, so that the formation of the ester may be regarded as a temporary termination[156-157,159-160]. Table 13 shows the rate of propagation in the polymerization of THF initiated by some initiators.

c) Living Polymerization of Oxazoline

A number of cyclic monomers containing imino ether linkage[166]($-N=C\text{-}O-$) have been successfully polymerized by cationic ring-opening polymerization, which include 2-oxazolines($\underline{3}$), 5,6-dihydro-4H-1,3-oxazines($\underline{4}$), 2-iminotetrahydrofurans($\underline{5}$), ethylene iminocarbonates($\underline{6}$) and 2-imino-1,3-oxazolidines($\underline{7}$).
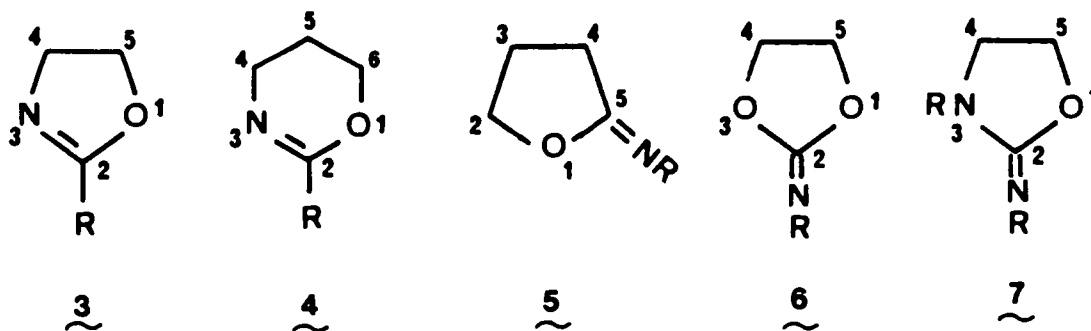
Table 13. Rate Constant of Propagation in the Polymerization of THF

Initiator	Solvent	Temp.($^\circ$ C)	k_p	Reference
$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	0	4.8×10^{-3}	139
$Et_3O^+BF_4^-$	CH_2Cl_2	-0.5	1.4×10^{-3} [a]	161
$Et_3O^+AsF_6^-$	CCl_4	0	9.8×10^{-3}	148
$Et_3O^+SbF_6^-$	CCl_4	0	9.8×10^{-3}	148
$CH_3CH_2\,^+COSbF_6^-$	bulk	0	3×10^{-3}	147
$CH_3CH_2\,^+COSbF_6^-$	CH_2Cl_2	25	2.7×10^{-3}	162
$CH_3CH_2\,^+COSbF_6^-$	bulk	25	3.1×10^{-3}	162
$Ph\,^+COSbF_6^-$	bulk	25	3.1×10^{-3}	162
$Ph_3C^+SbCl_6^-$	bulk	50	1.4×10^{-2}	163
FSO_3Me	CH_2Cl_2	0	1.7×10^{-3} [b]	164
CF_3SO_3Et	CH_2Cl_2	0	1.7×10^{-3} [b]	157
CF_3SO_3Et	CCl_4	0	8.4×10^{-4} [b]	157
$Et_3Al + H_2O + P$ [c]	bulk	0	6.4×10^{-3} [b]	165

[a] Ion pair reactivity.
[b] Apparent rate constant.
[c] p = Epichlorohydrin, propylene oxide, or β-propiolactone.

Among these, 2-oxazolines are the most exclusively studied monomers. The main driving force of these polymerizations is the isomerization of the reactive imino ether linkages to produce the thermodynamically more stable amide bond $-\overset{\mid}{\underset{\mid}{N}}\text{-}C = O$. Hence, polymerization usually reaches completion, without the formation of macrocyclization or equilibrium monomer concentration which is often observed in a ring-opening polymerization.

Cyclic imino ethers are highly nucleophilic monomers, perhaps second only to cyclic amines. Their polymerization can be initiated by various kinds of cationic initiators[166-167]. They may be classified into several categories: Metal halides of the Friedel-Crafts type and stable salts such as $BF_3O(C_2H_5)_2$ or SbF_5, Lewis acids of metal halides such as $SnCl_4$ or $TiCl_4$, strong protic acids and their salts with monomers such as sulfuric acid or p-toluenesulfonic acid, esters of sulfuric, sulfonic, and picric acids, and acid anhydrides such as dimethyl sulfate or methyl p-toluenesulfonate, and weak cationogenic compounds such as alkyl halides.

2-Alkyl-2-oxazolines are nucleophilic enough to be polymerized in the presence of Br^- or I^- gegenions, i.e., it successfully competes with Br^- and I^- during propagation. Also molecular iodine is usable[168]. With Cl^-, however, polymerization proceeds very slowly. n-Butyl chloride was found to be inactive for polymerization of 2-oxazoline[169].

The polymerization of 2-oxazoline has been studied by several workers since the 1960's [170-174] and has been further developed by Saegusa et al. The latter authors observed directly the active species for the first time by using NMR spectroscopy, and determined the rate constants of initiation and propagation in the presence of different initiators[175]. An interesting finding in a series of mechanistic studies of the polymerization of various oxazolines is the fact that there are two different mechanisms concerning the nature of propagating species[169,176-181]. Depending on the nature of the counter anion which is derived from the initiator, the propagation of polymerization

proceeds via either ionic or covalent species. There is also a difference between unsubstituted oxazoline and a substituted one. When the polymerization of unsubstituted oxazoline is initiated with MeI, polymerization proceeds via a propagating species of a covalent alkyl iodide which has electrophilic reactivity.

MeI + [oxazoline] $\xrightarrow[\text{slow}]{k_i}$ [oxazolinium I⁻] $\xrightarrow{\text{fast}}$ MeNCH₂CH₂I, HC=O

$$Me\underset{HC=O}{N}CH_2CH_2I$$

[oxazoline] $\xrightarrow{k_p}$ [Me−N(HC=O)−CH₂CH₂−N(oxazolinium) I⁻] $\longrightarrow$ MeNCH₂CH₂NCH₂CH₂I, HC=O HC=O

(36)
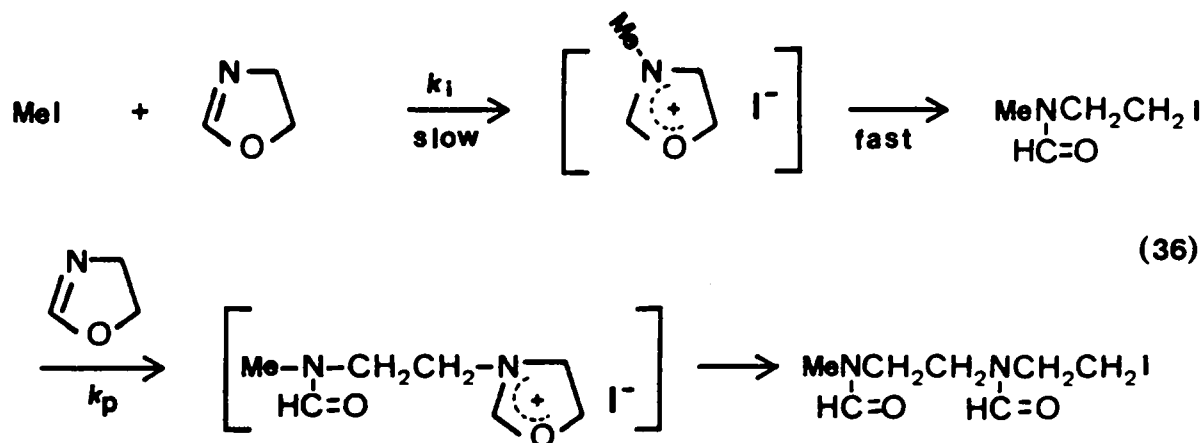
When the polymerization is initiated with methyl tosylate(MeOTs), however, polymerization proceeds via an ionic propagating species, oxazolinium tosylate.

MeOTs + [oxazoline] $\xrightarrow{k_i}$ [oxazolinium] ⁻OTs

[oxazoline] $\xrightarrow{k_p}$ Me−N(HC=O)CH₂CH₂−N[oxazolinium] ⁻OTs

(37)
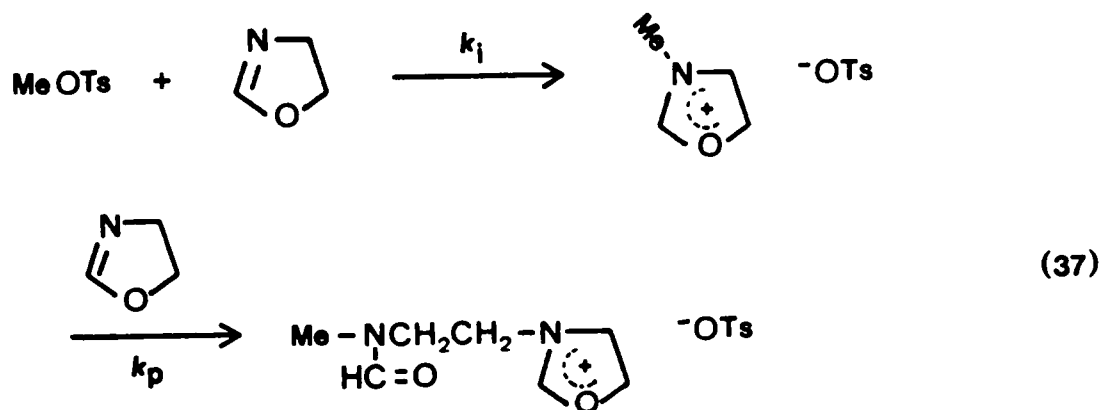
Nucleophilicity of a gegenion is, therefore, closely related to the nature of a propagating species. A highly nucleophilic gegenion tends to make covalent active species and a poor nucleophile makes ionic active species. The presence of an electron donating substituent in the oxazoline monomer, on the other hand, stabilizes the cation in the

ionic intermediates, and so promotes ionic active species. This relation can be seen in Table 14[182]. The rate of polymerization of an ionic intermediate is much faster than that of a covalent intermediate.
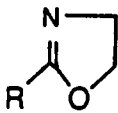
The rate of polymerization becomes faster in polar solvents than in nonpolar ones[176]. A solvent of great nucleophilicity such as pyridine or DMSO, however, coordinates strongly to the propagating end, thereby preventing the coordination of the incoming monomers; k_p is, therefore, decreased[176,183]. The nucleophilic reactivity of 2-substituted 2-oxazolines toward methyl p-toluenesulfonate(reflected in the k_i values) has been found to be in the order 2-CH$_3$ > H > 2-C$_6$H$_5$; The order of polymerizability by methyl p-toluenesulfonate initiator is H > 2-CH$_3$ > 2-C$_6$H$_5$. Assuming that the polymerizability, which is estimated from k_p values, is governed by the nucleophilic reactivity of a monomer and the ring-opening reactivity of the corresponding oxazolinium ion, it can be concluded that the ring-opening reactivity of propagating ions is in the order of H > 2-C$_6$H$_5$ > 2-CH$_3$[184]. In the copolymerization of 2-oxazolines the ease of monomer incorporation into the polymer parallels the monomer basicities, benzyl > methyl > isopropyl > phenyl[185].

d) Living Polymerization of N-Vinyl Carbazole

N-Vinyl carbazole(NVC)[186] is among the most reactive vinyl monomers in cationic polymerization. Its high cationic polymerizability arises from the electron-donating carbazolyl pendant, which also serves to stabilize the propagating NVC cation by providing a conjugating system where the positive charge is delocalized as in equation 38.

Due to its high reactivity the polymerization of NVC can be initiated by various kinds of cationic initiators: protic acids such as HCl, HBr, HI[187], AcOH[188], or

Table 14. Polymerization Mechanisms of Oxazoline in CH_3CN[a]

R in	Initiator	$k_p \times 10^4$(° C) (l/mole.s)	Ionic(I) or Covalent(C)	$\Delta E_p^{\neq}$ (kcal/mole)	$A_p^{\neq}$ (l/mole.s)
H	MeOTs	19(40)	I	25	7.5×10^{14}
H	MeI	0.18(40)	C	13.5	5.0×10^5
CH_3	MeI	1.14(40)	I	17.4	1.7×10^8
CH_3	$PhCH_2Br$	1.2(40)	I	17.1	1.1×10^8
CH_3	$PhCH_2Cl$	0.03(40)	C	14.8	6.5×10^4

[a] Data from [182].

HNO$_3$[189], stable carbenium salts such as tropylium salts[41b,190-191] or trityl salts[41a,132a], esters such as diethyl sulfate[192], metal perchlorate such as AgClO$_4$[193-194], Grinard reagents such as n-BuMgBr[195-196], phosphorus derivatives such as PCl$_3$[197], and various oxides[198-200]. Among these catalysts, only I$_2$, HI, and HI/I$_2$ are known to produce living polymerization[201].

$$\sim CH_2\text{-}CH^+ \quad \longleftrightarrow \quad \sim CH_2\text{-}CH \quad\quad (38)$$
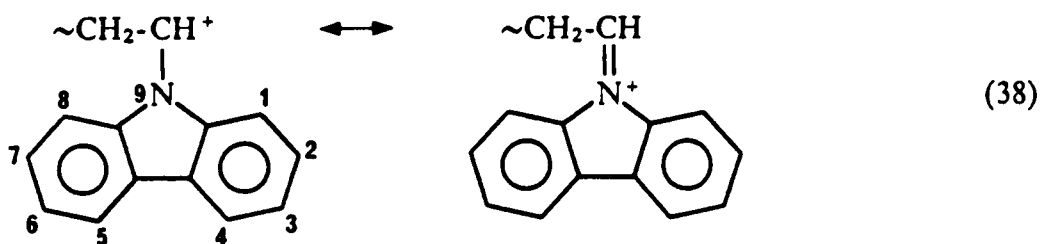
When polymerization was conducted by either HI, I$_2$, or HI/I$_2$ in a nonpolar solvent such as toluene[24], at low temperatures, it showed living behavior, but poly(NVC) has limited solubility in the nonpolar solvent. Therefore precipitation occurred. Also, when polymerization was initiated by iodine in either CH$_2$Cl$_2$ or CH$_2$Cl$_2$/CCl$_4$ mixed solvent at -50°C[202], the number average molecular weight of the polymers increased linearly with increasing monomer conversion, and by further addition of a new monomer feed to a completely polymerized solution. However, when polymerization was conducted in CH$_2$Cl$_2$ at -78°C[203], the iodine alone could not make living polymerization, but needed the presence of common ion salt, n-Bu$_4$NI, in the range of $0.5 \leq$ [n-Bu$_4$NI]/[I$_2$]$_0 \leq 1.0$. The number of polymer chains formed was half the amount of the initial iodine concentration, i.e., one living chain was formed from two iodine molecules. At higher temperatures($\geq$ -30°C) the system was not living. The best result(MWD: 1.18~1.26) was obtained when the polymerization was initiated with HI in CH$_2$Cl$_2$ at -78°C[24], in the presence of n-Bu$_4$NI(1 mole % to HI concentration), which suppresses the ionic dissociation of the propagating species in polar media[201].

The polymerization in salt free CH_2Cl_2 was very rapid and was not living. Addition of a small amount of the common ion salt retarded the polymerization remarkably and gave quantitative conversion of NVC. Whereas a higher salt concentration(salt/HI = 1/40) retarded the polymerization so much that the conversion apparently leveled off at a low percentage.

In the absence of the salt, the propagating species is dissociated and becomes reactive because of the polarity of CH_2Cl_2, and it induces a rapid polymerization where initiation is slower than propagation. Thus a broad molecular weight distribution results though the lifetime of the intermediate is long enough to maintain the linear increase in the polymer molecular weight given sequential addition of the monomer. In contrast, the added common ion salt suppresses the dissociation of the growing chain end, in turn rendering propagation slower than initiation, and creating a narrow molecular weight distribution of the polymers. This concept of dissociation suppression via common ion salts is closely related with two internal factors: the stability of the growing carbocation derived from a monomer and the nucleophilicity of the gegenion derived from an initiator. The relationship is represented in Figure 2.

e) Polymerization by the "Inifer" Technique

When a polymerization is initiated with halogen containing Lewis acids, the modes of termination(or transfer) become different depending on the types of halogen in the catalyst. One example is the different behavior between similar two catalysts such as BCl_3 and BF_3. For BF_3 initiated polymerization, the major mode of termination is via the chain transfer to the monomer with the generation of a double bond at the polymer chain end. Combination with an OH^- gegenion also creates a minor contribution.

However, the termination in the BCl_3-initiated polymerizations of isobutylene and styrene occurs almost exclusively by combination with chloride as in equation 39[47].

$$\sim CH_2C^+(CH_3)_2(BCl_3OH)^- \rightarrow \sim CH_2\text{-}C(CH_3)_2Cl + BCl_2OH \qquad (39)$$

When isobutylene is polymerized with BCl_3 in the presence of p-dicumylbenzene chloride, i.e., when the gegenion is BCl_4^-, the polymer formed consists of α,ω-bifunctional polyisobutylenes which contain chloride at the both ends of a chain[204-205]. The existence of the chloride is further confirmed by block copolymerization with α-methylstyrene[9]. In this polymerization the alkyl halide, 8 , functions

$$Cl - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \bigcirc - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Cl \qquad (\equiv \text{X-R-X})$$

<u>8</u>
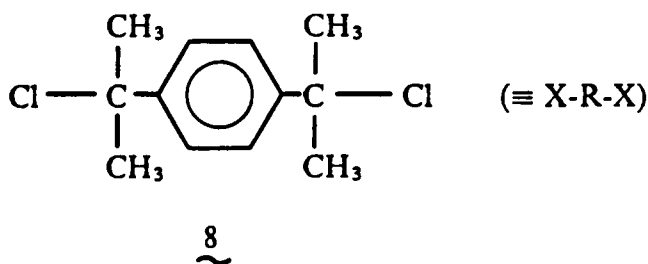
simultaneously as the initiator and transfer agent, so the name "inifer" was introduced(initiation-transfer agent). Inifers X-R-X must fulfill two functions simultaneously: as initiators they must initiate two-kinetic chains $^+$C-R-C$^+$, and as bifunctional transfer agents they must affect the following chain transfer sequence:

$$\sim C^+ + \text{X-R-X} \rightarrow \sim CX + \text{X-R}^+$$

$$\text{X-R}^+ + M \rightarrow \text{X-RM}^+ \xrightarrow{nM} \text{X-R}^+ \qquad (40)$$
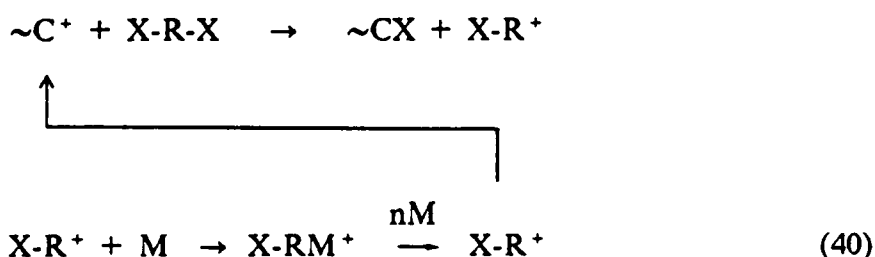
The collapse of the ion pair in this polymerization, which is a similar reaction to that in equation 38, is regarded as an irreversible termination. The frequency of these events is considered to be low compared to that of the transfer to inifer. According to a thorough analysis of the mechanism, the molecular weight distribution of Cl-polyisobutylene-Cl prepared by the inifer technique must be 1.5, and this was corroborated by experiments[206]. However, when the inifer was monofunctional(cumyl chloride) rather than di- or tri-functional[207], the polymerization was not ideal but needed a *proton trap*(2,6-di-t-butyl pyridine) to control the functionality of the product[208-209].

The concept of inifer is certainly of importance in the preparation of telechelic polymers[210] in the field of cationic polymerization. But the negligible influence of ion pairs[211] and possibility of self ionization of BCl_3[212] make it difficult for one to refine the description of the polymerization by "inifer" technique. Interestingly, the initiation system of bifunctional acetates/BCl_3 was reported to have the capability to make a living polymerization of isobutylene[11,213]. Terminal chain ends of the resultant polymers after polymerization were found to have one chlorine atom at each end in order to be telechelic. This inifer system can be compared with the lactone/BCl_3 initiation system in the ring expansion polymerization[214].

f) Polymerization via Modified Carbocation or Oxonium Ions

In order to achieve living cationic polymerization of vinyl compounds, the counter ions have to interact strongly with the propagating carbocations and thereby stabilize the active chain ends[201]. One way is to make the lifetime of the growing species longer by stabilization via the strong cation-anion interaction, as in the 'covalent' propagating

species. And another way is to create a less reactive active chain end by some modifications.

Recently, the polymerization of isobutyl vinyl ether was investigated in the presence of ether compounds[15]. When the polymerization was initiated with ethylaluminum dichloride in conjunction with a stoichiometric excess of dioxane(5~10%) in n-hexane at 0°C, well-defined living polymers were obtained. This finding is quite interesting when one compares it with the non-living behavior of the polymerization initiated by ethyl aluminum dichloride in the absence of any other compound. In the presence of dioxane, the number-averaged molecular weight of the polymers increased in direct proportion to polymerization conversion and the molecular weight distribution stayed quite narrow(Mw/Mn = 1.1~1.25). As the amount of ether compounds increased, the rate of polymerization became slower, and the molecular weight distribution became narrower.

A good result was (MWD = 1.1~1.25) obtained for a rather high concentration of dioxane(10 volume % which was the same concentration as that of the initial monomer). Similar behavior was observed for THF and Et$_2$O. Interestingly, the amount of added ethers needed for living polymerization depended on their basicity; Et$_2$O > Dioxane > THF.

(41)
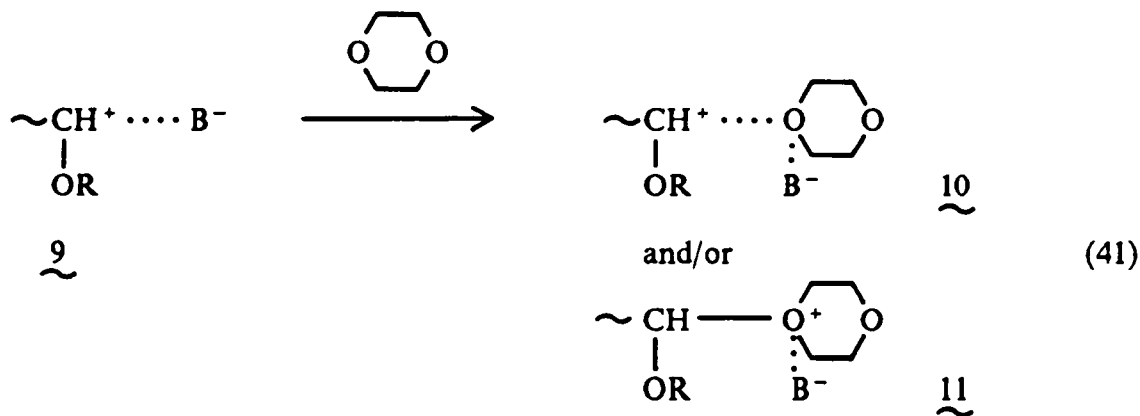
From the above observations, the role of an ether compound in the polymerization was proposed that the ether may solvate the growing carbocation(as in 10) and/or may even form an oxonium ion 11 that is much more stable than the carbocationic species 9. Therefore the stabilization mechanism is different from the mere cation-counteranion interaction. This reveals that not only a gegenion, but also an externally added basic compound can prolong the lifetime of the propagating carbocation.

6. Synthesis of Functionally Terminated Prepolymers

The term *prepolymer* originated in the field of thermoset plastics, and refers to an incompletely polymerized polymer which can be poured into an appropriate mold and can then be cured[215]. But generally, a prepolymer refers to a low-molecular-weighted polymer that can be reacted to increase its molecular size.

When a prepolymer has its reactive functional groups at its chain ends, it may be called a functionally terminated prepolymer or an end-functionalized prepolymer. This in turn can be further divided into more categories such as macromonomers, telechelic prepolymers, and others. For these species the molecular weights generally range from 1,000 or less to 20,000 or more. But the distinction between these species is not always clear because the definitions of these species are based on different criteria. If a polymer has an end-functional group which can participate further in the polymerization processes, giving access to graft copolymers, then it is called a **macromonomer**[2]. But if a polymer has end-functional groups at both ends of the chains or at every end of the chain, then it is called a telechelic polymer. The difference is well-represented in Figure 4.

Macromonomers

$$—CH{=}CH_2$$

$$—CH{-}CH_2 \atop \diagdown O \diagup$$

$$—CH{\diagup X \atop \diagdown X}$$

$$CH_2{=}CH———CH{=}CH_2$$

$$X———X$$

Telechelics

$$———X$$
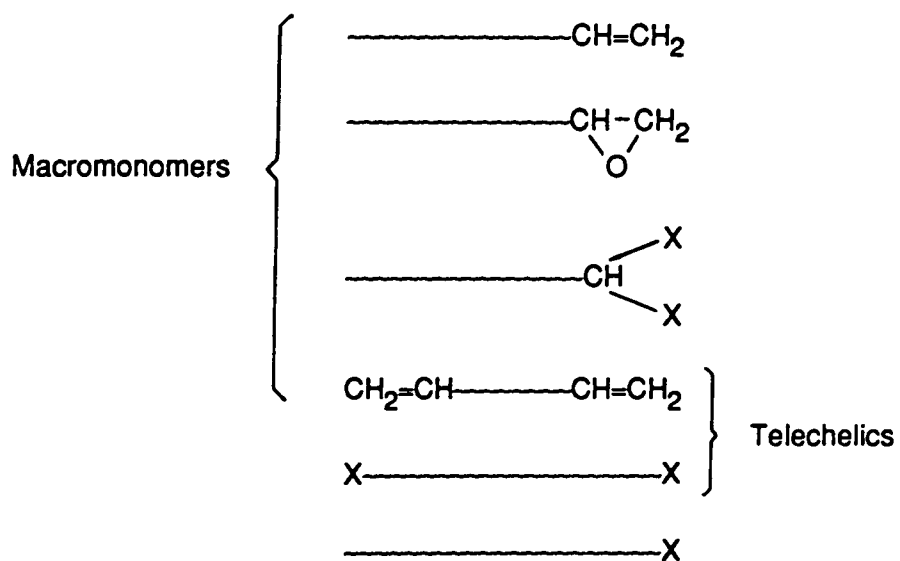
Figure 4. Functionally terminated prepolymers: X = -OH, -NH$_2$, -COOH, -Cl, etc.

Macromonomers, often called macromolecular monomers or **Macromer®**(trade mark of CPC International Inc.), are linear macromolecules carrying at their chain end some polymerizable functional groups[216]. In most cases, this functional group is an unsaturated group, but it also be an oxirane ring or another heterocycle that can undergo polymerization. Macromonomers can also be bifunctional carrying an active double bond or an adequately reactive heterocycle at each end of their chains. Polymerization of such species should result in network formation. Polymer chains bearing at one end two functions which are able to participate in a stepwise growth process(polycondensation reaction) can also be referred to as macromonomers. But if the functional groups are at both chain ends, they are called telechelic polymers because they can be incorporated into a linear polycondensate, but not as a chain extension involving branching. On the other hand, polymer chains bearing only one functional group which is able to participate in a condensation reaction, cannot be referred to as macromonomers or telechelics but as just functionally-terminated polymers.

A considerable amount of work has been done in recent years in universities and in industrial laboratories to synthesize well-defined prepolymers of various kinds, to characterize them thoroughly and to examine their ability in copolymerizations. The interest devoted to these species arises from the fact that they are useful intermediates in polymer synthesis. In particular, they give easy access to the structural design of copolymers via graft and block copolymers. The important parameters/properties of the polymer such as thermal, processability, mechanical, optical, chemical resistance, transport, surface behavior, and blending characteristics can be well controlled, by a proper structural design of a polymer. The area of block and graft copolymers has been well reviewed by many workers[3,217-229].

A great variety of methods have been developed to synthesize functionally-terminated prepolymers by ionic, radical, or two step processes. In this review, the gen-

eral synthetic features of the variety of methods will be discussed. Furthermore, the synthetic methods involving ionic living polymerizations - *initiator and end-capping methods* - will be discussed because the ionic living polymerization techniques are well suited to synthesize prepolymers, of molecular weight chosen at will, of narrow MWD, and carrying quantitative functionality.

a) General Synthetic Features of Functionally Terminated Prepolymers

Functionally terminated prepolymers are prepared by many techniques, for example, by step polymerizations or by chain polymerizations such as radical, anionic, and cationic polymerizations. Among these, the preparation methods by step polymerizations are quite obvious. Stoichiometric imbalance of A-A and B-B types of monomers leads to the preparation of telechelic prepolymers of designed molecular weight utilizing the Carothers equation[230-231]. Some elegant applications of this equation can be seen in many areas of polymer synthesis. The synthesis of an amine-terminated poly(ether sulfone) or a maleimide-terminated poly(ether ether ketone) is one good example of the application[232] of that equation. In polymerization, the third type of monomer such as B-C as well as A-A and B-B is employed. The functional group C does not react with A nor B during the polymerization reaction. The resultant polymer becomes a C-terminated telechelic polymer if the stoichiometric balance is provided between A and B. The molecular weight is determined by the relative ratio of B-C to the A-A and B-B. This relationship is represented in equation 42.

$$x \text{ A-A } + (x-1) \text{ B-B } + 2 \text{ B-C } \rightarrow \text{ C-B-(-A-A-B-B-)}_{x-1}\text{-A-A-B-C} \qquad (42)$$

The derivatization of a functional group into a different functional group is another method of preparation. For example, the hydroxyl group in polyethylene oxide is reacted with succinic anhydride to make a carboxylic acid functional group. This then is reacted with glycidyl methacrylate[233].

Another example is the preparation of amine-terminated polysiloxane via equilibrium polymerization(ionic polymerization)[234]. In this polymerization, tetra dimethylsiloxane("D_4") is reacted in the presence of a bifunctional compound such as bis(3-aminopropyl) tetramethyl disiloxane or similar acid[235]. Again, the amine functional group is not involved in the polymerization reaction. The molecular weight of the resulting polymer is controlled by the amount of the disiloxane which acts as an endblocker.

The preparation method of a functionally terminated prepolymer by chain polymerization reaction is very versatile. Many attempts have been made to utilize anionic polymerization, radical polymerization and recently, cationic polymerization. However, all these preparation methods by chain polymerization reaction have two common features in their synthetic schemes, i.e., the polymerizations are either initiated with functional initiators or terminated with end-capping agents.

In living ionic polymerizations, these two schemes are quite simple because the reactions themselves are quite predictable. And even in the radical polymerizations which are more complex than the living ionic systems, those two schemes are well applied. The preparation methods via ionic polymerization will be reviewed in the next two sections.

In a radical polymerization, a radical formed upon homolytic cleavage of a functional initiator carries the corresponding functional group. Since upon initiation the primary radical adds to a monomer, this functional group remains attached to the formed polymer molecule. Typical functional free radical initiators include the derivatives of azobisisobutyronitrile, such as 4,4'-azobis(4-cyanovaleric acid), 12, and

4,4'-azobis(4-cyano-n-pentanol)[236-239], 13, or diethyl 2,2'-azobis(isobutyrate)[240]. The hydroxyl groups are also incorporated by the initiation with H_2O_2[241-242].

$$HOOC-(CH_2)_2 \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} - N=N - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} (CH_2)_2-COOH$$

12

$$HO-(CH_2)_3 \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} - N=N - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} (CH_2)_3-OH$$
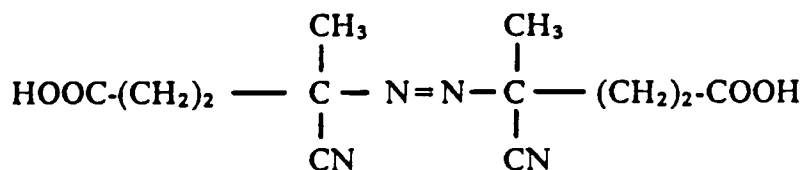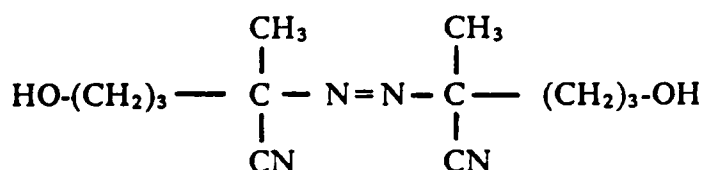
13

However, this functionalization procedure, i.e., the initiation by a radical initiator, is far from being ideal due to chain transfer to monomer or solvent, and due to the concurrence of disproportionation and recombination. Control of the molecular weights of the polymers formed under standard experimental conditions is not possible. Only by carrying out polymerization in the presence of a large amount of a functional radical initiator, it is possible to lower the molecular weight of the formed polymer[243].

On the other hand, the functionalization by radical chain transfer is more successful in the control of molecular weight and functionality. Functionalization at only one chain end can be achieved by means of efficient functional transfer agents which simultaneously allow functionalization and adequate control of the molecular weight. A large value of chain transfer coefficient, C, , is essential for this purpose. Typical functional chain transfer agents include 2-mercaptoethanol, $HS-CH_2CH_2-OH$[244], thioglycolic acid, $HS-CH_2-COOH$[245-246], thiomalic acid, $HOOC-CH_2CH(SH)-COOH$[247], α-thioglycerol, $HS-CH_2-CH(OH)CH_2OH$[248], and iodoacetic acid[249].

The combination of a functional initiator and a functional chain transfer agent can be used for functionalization[250], and a telomerization reaction can also be used[251]. Equation 43 shows the functionalization process by using thioglycolic acid.

$$\sim CH_2\text{-}\underset{\underset{R}{|}}{CH}\cdot \quad + \quad HS\text{-}CH_2\text{-}COOH \quad \rightarrow \quad \sim CH_2\text{-}\underset{\underset{R}{|}}{CH_2} \quad + \quad \cdot S\text{-}CH_2COOH$$

$$HOOC\text{-}CH_2\text{-}S\cdot \quad + \quad CH_2 = \underset{\underset{R}{|}}{CH} \quad \rightarrow \quad HOOC\text{-}CH_2\text{-}S\text{-}CH_2\text{-}\underset{\underset{R}{|}}{CH}\cdot \tag{43}$$
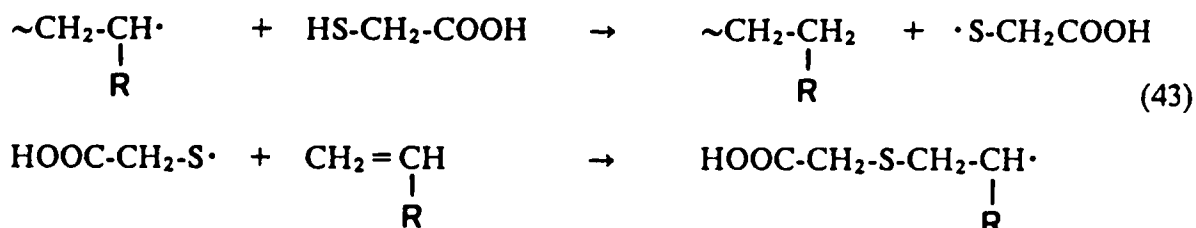
In the polymerization, the existence of a mixture of functional and nonfunctional ends is expected. Experimental data, however, reveals that there is greater functionality than is predicted due to the selective reaction of the initiator with the chain-transfer agent in the initiation process[252].

Besides chain polymerization, functionalization can be attained by addition polymerization. A good example is the Michael addition reaction of an amine to the styrenic double bond[253-256]. p-Divinyl benzene is reacted with N,N'-diethyl ethylenediamine in the presence of a lithiated diamine. The reaction is fast and a monoadduct is formed by using a stoichiometric amount of the amine to the double bond. After purification, the monoadduct is further reacted via the Michael type self addition reaction in the presence of lithium diisopropylamide.

$$CH_2 = CH\text{-}\langle\bigcirc\rangle\text{-}CH = CH_2 \quad + \quad \underset{\underset{C_2H_5}{|}}{HN}\text{-}CH_2CH_2\text{-}\underset{\underset{C_2H_5}{|}}{NH} \quad \xrightarrow{\quad BuLi \quad}$$

$$CH_2 = CH\text{-}\langle\bigcirc\rangle\text{-}CH_2\text{-}CH_2\text{---}\underset{\underset{C_2H_5}{|}}{N}\text{-}CH_2CH_2\text{---}\underset{\underset{C_2H_5}{|}}{NH} \quad \xrightarrow{\quad (iPr)_2NLi \quad} \tag{44}$$
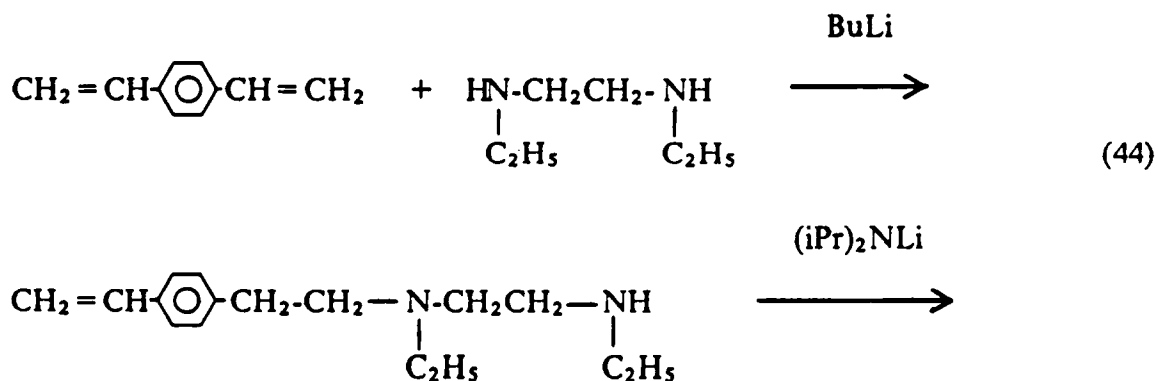
Functionally terminated prepolymer

The same kind of addition reaction can be performed with substituted bisacryl amides such as bisacryloyl piperidide and N,N'-dimethyl ethylenediamine. However, the difference in the reactivity between the two acrylic double bonds is much less pronounced than in the case of p-divinyl benzene, so that a mere polyaddition reaction occurs. Using a proper stoichiometric imbalance, telechelic prepolymers of a known molecular weight have been obtained[257-258].

$$CH_2=CH\text{-}CO\text{-}N\underbrace{}N\text{-}CO\text{-}CH=CH_2 \quad + \quad \underset{\underset{CH_3}{|}}{NH}-CH_2\text{-}CH_2-\underset{\underset{CH_3}{|}}{NH} \quad \longrightarrow$$

$$\tag{45}$$

$$CH_2=CH\text{-}CO\left[N\underbrace{}N\text{-}CO\text{-}CH_2CH_2\underset{\underset{CH_3}{|}}{N}CH_2CH_2\text{-}\underset{\underset{CH_3}{|}}{N}\text{-}CH_2CH_2\text{-}CO\right]_n N\underbrace{}N\text{-}CO\text{-}CH=CH_2$$
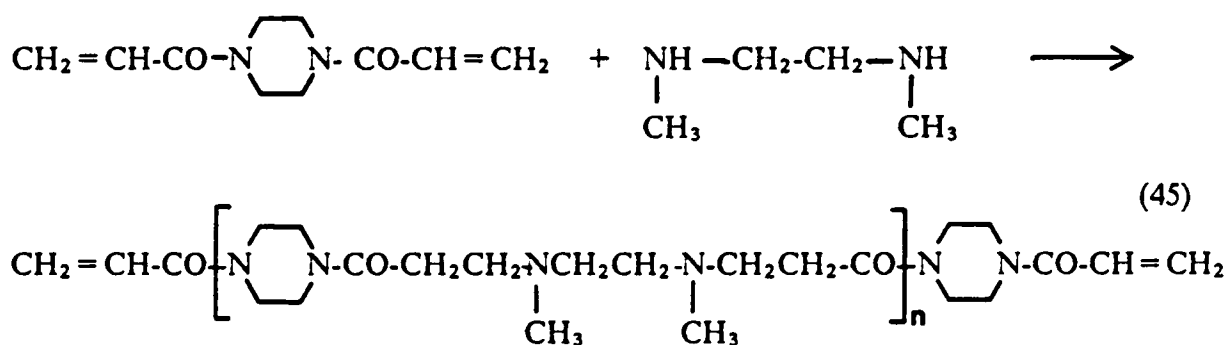
b) Synthesis via Functional Initiators

In this and the next sections, preparation methods utilizing ionic living polymerizations will be reviewed.

In a living polymerization, the absence of spontaneous termination and transfer reactions makes the synthesis of well-defined functionally terminated prepolymers possible. If the initiation by a functional initiator proceeds by addition to the monomer chosen and if the functional group of the initiator is insensitive to the attack by the active intermediate(anion or cation), the process should yield a functionally terminated prepolymer. Most frequently used functional groups include the carbon-carbon double bond, and cationically or anionically polymerizable monomers.

However, when a functional initiator utilized in an anionic polymerization contains an unsaturated double bond, there are some drawbacks:
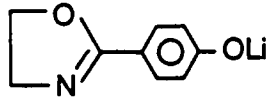
1. Efficiency is impeded by the fact that the unsaturated double bond is generally sensitive to the attack by reactive carbanions whereby branched structures are formed. But if the polymerization involves oxirane monomers, the functional group(the carbon-carbon double bond) is quite insensitive to the attack of an alkoxide.

2. The rate of initiation by a less reactive initiator such as a vinyl lithium compound is fairly slow for the styrene monomers, so the molecular weight distribution becomes broader.

3. An allylic type double bond at the chain end is not adequate for the subsequent radical copolymerization because of its low reactivity towards radicals and of the isomerization that can take place.

Thus, the use of functional initiators in anionic polymerizations is good for the polymerization of heterocyclic monomers. Recently a protected functional initiator is used in group transfer polymerization in order to make telechelic hydroxyl functional PMMA. After the polymerization, p-(bromomethyl) benzyl bromide is added to induce coupling, and the protecting group(trimethyl silyl) is replaced by a proton[121].

Table 15 shows the available combinations of monomers and functional initiators in anionic polymerization.

In cationic polymerization, functional initiators were used usually in the polymerizations of heterocyclics because almost olefinic and vinylic monomers do not produce living cationic species. THF and oxazolines are the most studied monomers because they undergo living polymerizations.

Table 15. Functional Initiators in Anionic Polymerization

Initiator	Monomer	Reference
$CH_2=CH$–⟨O⟩–MgCl	MMA vinylpyridine	259 259
$CH_2=CHLi$	styrene	260, 261
$CH_2=CH\text{-}CH_2Li$	styrene	262
![H2C=C(CH3)–⟨O⟩–CH2OK]	![epoxide]	263, 264
![oxazoline–⟨O⟩–OLi]	![epoxide]	265, 266
$(CH_3)_2C=C(O\text{-}CH_2CH_2\text{-}O\text{-}Si(CH_3)_3)(O\text{-}Si(CH_3)_3)$ + HF_2^-	MMA	113
trans-PhCH=CHCHO + ZnBr$_2$	$H_2C=CHOSiMe_2(tBu)$	121

For THF, propagation is a reversible process and an equilibrium monomer concentration can be defined at each temperature. The polydispersity of the prepolymer tends to be broader if the polymerization conditions approaching the *ceiling temperature* are used[267]. Many polymerizations of THF are initiated by using functional initiators which contain the methacryloyl group because the methacrylic carbon-carbon double bond does not polymerize cationically. The initiators are conveniently prepared in situ by a metathetic reaction between the corresponding acyl halides and $AgSbF_6$.

$$R\text{-}\overset{\displaystyle O}{\underset{\displaystyle X}{C}} \quad + \quad AgSbF_6 \quad \rightarrow \quad R\text{-}\overset{\displaystyle O}{C^+}\, SbF_6^- \quad + \quad AgX \qquad (46)$$
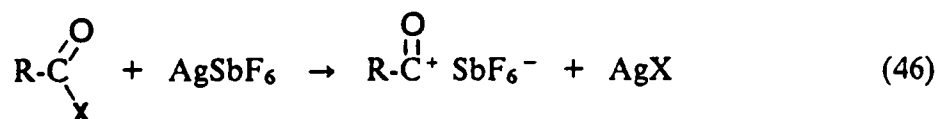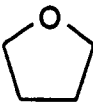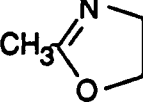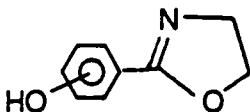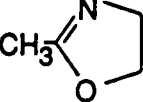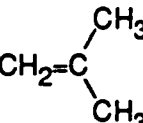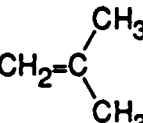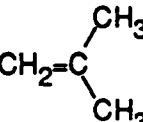
In the polymerization of THF, the polymerization process is carried out preferably in bulk, and around $0\sim10°C$, in order to prepare samples of low polydispersity. The process is stopped when the chains have reached the desired molecular weight. Deactivation is performed by the addition of an efficient nucleophile such as phenoxide[268], amine, phosphine[269], or lithium bromide.

Besides the carbon-carbon double bond, phenolic -OH terminated prepolymers are synthesized by the initiator method using oxazoline and isobutylene. The polymerization of isobutylene is not living, but the molecular weight is controlled by the inifer technique. Table 16 shows some functional initiators used in cationic polymerization.

c) Termination with Functional End Capping Agents

This method of deactivation has been more successful than the initiation method in the preparation of functionalized prepolymers. When a living ionic polymer is reacted with a functionalized capping agent in order to make a good prepolymer, the rate of

Table 16. Functional Initiators in Cationic Polymerization

Initiator	Monomer	Reference
$CH_2=\overset{\displaystyle CH_3}{\underset{\displaystyle}{C}}\text{-COCl}$ + AgSbF$_6$	(tetrahydrofuran)	264, 270
$CH_2=\overset{\displaystyle CH_3}{\underset{\displaystyle}{C}}$-⟨O⟩-CH$_2$Br + AgSbF$_6$	(tetrahydrofuran)	264
CH_2=CH-⟨O⟩-CH$_2$Br + AgSbF$_6$	(tetrahydrofuran)	264
⟨O⟩-CH=CH-CH$_2$Br + AgSbF$_6$	(tetrahydrofuran)	271
CH_2=CH-⟨O⟩-CHI	CH$_3$-(oxazoline)	272
HO-⟨O⟩-(oxazoline) + TfOMe [a]	CH$_3$-(oxazoline)	266
HO-⟨O⟩-$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}$-Cl + BCl$_3$	$CH_2=C\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}}$	273
$(CH_3)_2$C=CH-CH$_2$Cl + BCl$_3$	$CH_2=C\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}}$	274
CH_2=CH-⟨O⟩-CH$_2$Cl + BCl$_3$ + H$_2$O	$CH_2=C\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}}$	275
$CH_2=\overset{\displaystyle CH_3}{\underset{\displaystyle}{C}}$-COO-(CH$_2$)$_2$OCH=CH$_2$ + HI/I$_2$	CH_2=CH-O-iBu	276

[a] Methyl trifluorosulfonate.

termination has to be faster than the side reaction which can occur between the active chain end and the functional group. Functional groups include the carbon-carbon double bond, the hydroxyl group, amines, etc. Among these, the double bond is the one which has been studied the most exclusively.

In anionic polymerization, the functional capping agent is usually an unsaturated electrophile. Thus, there is possible competition between the termination reaction and the side reaction as in equation 47. Because these reactions are determined mainly by the nucleophilicity of the active chain end, electrophilicity of the end-capping agent and the polymerizability of the double bond have to be taken into consideration. Only the right combinations of the above two creates efficient capping reactions.

$$\tag{47}$$
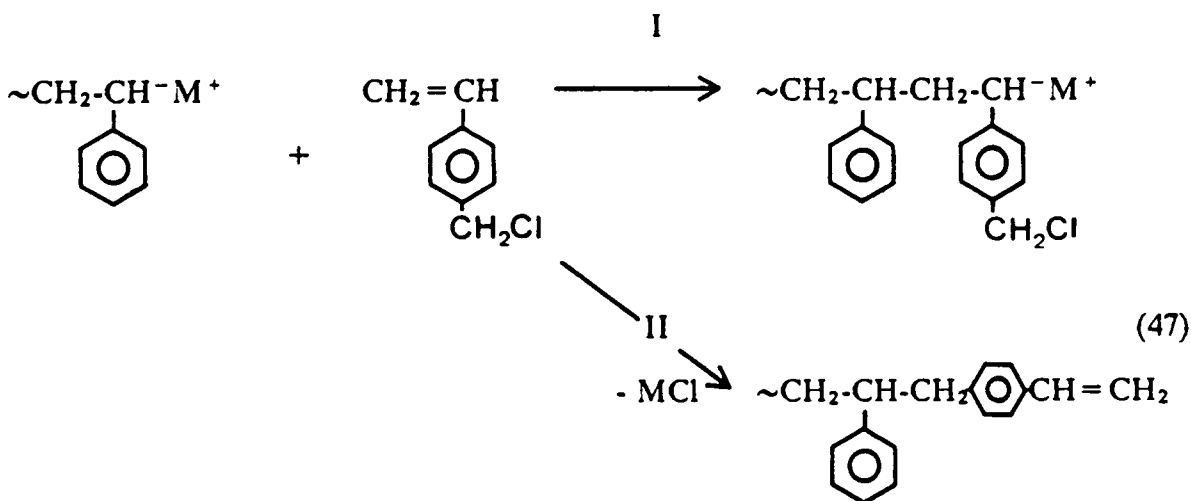
In order to suppress the side reaction I, a modification of the reactivity of the carbanion is necessary. When the gegenion is lithium, the reaction depends strongly upon the reaction medium, so the use of polar aprotic solvent such as THF is needed in order to suppress the side reaction[277]. However, the living carbanionic polystyrene formed with lithium or potassium gegenions cannot be reacted directly with an unsaturated electrophile such as methacryloyl chloride, because the high nucleophilicity of styrene carbanions gives rise to side reactions involving the double bond. An intermedi-

ate addition of diphenylethylene[278-279] or oxirane[278,280] is required to lower the nucleophilicity of the end-standing site, prior to the reaction with the end-capping agent. This has been extensively tested by Milkovich[278].

As the nucleophilicity of the living chain end decreases - polystyrene > polyvinylpyridine > polyalkylmethacrylate > polyethylene oxide - the chance of side reactions decreases. The nucleophilicity of vinyl pyridine carbanions is still rather high and therefore, an intermediate addition of oxirane is required when methacryloyl chloride is used as the capping agent. For alkyl methacrylate carbanion the intermediate addition of oxirane is of no help because this reaction is far from being quantitative. Direct deactivation by p-vinylbenzyl bromide at low temperature is preferable.

The right choice of end capping agent is also important in the successful preparation of prepolymers. Allyl halides, vinylbenzyl halides, methacryloyl chlorides, and vinylsilyl chlorides are the most frequently used end-capping agents. Among them, allyl bromide and vinylbenzyl bromide were tested to be good for living poly MMA[281], but the direct use of allyl halides in polystyrenic living polymer is accompanied by side reactions, and the use of the allyl group is not that desirable due to the low reactivity toward radical polymerization. Methacryloyl chloride is a good end-capping agent for less reactive nucleophiles such as alkoxides, but it is accompanied by side reactions for reactive nucleophiles such as styrenic or acrylate carbanions. On the other hand, there is a broader spectrum in its choice of nucleophiles if vinyl silyl chloride is used. It can be reacted indirectly after the addition of oxirane[282a].
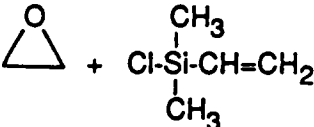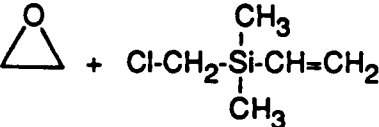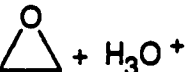
Generalizations about the correct combinations of nucleophiles and electrophiles cannot be made easily, since they are dependent upon the natures of each species in a reaction at given reaction conditions. Table 17 shows the list of some end-capping agents in anionic polymerization. This includes functional groups, other than the carbon-carbon double bond, as well as the carbon-carbon double bond.

Table 17. Functional Capping Agents in Anionic Polymerization

Monomer	Initiator	Deactivator	Reference
Styrene	BuLi	$BrCH_2CH=CH_2$	278
Styrene	CuK (Cumyl Potassium)	$BrCH_2CH=CH_2$	278
Styrene	BuLi	$ClCH_2$-⟨O⟩-$\underset{\underset{H(R)}{\mid}}{C}=CH_2$	277
Styrene	CH_3-⟨O⟩-CH_2K	$BrCH_2$-⟨O⟩-$CH=CH_2$	264
Styrene	CH_3-⟨O⟩-CH_2K	$CH_2=\underset{\underset{Ph}{\mid}}{C}$-Ph + $BrCH_2$-⟨O⟩-$CH=CH_2$	264
Styrene	CH_3-⟨O⟩-CH_2K	$CH_2=\underset{\underset{Ph}{\mid}}{C}$-Ph + $BrCH_2$-⟨O⟩-$\underset{\overset{CH_3}{\mid}}{C}=CH_2$	264
Styrene	BuLi	△O + $ClCH_2$-⟨O⟩-$CH=CH_2$	264
Styrene	CuK	△O + $ClCH_2$-⟨O⟩-$CH=CH_2$	278
Styrene	CH_3-⟨O⟩-CH_2K	△O + $BrCH_2$-⟨O⟩-$CH=CH_2$	264
Styrene	BuLi	$Cl-CO-\underset{\overset{CH_3}{\mid}}{C}=CH_2$	278
Styrene	BuLi	△O + $Cl-CO-\underset{\overset{CH_3}{\mid}}{C}=CH_2$	264
Styrene	CuK	△O + $Cl-CO-\underset{\overset{CH_3}{\mid}}{C}=CH_2$	278, 283

(to be continued)

Table 17 (continued)

Monomer	Initiator	Deactivator	Reference
Styrene	CuK	$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Cl\text{-}Si\text{-}CH\text{=}CH_2}}$	282
Styrene	CuK /BuLi	$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Cl\text{-}CH_2\text{-}Si\text{-}CH\text{=}CH_2}}$	282
Styrene	CuK /BuLi	$\triangle\!\!O$ + $Cl\text{-}Si\text{-}CH\text{=}CH_2$ (with CH_3 groups)	282
Styrene	CuK /BuLi	$\triangle\!\!O$ + $Cl\text{-}CH_2\text{-}Si\text{-}CH\text{=}CH_2$ (with CH_3 groups)	282
Styrene	CuK /BuLi	(succinic anhydride structure)	278
Styrene	CuK /BuLi	$Cl\text{-}CH_2CH_2\text{-}O\text{-}CH\text{=}CH_2$	278
Styrene	CuK /BuLi	$CH_2\text{=}\underset{Ph}{C}\text{-}Ph$ + $ClCH_2\overset{O}{C}\text{-}O\text{-}CH\text{=}CH_2$	278
Styrene	BuLi	CO_2 + H_3O^+	284
Styrene	BuLi	$ClCH_2\!\!\triangle\!\!O$ + H_3O^+	278
Styrene	BuLi	$\triangle\!\!O$ + H_3O^+	280

(to be continued)
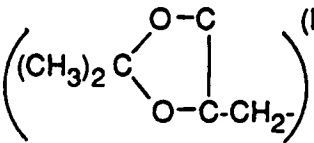
Table 17 (continued)

Monomer	Initiator	Deactivator	Reference
2-Vinylpyridine	C-C-Ċ-C-Ċ-Li (with C and Ph, Ph substituents)	BrCH$_2$-C$_6$H$_4$-C(CH$_3$)=CH$_2$	264
2-Vinylpyridine	(Ph)$_2$CHK	BrCH$_2$-C$_6$H$_4$-C(CH$_3$)=CH$_2$	264
2-Vinylpyridine	(Ph)$_2$CHK	(epoxide) + ClCO-C(CH$_3$)=CH$_2$	264
4-Vinylpyridine	(Ph)$_2$CHK	BrCH$_2$-C$_6$H$_4$-C(CH$_3$)=CH$_2$	264
MMA	BuLi	BrCH$_2$-CH=CH$_2$	281
MMA	BuLi	BrCH$_2$-C$_6$H$_4$-CH=CH$_2$ (I)	281
MMA	C-C-Ċ-C-Ċ-Li (with C and Ph, Ph substituents)	ClCH$_2$-C$_6$H$_4$-CH=CH$_2$ (Br)	264
MMA	C-C-Ċ-C-Ċ-Li (with C and Ph, Ph substituents)	BrCH$_2$-C$_6$H$_4$-C(CH$_3$)=CH$_2$	264
MMA	(Ph)$_2$CHNa	BrCH$_2$-C$_6$H$_4$-C(CH$_3$)=CH$_2$	264
MMA	(Ph)$_2$CHK	(epoxide) + ClCO-C(CH$_3$)=CH$_2$	264
nBuMA	(Ph)$_2$CHNa	BrCH$_2$-C$_6$H$_4$-C(CH$_3$)=CH$_2$	264

(to be continued)

Table 17 (continued)

Monomer	Initiator	Deactivator	Reference
t-BuMA	(Ph)$_2$CHK	BrCH$_2$—C$_6$H$_4$—C(CH$_3$)=CH$_2$	264
Methacrylate (-CH$_2$CH$_2$Si(CH$_3$)$_3$)	(Ph)$_2$CHK	BrCH$_2$—C$_6$H$_4$—C(CH$_3$)=CH$_2$	264
Methacrylate ((CH$_3$)$_2$C(O-C)(O-C-CH$_2$-))	(Ph)$_2$CHK	BrCH$_2$—C$_6$H$_4$—C(CH$_3$)=CH$_2$	264
Ethylene oxide	(Ph)$_2$CHK	Cl-CO-C(CH$_3$)=CH$_2$	263, 264
Ethylene oxide	CH$_3$O(CH$_2$)$_2$OK	Cl-CO-C(CH$_3$)=CH$_2$	263, 264
Propylene oxide	Bis-A + Al-porphyrin	MeOH	285
D$_3$	(CH$_3$)$_3$SiOLi	Cl-Si(CH$_3$)$_2$—C$_6$H$_4$—CH=CH$_2$	286, 287
D$_3$	(CH$_3$)$_3$SiOLi	Cl-Si(CH$_3$)$_2$-(CH$_2$)$_3$O(CH$_2$)$_2$OC(=O)-C(CH$_3$)=CH$_2$	286
D$_3$	-	Cl-Si(CH$_3$)$_2$-(CH$_2$)$_5$OC(=O)-C(CH$_3$)=CH$_2$	287
D$_3$	sec-BuLi	Cl-Si(CH$_3$)$_2$-(CH$_2$)$_3$OC(=O)-C(CH$_3$)=CH$_2$	288

Most cationic polymerizations involve transfer and/or termination reactions, and are not suited for direct functionalization. It is only feasible to make functionalized prepolymers with certain monomers. Monomers with the carbon-carbon double bond, such as alkyl vinyl ethers, isobutylene, p-methoxystyrene, and N-vinyl carbazole, are known to undergo living polymerization. But research efforts into the preparation of functionalized prepolymers with these living polymerizations are at the very beginning stage of development because discoveries about living polymerizations are relatively new and there is a greater possibility of side reactions compared to those in anionic polymerizations. In contrast, the living polymerizations of cyclic monomers such as oxolane, dioxolane, N-substituted aziridines, and oxazolines, have been known for many years and thus the majority of research efforts concerning functionalizations have been devoted to these cyclic monomers.

Frequently used functional deactivators include unsaturated nucleophiles such as p-vinylphenoxide, p-vinylbenzylate, sodium methacrylate, or p-vinylpyridine, and ordinary nucleophiles such as amines, carboxylates, or hydroxides. When these deactivators are reacted with living polymers of cyclic monomers, especially poly(THF), the efficiencies of deactivations are usually high, giving rise to well-defined functionally-terminated prepolymers. If living poly(THF) is reacted with pyridine or tertiary amines, the resultant polymers contain quarternary ammonium sites and therefore their characterization becomes difficult.

Sometimes transfer reactions are used for preparations of functionally terminated prepolymers. A representative example is the inifer technique developed by Kennedy et.al.[289-292]. This preparation method utilizes the fact that transfer to the gegenion is the predominant mode of termination reaction when the polymerization of isobutylene is initiated by BCl_3 and cumyl chloride compounds. Though the polymerization system is not living, the molecular weight can be accurately controlled. The polymerization

generates a chloride-terminated polyisobutylene and this becomes the precursor of functionally terminated polyisobutylene. The ω-chloro-polyisobutylene is dehydrochlorinated in order to make a terminally unsaturated prepolymer, and this reaction can be followed further by hydroboration and selective oxidation to yield the ω-hydroxy-polyisobutylene.
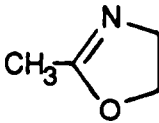
Besides this inifer technique, other modes of transfer reactions were applied in the preparation of functionally terminated prepolymers. Examples of these include the synthesis of functionalized polyisobutylenes via substitution reaction and elimination reaction[293]. If 2-methylfuran is added to the growing chain of polyisobutylene initiated by $EtAlCl_2$, the carbocation of the growing chain end attacks the furan ring and the substitution reaction takes place as in an electrophilic aromatic substitution reaction. Though the reaction yield is not that high, 50~70%, this method provides a convenient means to prepare functionalized prepolymers.

On the other hand, if 1,3-pentadiene is added to the growing chain end of polyisobutylene initiated by BF_3, proton transfer occurs predominantly from the polyisobutylene active chain end to the 1,3-pentadiene. Hence, a double bond is formed at the chain end of polyisobutylene. The newly formed active center on 1,3-pentadiene becomes allylic carbocation and propagates much more slowly.

Therefore, if one knows the exact modes of termination, and can promote a specific mode of termination by proper use of reactant and by modification of reaction conditions, the specific mode of termination can be utilized for the preparation of a functionalized prepolymer.
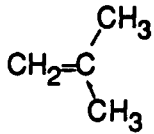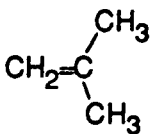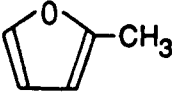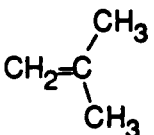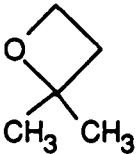
Table 18 shows the lists of some end-capping agents in cationic polymerization. Also this table includes chain transfer agents which are used for the preparation of functionally terminated prepolymers.

Table 18. Functional Capping Agents in Cationic Polymerization

Monomer	Initiator	Deactivator	Reference
$CH_2=CHO$-iBu	$HI + I_2$	$NaCH(COOEt)_2 + OH^-$	294
$CH_2=CHO$-iBu	$HI + I_2$	H_2N—⟨○⟩—$COOH$	295
THF	$Et_3O^+BF_4^-$	NaO—⟨○⟩—$CH=CH_2$ (f = 0.95)	146, 296
THF	$Et_3O^+BF_4^-$	$NaOCH_2$—⟨○⟩—$CH=CH_2$	146, 297
THF	$CH_3CH_2COCl + AgSbF_6$	$KOCH_2$—⟨○⟩—$\overset{CH_3}{\underset{}{C}}=CH_2$	147
THF	$Et_3O^+BF_4^-$	$NaOOC-CH=CH_2$	146
THF	$Et_3O^+BF_4^-$	$NaOOC-\overset{CH_3}{\underset{}{C}}=CH_2$ (f = 1.0)	146, 298
THF	-	N⟨○⟩—$CH=CH_2$	299
THF	-	$(CH_3)_2N$—⟨○⟩—$CH=CH_2$	299
CH_3—C(=N, O ring, oxazoline)	MeOTs [a]	$H_2N(CH_2)_2\overset{CH_3}{\underset{}{N}}(CH_2)_2$—⟨○⟩—$CH=CH_2$	272
t-Bu-N⊲	$CH_3OSO_2CF_3$	$NaOOC-\overset{CH_3}{\underset{}{C}}=CH_2$ (f = 1.0)	300

(to be continued)

Table 18 (continued)

Monomer	Initiator	Deactivator	Reference
$CH_2=C(CH_3)CH_3$	BF_3 + Cl-C(CH$_3$)$_2$-C$_6$H$_4$-C(CH$_3$)$_2$-Cl	initiator-transfer	210, 301
$CH_2=C(CH_3)CH_3$	EtAlCl$_2$	(furan with CH$_3$) (f = 0.5-0.7)	293
$CH_2=C(CH_3)CH_3$	BF_3	1,3-pentadiene (f = ~ 0.5)	293
(oxetane with CH$_3$ CH$_3$)	Et$_3$O$^+$PF$_6^-$	generation of H$^+$PF$_6^-$ (f = 0.3-0.9)	302

a Methyl tosylate.

B. Cationic Polymerization of Alkyl Vinyl Ethers

1. Introduction

Vinyl ethers form one of the most important group of monomers that can be polymerized by cationic methods.

The first polymerization of a vinyl ether was reported in 1878 by Wislicenus[303]. The attempted synthesis of a 1,2-diiodo compound led to the discovery that the addition of iodine to ethyl vinyl ether produces a violent reaction resulting in the formation of a resinous material. However, the major impetus for the study of vinyl ethers began with the discovery of a simple method of producing the monomers by Reppe and co-workers at I. G. Farbenindustrie[304]. Lewis acids, such as boron trifluoride, were found to be excellent catalysts for the polymerization and a rubbery poly(isobutyl vinyl ether) produced in this way was sold in Germany under the trade name Oppanol C even before the World War II.

Due to the high nucleophilicity of these monomers many cationic initiation systems can initiate polymerization of these monomers. But, it is known that vinyl ethers produce only low molecular weight polymers when initiation is carried out with free radical catalysts, ultraviolet radiation, or heat alone. Anionic initiation systems apparently fail the initiation completely, as would be expected from the electron donating nature of the ether substituent.

On the other hand, when vinyl ethers are copolymerized with electron deficient monomers such as the acrylates, methacrylates, maleic anhydride, vinyl chloride, vinyl acetate, etc. Polymerization occurs by using a free-radical initiation system. Alternating

copolymers are obtained by using a highly electrophilic monomer such as maleic anhydride[305].

Vinyl ethers are used in many areas of chemistry as well as other related areas, e.g., in the manufacture of glutaraldehyde[306], as synthetic intermediates[307], as monomers or comonomers in vinyl polymers, or as a general inhalation anesthetic for procedures of short duration[308]. Vinyl ether copolymers are used largely in specialty polymeric areas such as adhesives, surface coatings, lubricants, greases, elastomers, molding compounds, fibers, films, and chemical processing[309].

2. Monomer Preparation and Properties

a) Preparation

There have been variety of routes taken in the synthesis of vinyl ether monomers starting with the early attempt to prepare ethyl vinyl ether from diethyl chloroacetal and sodium[303]. The major commercial process used in the manufacture of vinyl ethers is the reaction of acetylene with alcohols under basic conditions, which was developed by Reppe and coworkers in Germany. The German plant used a reaction tower packed with Raschig rings and filled with the alcohol containing 1~5% KOH at 160~180°C. Acetylene was continuously recycled up through the tower. Heat of reaction(ca. 125 kJ/mole, or 30 kcal/mole) was removed by cooling coils. Fresh alcohol and catalyst were added continuously at the top and the product was withdrawn from the base of the tower. Yields of purified distilled product were quantitative[310]. The vinylation of alcohols from methyl to butyl was carried out under pressure; 2~2.3 MPa(20~22atm) for methyl at 160~165°C and 0.4~0.5MPa(4~5atm) for isobutyl at 150~155°C,

respectively[311]. Vinylation of high boiling alcohols can be carried out at atmospheric pressure.

On the other hand, a typical procedure for a batch vinylation would be conducted in a high-pressure autoclave with a suitable safety barricade. The reactor would be half charged with alcohol containing either alkali metal hydroxide or alkoxide, purged of air with nitrogen, and the temperature raised to 120~180°C. A gas mixture of acetylene and nitrogen(usually 1 part acetylene to 2 parts nitrogen) is introduced in at an operating pressure of 100 psi or above and held at that pressure by continuous feed until there is no further uptake of acetylene[304,312]. A likely mechanism for the reaction involves addition of the metal alcoholate to the triple bond in the rate-controlling step followed by metal-alcohol exchange[304].

$$HC \equiv CH \ + \ ROM \ \rightarrow \ ROCH = CHM \qquad (48)$$

$$ROCH = CHM \ + \ ROH \ \rightarrow \ ROM \ + \ ROCH = CH_2 \qquad (49)$$

Another important commercial process for the preparation of vinyl ethers is the thermal cracking of acetals. The cracking reactions are usually conducted at 250 - 400°C over catalysts such as palladium on asbestos[313], thoria[314], or metal sulfates on alumina[315].

$$CH_3CH(OR)_2 \ \rightarrow \ CH_2 = CH\text{-}OR \ + \ ROH \qquad (50)$$
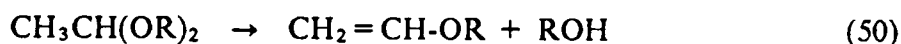
The acetal precursors are prepared by the reaction of acetaldehyde with appropriate alcohols using acid catalysts. Calcium chloride is an especially advantageous catalyst since it also functions to remove water and drive the polymerization to completion. Acetals are also formed in good yield by the reaction of acetylene with alcohols in the presence

of acidic mercuric catalysts(HgO + BF_3)[316]. Also the reaction of primary alcohols with vinyl acetate in the presence of a similar type of catalyst[317], or the reaction of ethylene with alcohols using platinum derivatives[318], can give acetals.

Some interesting synthetic routes which use ethylene were reported as in equation 51. Another method that gives very high yields by exchange reaction was reported as in equation 52[319-320].

$$ROH + CH_2=CH_2 + \tfrac{1}{2} O_2 \xrightarrow{\quad PdCl_2.CuCl_2.HCl \quad} ROCH=CH_2 + H_2O \qquad (51)$$

$$ROH + CH_2=CH\text{-}O\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{\quad PdCl_2.Na_2WO_4 \quad} ROCH=CH_2 + CH_3\overset{O}{\overset{\|}{C}}OH \qquad (52)$$
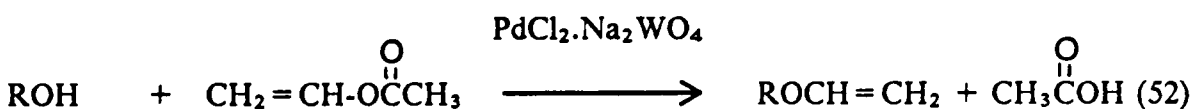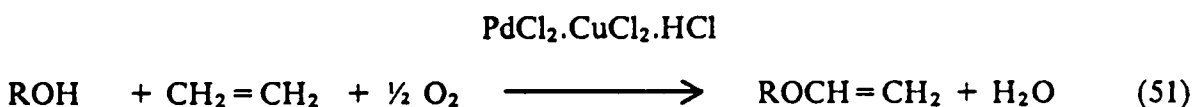
If the acetal precursor is difficult to prepare or if the vinyl ether cannot withstand the hot basic conditions of the vinylation reaction, the exchange or trans-vinylation reaction can be used as in the equation 53. This reaction is catalyzed by mercuric salts and is carried out in vapor phase[321]. This method is good for the laboratory preparation of the vinyl ethers.

$$CH_2=\underset{\underset{R}{\overset{|}{O}}}{\overset{|}{CH}} + R'OH \xrightarrow{\quad Hg^{2+} \quad} CH_2=\underset{\underset{R'}{\overset{|}{O}}}{\overset{|}{CH}} + ROH \qquad (53)$$
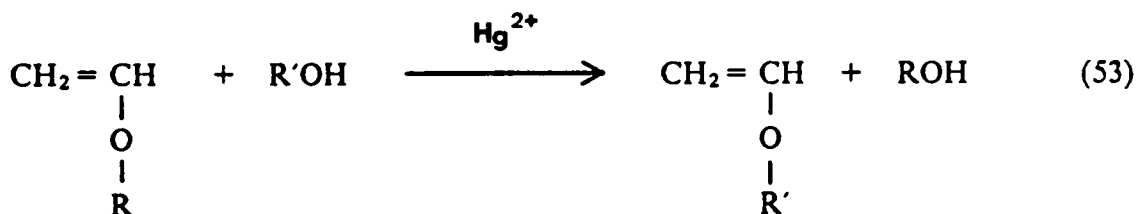
Certain vinyl ethers have been produced by dehydrochlorination reactions both commercially and in laboratory preparations. Reaction of 2,2'-dichlorodiethyl ether with sodium hydroxide is used commercially to manufacture 2-chloroethyl vinyl ether as in Equation 53[322]. Pyrolytic dehydrochlorination of 1,1'-dichlorodiethyl ether, on the other hand, is used to manufacture divinyl ether[308].

$$ClCH_2CH_2OCH_2CH_2Cl + NaOH \rightarrow CH_2=CHOCH_2CH_2Cl + NaCl + H_2O \quad (54)$$
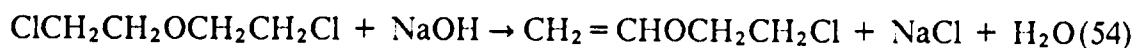
Polyhydric alcohols and saccharides can be vinylated if the hydroxyl groups are separated by two or more carbon atoms or adjacent hydroxyls are protected by ketal formation with acetone. Unless this is done, intramolecular acetals result by addition of a free hydroxyl group across a vinyl ether. Primary and secondary hydroxyl groups are readily vinylated, whereas tertiary alcohols require more vigorous conditions or special techniques such as the use of potassium *tert*-butoxide. Vinyl ethers have been prepared from most simple alcohols, glycols, triols, sugars, phenols, pentaerythritol, cyclic hydroxyl compounds, terpene alcohols, and a number of miscellaneous hydroxyl compounds[323].

b) Physical Properties

Table 19 lists the physical properties of the $C_1 \sim C_4$ vinyl ethers[310a,324]. The ethers are soluble in solvents such as hexane, CCl_4, methanol, ethanol, ether, dioxane, ethyl acetate, benzene, and ethoxyethanol. These monomers are the principal commercially available monomers. Table 20 shows the physical properties of some of other alkyl, aryl, divinyl, α- and β-substituted, and functionally substituted vinyl ethers[324-325].

c) Reactions and Applications

The chemical reactions of the vinyl ethers are typical of most vinyl compounds. Extensive discussion of their polymerizations can be found in references, 309b, 324, 326, and 327.

Table 19. Physical Properties of the C_1 - C_4 Vinyl Ethers[a]

	Methyl	Ethyl	Isopropyl	n-Butyl	Isobutyl
Freezing point (° C)	-122.8	-115.4	-140	-91.9	-112.1
Boiling point (° C, 760 torr)	5.5	35.7	55-56	93.5	83.0
Specific gravity (d_4^{20})	0.7511	0.7541	0.753	0.7790	0.7682
Refractive index (n_D^{20})	1.3730 (0 ° C)	1.3767	1.3829 (25 ° C)	1.4020	1.3966
Flash point (° C)	-56	<-18	-	-1	-7
Heat of vaporation (1 atm, cal/g)	-	87.8	-	75.6	77.2
Solubility in water (20 ° C, wt %)	1.5	0.9	-	0.2	0.3
Odor	sweet pleasant	pleasant	pleasant	pleasant	pleasant

[a] Data from [310a, 324].

Table 20. Physical Properties of Various Vinyl Ethers[a]

Vinyl ethers R or Ar	Boiling point, °C (mm Hg)	n_D^{20} (°C)	d_4^{20}
s-Butyl	81	1.3970	0.7715
t-Butyl	75	1.3922	0.7691
n-Amyl	119	1.4105(30)	-
Isoamyl	110	1.4070	0.7833
n-Hexyl	143.5	1.4171	0.7966
n-Octyl	58(4)	1.4268	0.8024
2-Ethylhexyl	178, 61-63(11)	1.4247(25)	0.8088
n-Decyl	101(10)	1.4346(25)	-
n-Tetradecyl	140-145(4)	1.4457(30)	-
n-Hexadecyl	160-165(4)	1.4490(30)	-
n-Octadecyl	182(3)(mp, 30 °C)	1.4515(25)	-
Phenyl	155-157	1.5226	-
o-Cresyl	170	-	-
p-Cresyl	174	1.5186	-
α-Naphthyl	259	1.6152	-
β-Naphthyl	264(mp, 64 °C)	-	-
$CH_2=CH-$	28.5(mp, -101 °C)	1.3989	0.773
$CH_2=CH-O-CH_2CH_2-$	126	1.4388	-
$CH_2=CH-O-CH_2-$	90	-	-
Methyl α–methyl	32.5-33.5	1.3788	0.73
Methyl α–chloro	122-123	-	-
Isopropyl β–methyl			
(cis-)	83(750)	1.400	-
(trans-)	90.5(750)	1.4018	-
$-CH_2CH_2OH$	140	1.4532	-
$-CH_2CH_2Cl$	108(mp, -70 °C)	1.4361	1.0493_{20}^{20}
$-CH_2CH-CH_2$ (with O bridge)	138-139	1.4458(11)	1.105_{11}^{11}

[a] Data from [324, 325].

Vinyl ethers are hydrolyzed to the corresponding alcohol and acetaldehyde in the presence of an acid[303,328-329].

$$ROCH = CH_2 + H_3O^+ \rightarrow ROH + CH_3CHO + H^+ \tag{55}$$
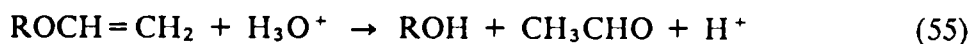
A kinetic study of the reaction showed the following order of reactivities: t-butyl > isopropyl > ethyl > methyl[328]. This is the same order observed in simple cationic polymerization and is related to the basicity of the oxygen rather than electron release to the double bond. This reaction, on the other hand, was used for the monomer analysis of the vinyl ethers by Reppe. In the analysis, the aldehyde formed is titrated as in a typical aldehyde analysis[312,330-331]. But this suffers from the disadvantage that aldehydes and acetals, typical impurities, act as interfering impurities and cannot be detected.

Vinyl ethers undergo the usual addition reactions of olefinic compounds. Catalytic hydrogenation proceeds smoothly to the corresponding ethyl ethers[312]. Chlorine and bromine add extremely vigorously giving high yields of 1,2-dihaloethyl ethers with a proper control[332]. In the presence of an alcohol, halogens add as hypohalites, giving a 2-haloacetal[333].

$$CH_2 = CHOR + X_2 + R'OH \rightarrow XCH_2CH(OR)(OR') + HX \tag{56}$$

This reaction is used in the analysis of vinyl ethers. Excess iodine in the presence of methanol gives the iodoacetal with the vinyl ether and is back titrated with thiosulfate as in equation 57[331].

$$CH_2 = CHOR + CH_3OH + I_2 \rightarrow ICH_2CH(OR)(OCH_3) + HX \tag{57}$$

In this method, aldehydes and acetals do not interfer. The pH must not be allowed to go below two if acid impurities are present, as this leads to iodine formation from the HI. High pH must also be avoided since under basic conditions vinyl ethers and acetaldehyde impurities can give iodoform by reaction with iodine.

Vinyl ethers have been used as protecting groups in organic synthesis. In particular they have been used to convert hydroxyl groups to acetals, which are stable under neutral or alkaline conditions and are easily hydrolyzed with dilute acid after other desired reactions have occurred[334-336].

$$ROH + CH_2 = CH\text{-}OR \rightleftharpoons ROCH(CH_3)(OR) \tag{58}$$

Besides alcohols, many labile hydrogen compounds add across the double bond as in equation 58. Carboxylic acids give 1-alkoxy ethyl esters[337], and thiols give thioacetals[338]. Addition occurs in the *Markovnikov direction.*

Vinyl ethers and α,β-unsaturated carbonyl compounds react by cycloaddition[306a] as in equation 59 by heating the two reactants in an autoclave, with a small amount of hydroquinone to inhibit polymerization. The resultant 2,3-dihydropyran is hydrolyzed in the synthesis of glutaraldehyde[339].

$$\tag{59}$$
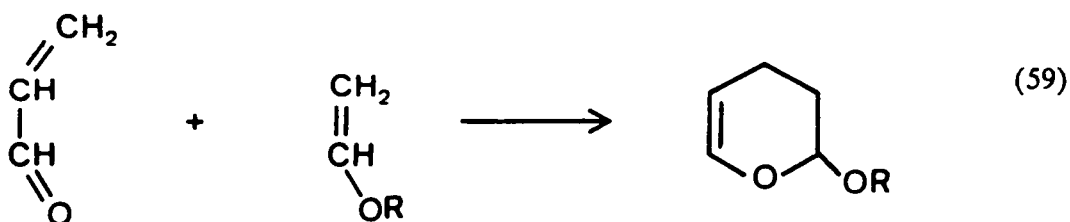
When ketene is used instead of unsaturated carbonyl compounds, vinyl ethers cyclize to cyclobutanones[340].

Since vinyl ethers are prone to hydrolysis and to polymerization by acidic materials, acids and water are to be avoided. Stabilizers ordinarily used are solid alkalies(KOH pellet), or high-boiling amines such as triethanolamine. No radical-trap stabilizers are ordinarily required if there is adequate removal of air during handling and distillation. Protected from air, moisture, and other contamination, vinyl ethers are stable for years.

Because of their high vapor pressure, the lower alkyl vinyl ethers represent a severe fire hazard and must be handled accordingly. Inhalation should be avoided. Although vinyl ethers form peroxide more slowly than saturated ethers, distillation residues must be handled with caution.

At a concentration of 64,000 ppm in air, methyl vinyl ether immobilized a group of test rats within one-half hour. When removed from the test atmosphere, all rats recovered and appeared normal after 72 hours. One died after 96 hours, the remaining five rats seemed normal for the total two week observation period.

Isobutyl vinyl ether showed a single oral LD_{50} (50% lethal dosage) for rats of 17 ml/kg and a single skin penetration LD_{50} for rabbits of 20 ml/kg. Concentration of 16,000 ppm in air gave 50% rat mortality in 4 hours[310a].

3. Polymerizations and Characteristics

Vinyl ethers are converted to high molecular weight polymers only by cationic initiators. Because of the ability of the alkoxide group to donate electrons, the π bond in vinyl ether is very nucleophilic. It is therefore attacked extremely readily by carbenium ions, even by the compounds as stable as the triphenylmethyl carbenium ion[341]. Furthermore, the carbenium ion resulting from the addition is stabilized by the ability of the

alkoxide group to delocalize the positive charge. Hence, the strong tendency of vinyl ethers to undergo cationic polymerization can be readily understood.

$$
\left[\begin{array}{ccc}
& \overset{\displaystyle H}{\underset{\displaystyle \underset{R}{\overset{|}{:O:}}}{\overset{|}{\sim CH_2-\overset{|}{C}{}^+}}} & \longleftrightarrow \quad \overset{\displaystyle H}{\underset{\displaystyle \underset{R}{\overset{|}{:O^+}}}{\overset{|}{\sim CH_2-\overset{\|}{C}}}}
\end{array} \right]
$$

$$\underset{\sim}{14}$$

$$(\underset{\sim}{14}) \quad + \quad CH_2 = CH\text{-}OR \quad \longrightarrow \quad \sim CH_2\text{-}\underset{\underset{R}{\overset{|}{:O:}}}{\overset{\overset{H}{|}}{C}}\text{-}CH_2-\underset{\underset{R}{\overset{|}{:O:}}}{\overset{\overset{H}{|}}{C}}{}^+ \qquad (60)$$
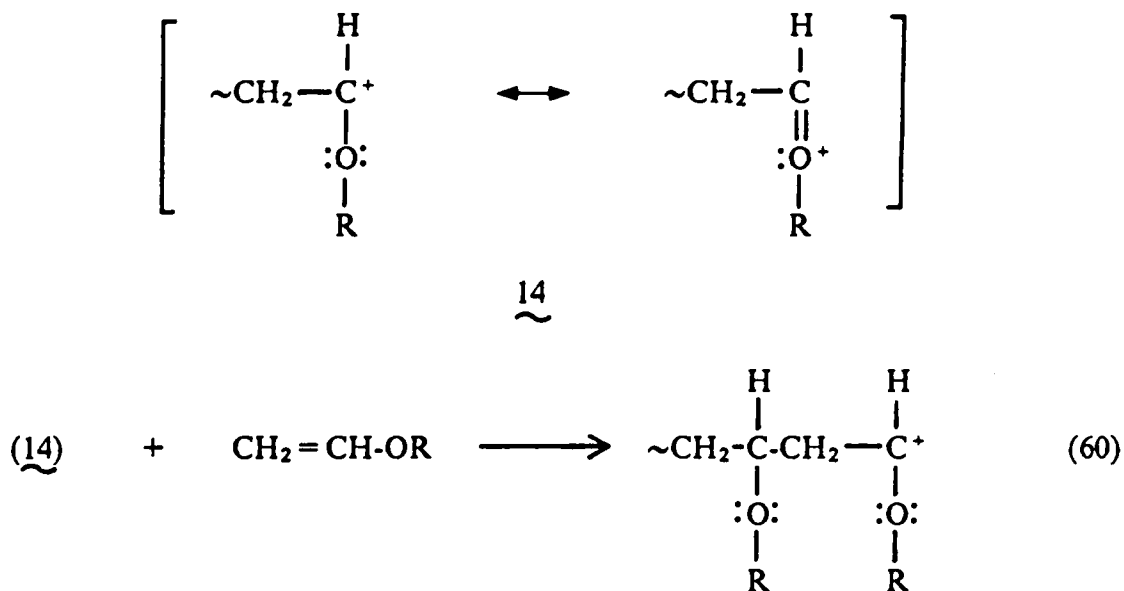
a) Reactivity

Vinyl ether monomers with highly branched alkyl groups generally exhibit greater reactivity[342], and a greater tendency to form stereoregular polymers than straight-chain monomers[343]. Long chain alkyl ethers are generally less reactive than the short chain homologues. Aromatic vinyl ethers are less reactive under cationic initiation than alkyl vinyl ethers and more susceptible to side reactions[326], but they have markedly greater reactivity than styrene[344].

The reactive polymerizability of selected alkyl and aryl vinyl ethers is shown in Table 21. In this Table, alkyl vinyl ethers cannot be compared directly with aryl vinyl ethers. In the first part(alkyl vinyl ethers) of the Table, reactivity of the monomers was determined by the rate of reaction with dichlorocarbene[345] as in equation 61, by the

rate of hydrolysis[328], and by the rate of polymerization initiated by cycloheptatrienyl hexachloroantimonate[346].

$$ROCH=CH_2 \quad + \quad :CCl_2 \quad \rightarrow \quad ROCH\!\!-\!\!-\!\!CH_2 \qquad\qquad (61)$$
$$\diagdown\;\diagup$$
$$CCl_2$$
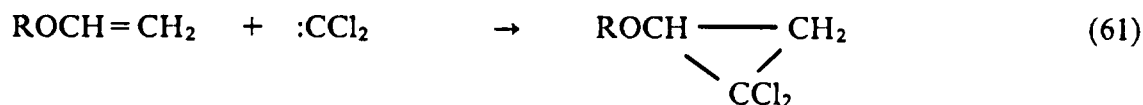
In the second part(aryl vinyl ethers) of Table 21, reactivity of the monomers was determined by the reactivity ratios in the copolymerization of phenyl vinyl ether(M_1) and its derivatives(M_2)[347].

The heat of polymerization of isobutyl vinyl ether was reported to be around 22.3 kcal/mole at 0°C[50].

With a complexed boron fluoride catalyst, the rate of polymerization changes by side group as follows: anisole > isopropyl ether > ethyl ether > n-butyl ether > tetrahydrofuran[305,348]. Also with a metal sulfate-sulfuric acid complex catalyst the rate of polymerization of alkyl vinyl ethers decreases as follows: ethyl > n-butyl > n-hexyl $\cong$ n-octyl [349].

But Schildknecht and others[326,350] reported a different tendency in the polymerization initiated by boron trifluoride etherate, in the following order: t-butyl > isopropyl > isobutyl > n-butyl > ethyl > methyl. The reactivity of the monomer, therefore, can be changed by a change of catalyst and reaction conditions.

Usually the reactivity of monomers in cationic polymerization is determined by (1) the use of the rate constant, (2) the use of reactivity ratios, or (3) ^{13}C NMR.

The knowledge of rate constants, particularly the propagation rate constant k_p, provides an estimate of monomer reactivity toward its own cation. However comparison of k_p's of different monomers is not always reliable for the evaluation of relative reactivities because in addition to experimental difficulties k_p is determined not only by the nature of the monomer, but also by the growing cation and experimental conditions. The

Table 21. Relative Polymerizability of Selected Alkyl and Aryl Vinyl Ethers

Alkyl vinyl ethers	Relative reactivity		Relative polymerizability [c]
	$:CCl_2$ [a]	H_3O^+ [b]	
Ethyl	1.0	1.0	1.0
Methyl	0.86	0.50	-
Isopropyl	1.3	3.6	7.4
Isobutyl	0.83	0.8	-
t-Butyl	2.0	6.6	25
2-Chloroethyl	0.40	0.09	0.1
Aryl vinyl ethers (M_2) [d]	r_1	r_2	Relative polymerizability $(1/r_1)$
Phenyl	-	-	1
p-Methoxyphenyl	0.42	2.1	2.38
p-Methylphenyl	0.55	1.76	1.82
m-Methylphenyl	0.79	1.50	1.27
m-Methoxyphenyl	0.71	1.1	1.41
p-Chlorophenyl	3.6	0.27	0.278
m-Chlorophenyl	21.6	0.19	0.217

[a] KO-tBu + $CHCl_3$, 0-5 ° C[345].

[b] HCl in 80% aqueous acetone, 25 ° C[328].

[c] $C_7H_7SbCl_6$ in CH_2Cl_2, 0 ° C[346].

[d] $SnCl_4$ in toluene, -78 ° C[347].

different degree of dissociation of an active species under different conditions is one of the biggest difficulties in the determination of the rate constant[351]. Also the different impurity level makes the data different. Table 22 shows some of the polymerization rate constants of vinyl ethers. Transfer constant k_{tr} has also been used to estimate the reactivity of growing ions of styrenic monomers[354-355].

Monomer reactivity ratios reflect relative monomer reactivities toward the same active species. According to Mayo and Lewis[356], or Alfrey and Goldfinger[357], four propagation steps were proposed in a copolymerization regardless of the nature of the active species. For cationic copolymerization the four propagation steps are as follows.

$$\sim M_1^+ \;+\; M_1 \;\xrightarrow{k_{11}}\; \sim M_1 M_1^+ \tag{62}$$

$$\sim M_1^+ \;+\; M_2 \;\xrightarrow{k_{12}}\; \sim M_1 M_2^+ \tag{63}$$

$$\sim M_2^+ \;+\; M_1 \;\xrightarrow{k_{21}}\; \sim M_2 M_1^+ \tag{64}$$

$$\sim M_2^+ \;+\; M_2 \;\xrightarrow{k_{22}}\; \sim M_2 M_2^+ \tag{65}$$
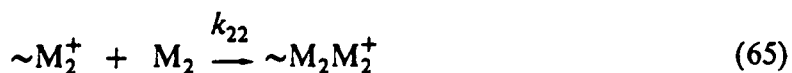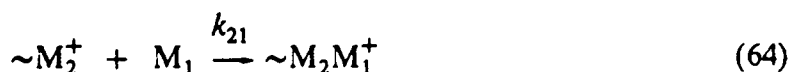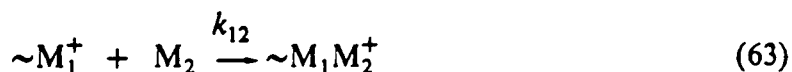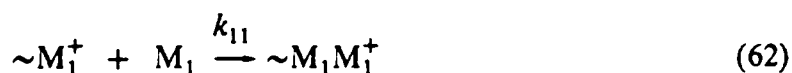
where M_1, M_2, M_1^+, and M_2^+ are the two monomers and corresponding carbenium ions, and k is a rate constant. Then reactivity ratios r_1, and r_2 for monomer 1 and monomer 2 are defined, respectively.

$$r_1 \;=\; \frac{k_{11}}{k_{12}} \tag{66}$$

Table 22. Rate Constant of Polymerization of Some Alkyl Vinyl Ethers

Monomer (Alkyl group)	Initiation system (° C / initiator / solvent)	$k_p \times 10^{-3}$ (M^{-1}sec^{-1})	Reference
Methyl	0 / C$_7$H$_7$$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	0.14	346
Ethyl	0 / C$_7$H$_7$$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	1.5	346
	0 / Ph$_3$C$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	5.1	352
	0 / ^{60}Co / bulk	8.3	352
	30 / ^{60}Co / bulk	60	353
Isobutyl	0 / Ph$_3$C$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	14.8	352
	0 / C$_7$H$_7$$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	6.8	346
	0 / ^{60}Co / bulk	38	352
Isopropyl	-25 / Ph$_3$C$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	0.32	351
	0 / Ph$_3$C$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	0.42	351
	15 / Ph$_3$C$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	1.0	351
	0 / ^{60}Co / bulk	900	352
	0 / γ-ray / bulk	390	351
	30 / γ-ray / bulk	1300	353
t-Butyl	0 / C$_7$H$_7$$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	3.5	346
	0 / ^{60}Co / bulk	50	352
Cyclohexyl	0 / C$_7$H$_7$$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	3.3	346
2-Chloroethyl	0 / C$_7$H$_7$$^+$SbCl$_6$$^-$ / CH$_2$Cl$_2$	0.2	346

$$r_2 = \frac{k_{22}}{k_{21}} \qquad (67)$$

When M_1 is a reference monomer the value of $1/r_1$ is a measure of the preference of the attack of $M_1{}^+$ on M_2 or its own monomer M_1. If k_{11} is taken to be unity, $1/r_1$ is a measure of the reactivity of M_2 toward cation $M_1{}^+$. Consequently, $1/r_1$ values for a set of M_2 monomers may be used to express their reactivity toward the same cation. Absolute values of $1/r_1$ depend on the nature of the reference monomer. In the absence of steric effects, monomer reactivities obtained by different methods give the same reactivity values[358-359].

Second part of Table 21 shows the reactivity relationship via reactivity ratios. Comprehensive compilation of reactivity ratios can be seen in Kennedy's book[8].

Following Karplus and Pople's[360] proposition that a ^{13}C NMR chemical shift reflects π electron density on carbon atoms, attempts have been made to correlate ^{13}C NMR chemical shifts with monomer reactivity[361]. Thus Higashimura et al.[362] correlated ^{13}C NMR chemical shifts with the reactivity of β-substituted styrenes and vinyl ethers. A β-methyl group was found to decrease the reactivity of styrene and increase the reactivity of vinyl ethers.

Table 23 shows ^{13}C NMR shifts of β-carbons for several vinyl or alkenyl ethers. Examination of the data in this Table shows that the chemical shift of β-carbon in n-butyl vinyl ether and isopropyl vinyl ether decreases upon methyl substitution. The decrease caused by an ethyl group is larger than that caused by a methyl group. The changes in chemical shift suggest that the π electron density on the β-carbon of an olefinic double bond decreases on introduction of an alkyl group on the β-carbon, and this change in chemical shift in vinyl ethers is similar to the general trend observed in substituted hydrocarbons.

Table 23. Carbon-13 NMR Chemical Shifts of β-Carbons[a]

Monomer	δ_c(ppm) (from CS_2)	AO Population of $(\beta-C)_\pi$[b]	
		Model compounds	AO Population of $(\beta-C)_\pi^*$
$CH_2=CHO\text{-}n\text{-}C_4H_9$	107.8	$CH_2=CHOCH_3$	1.131
cis-$CH_3\text{-}CH=CHO\text{-}n\text{-}C_4H_9$	93.5	cis-$CH_3\text{-}CH=CHOCH_3$	1.043
cis-$C_2H_5\text{-}CH=CHO\text{-}n\text{-}C_4H_9$	84.5	cis-$C_2H_5\text{-}CH=CHOCH_3$	1.043
$CH_2=CHO\text{-}i\text{-}C_3H_7$	102.2	$CH_2=CHOCH_2CH_3$	1.131
cis-$CH_3\text{-}CH=CHO\text{-}i\text{-}C_3H_7$	93.0	-	-
$CH_2=CHOCH_2CH_2Cl$	104.6	-	-

[a] Data from [362].
[b] Atomic orbital population in the π orbital(π electron density).

Evidently the increase of reactivity due to β-alkyl substitution is not due to an increase of π electron density on the β-carbon. Also chemical shift does not reflect reactivity of vinyl ethers. The reactivity of vinyl ethers decreases in the following order; $CH_2 = CH\text{-}O\text{-}iPr > CH_2 = CH\text{-}O\text{-}nBu > CH_2 = CH\text{-}O\text{-}CH_2CH_2Cl$, whereas the downfield shift of β-carbon resonance is $CH_2 = CHO\text{-}nBu > CH_2 = CH\text{-}O\text{-}CH_2CH_2Cl > CH_2 = CH\text{-}O\text{-}iPr$.

Since an upfield shift usually indicates increased π electron density on the carbon atom as in styrenic monomer, the reactivity of vinyl and alkenyl ethers does not parallel π electron density on the β-carbon. Thus the carbocation attack on the β-carbon is not the rate-determining step[328,363].

Hatada et al.[364] noted that with increasingly electron-donating alkyl groups in vinyl ethers, the chemical shift of the α-carbon of the vinyl group shifts to a higher field and that of the β-carbon to a lower field. These observations were explained by assuming that the contribution of the $CH_2^-\text{-}CH = O^+\text{-}R$ of resonance structure decreases with increasing electron-repelling power of the alkyl group. A good correlation between the chemical shifts of the vinyl groups and monomer reactivity was obtained as in Table 24.

b) Initiation System

Polymerization of a vinyl ether was first observed by Wislicenus in 1878, using iodine as catalyst[303]. In 1932, Charmers obtained polymers using Friedel-Crafts catalysts[366]. A few years later, I.G. Farben obtained a patent in which the polymerization of isobutyl vinyl ether by boron trifluoride was described in considerable detail[367]. Since that time many catalyst systems have been found for the polymerization of vinyl ethers, and many systems generate stereoregular polymers. Good reviews on the catalyst systems of vinyl ethers can be found in the

Table 24. Carbon-13 NMR Chemical Shifts of α- and β-Carbons and Monomer Reactivity[a]

Alkyl group in $R\text{-}O\text{-}HC_\alpha= C_\beta H_2$	Chemical shift from CS_2(ppm) [a]		Reactivity [b] $(1/r_1)$
	α	β	
Methyl	40.5	109.6	0.18
Ethyl	39.7	108.5	0.49
n-Butyl	40.6	108.1	1.0
Isobutyl	40.8	108.7	1.37
Isopropyl	42.3	106.2	2.63
t-Butyl	46.9	103.5	5.26

[a] Data from [364].
[b] $EtAlCl_2$ catalyst in toluene at -78 °C[365].

literature[309a,327,348,368-369]. Some of the representative examples are shown in Table 25.

Atactic vinyl ether homopolymers can be readily prepared by initiation with acid catalysts, especially by Friedel-Crafts type catalysts such as boron fluoride, aluminum trichloride, stannic chloride, etc., either in bulk or in inert dry solvents. The reaction may be extremely vigorous, so it is important to moderate it for safety and in order to control the molecular weight. The extraordinary rapid polymerization brought about the term "flash polymerization"[370], especially in the polymerization of the lower alkyl vinyl ethers by boron trifluoride.

Much greater control of the polymerization reaction can be obtained if polymerization is carried out at low temperatures(-40 to -70°C) and if the Lewis acid is complexed(e.g. boron trifluoride etherate). Some heterogeneous initiators such as molecular sieves and vanadium pentoxide make atactic homopolymers at room temperature[371-372].

Often slight modification of the reaction conditions or the catalyst system changes the tacticity. A good example is the polymerization of isobutyl vinyl ether[348,373-376]. When liquid propane(~ -70°C) containing a boron trifluoride catalyst(0.01% or more) is rapidly added to cooled isobutyl vinyl ether diluted with liquid propane, nearly instantaneous or "flash polymerization" takes place. The polymer obtained is tacky, rubberlike and amorphous. On the other hand, when boron trifluoride etherate is used at -80° to -60°C, polymerization proceeds slowly and the polymer grows around the catalyst as a separate phase. This type of polymerization is termed[376] "polyphase" or "proliferous polymerization." The polymer is a nontacky solid which gives a crystalline x-ray diffraction pattern in the unstretched condition and a sharp fiber diagram on stretching.

Table 25. Some Initiation Systems for the Polymerization of Alkyl Vinyl Ethers[a]

Monomer[b] (Alkyl group)	Initiation system (° C / initiator / solvent)	Remark
Methyl	3-5 / $BF_3.2H_2O$ / bulk	-
Ethyl	-10 / SO_2 / bulk	-
Isobutyl	12 / $SnCl_2$ / bulk	-
Isobutyl	25 / I_2 / ethyl ether	-
-	0-8 / CrO_2Cl_2 / hexane	-
Isobutyl	-70 / $BF_3.Et_2O$ / propane	-
n-Butyl	5-100 / $Al_2(SO_4)_3.3H_2SO_4$ / heptane	crystalline
n-Butyl	-78 / $AlClEt_2$ / toluene-propylene(5/3)	crystalline
n-Butyl	-78 / $AlCl_2Et$ / toluene-propylene(5/3)	crystalline
n-Butyl	-78 / $AlCl_2(OEt)$ / toluene-propylene(5/3)	crystalline
Isobutyl	-78 / I_2 / ethyl ether	syndiotactic
Isobutyl	0 / $C_7H_7^+SbCl_6^-$ / CH_2Cl_2	isotactic
Isobutyl	30 / V_2O_5 + $AlEt_3$ / benzene	isotactic
Isobutyl	30 / $POCl_3$ + $AlEt_3$ / benzene	isotactic
Isobutyl	30 / V_2O_5 + $AlEt_3$ / benzene	isotactic
Isobutyl	25 / Fe_2O_3 / toluene	isotactic
Ethyl	-20 / Fe_2O_3 / toluene	-
Allyl	-10 / $SbCl_5$ / toluene	isotactic
t-Butyl	-76 / $(C_6H_5)_3C^+BF_4^-$ / CH_2Cl_2-toluene(7/3)	isotactic

[a] Data from [309, 327, 368-369].

Another example is the change of coinitiator in the polymerization of isobutyl vinyl ether initiated with vanadium pentoxide. Addition of benzaldehyde causes a 50% increase in the rate of the polymerization in benzene at room temperature, whereas replacement of benzaldehyde with triethylaluminum changes the nature of the polymerization from atactic to stereoregular in the same medium[373].

In the polymerization of t-butyl vinyl ether at -78°C by BF_3OEt_2, 8/1(volume/volume) ratio of CH_2Cl_2-toluene solvent makes an atactic polymer, a 1/1(v/v) ratio of toluene-nitroethane solvent makes a syndiotactic polymer, and toluene makes an isotactic polymer[377-378].

The formation of stereoregular vinyl ether homopolymers produced by cationic polymerization has been the subject of numerous investigations. Historically, the poly(vinyl ethers) occupy an important place in the development of polymer science, since crystalline polymers recognized later to be isotactic, were prepared as early as 1948[348]. Initiators for the stereoregular polymerization of vinyl ethers can be classified into eight categories[309,379]: metal halides, organometallic halides, metal organic or inorganic halides, metal oxides and metal oxyhalides, organometallic or metal alkoxide-sulfuric acid, metal sulfates, Ziegler-Natta initiators, and Grinard reagents.

Heterogeneous initiator systems frequently provide alkyl vinyl ether polymers with greater stereoregularity than homogeneous initiators, especially at near room temperature. Pioneering research on complex catalysts prepared from sulfuric acid and an aluminum salt shows the preparation of high crystalline alkyl vinyl ethers[349,380]. Fe_2O_3 initiator system also creates high yields of semicrystalline polymers[381].

Besides the chemical initiation systems mentioned above, many physical initiation systems have been applied in the polymerization of vinyl ethers. Initiation by high energy radiation, initiation by electrochemical reaction, etc., are the examples. A recent

review by Gandini and Cheradame[97] documents well many cationic initiation processes of vinyl ethers.

c) Polymerization Mechanisms

Eley and his coworkers investigated in detail the kinetics of polymerization of several alkyl vinyl ethers using different catalysts under a variety of conditions[382]. The ionic nature of the polymerization reaction is clearly demonstrated[341] by the acceleration effect[383] of solvents of high dielectric constant. In the polymerization of n-butyl vinyl ether with stannic chloride, Eley and Richards[341] proposed a basic scheme of elementary reactions which include initiation, propagation, termination, and chain transfer to the monomer. Each of these elementary reactions is very similar to the corresponding general reaction of cationic polymerization reviewed well by Kennedy[8].

In this section, the differences between the polymerization of vinyl ethers and other cationic processes will be reviewed. The focus will be upon the chain transfer reaction, the initiation with iodine catalyst, and steric control mechanisms.

1) Chain Transfer Reaction: Among the elementary reactions, the chain transfer to the monomer has been studied extensively by many workers. It has been suggested that it is one of the most important reactions that control the molecular weight of the polymer[384]. Ledwith and his coworkers[50] have shown that the propagation reaction in the polymerization of isobutyl vinyl ether is faster only 30~50 times than the transfer reactions, with both processes having rather similar activation energies.

Direct proton transfer to the monomer, for example, functions as in equation 68, but the tremendous efficiency of monomer transfer in this case suggests that other forms

of monomer transfer may be operative. At least two alternative reactions may account for the ease of monomer transfer.

$$\underset{\underset{R}{\overset{\overset{\displaystyle O}{|}}{|}}{\sim CH_2 - \overset{..+}{CH}} \ X^- \ + \ \underset{\underset{R}{\overset{\overset{\displaystyle O}{|}}{|}}{CH_2 = CH} \ \longrightarrow \ \underset{\underset{R}{\overset{\overset{\displaystyle O}{|}}{|}}{\sim CH = CH} \ + \ \underset{\underset{R}{\overset{\overset{\displaystyle O}{|}}{|}}{CH_3 - \overset{..+}{CH}} \ X^- \qquad (68)$$

Studies of carbocation behavior were established beyond a doubt that protonated cyclopropanes constitute active intermediates in many reactions of simple alkyl cations[385], as in equation 69. There is still some uncertainty regarding the exact structure of protonated cyclopropanes, as to whether the ring is *face protonated, edge protonated,* or *corner protonated*, but a primary alkyl cation may be represented as an equilibrium between classical and non-classical structures.

$$RCH_2CH_2CH_2{}^+ \ \underset{\longrightarrow}{\overset{\longleftarrow}{}} \ RCH \underset{CH_2 \ H^+}{\overset{\displaystyle \diagup \ \diagdown}{\diagdown \times}} CH_2 \qquad (69)$$

For a simple alkane structure the order of carbenium ion stability falls in the following sequence, *tert- > sec- > protonated cyclopropyl- > primary-*. However, for substituted derivatives, the free energy differences between protonated cyclopropyl and secondary or tertiary classical structures are not very great[386]. It is plausible, therefore, that the propagating classical cation in vinyl ether polymerization is in equilibrium with a very small concentration of the non-classical protonated cyclopropyl derivatives, for example as in equation 70. In this particular example, the presence of stabilizing alkoxy groups would overwhelmingly favor the open chain classical structure, but cyclopropanes are much less basic than similarly substituted olefins, and this provides a simple explanation for the observed facile monomer transfer reaction. The proposition of the cyclic intermediate was introduced for the explanation of head-to-tail type structures of the polymer[368,387], and supported by theoretical calculations as well as by the

enhancement of the polymerization reactivity of the vinyl ether resulting from methyl group substitution for hydrogen on the β-carbon of the vinyl ether monomers[371,388].

$$\sim CH_2\text{-}CH\text{-}CH_2\text{---}CH \quad \rightleftharpoons \quad \sim CH_2\text{---}C\text{---}CH_2 \qquad (70)$$

$$\underset{OR}{|} \qquad \underset{OR}{|\overset{..}{:}+} \qquad \qquad RO \diagup \diagdown \overset{|}{C} \overset{\times}{H^+}$$

$$\diagup \diagdown$$

$$H \quad OR$$

$$\big\Updownarrow \; CH_2 = CHOR$$

$$\sim CH_2\text{---}C\text{---}CH_2 \; + \; CH_3\text{-}CH$$

$$RO \diagup \diagdown \diagup \qquad \qquad |\overset{..}{:}+$$

$$CH \qquad\qquad OR$$

$$|$$

$$OR$$

Another alternative monomer transfer process would be possible if the propagating carboxonium ion attains stabilization by neighboring group effects of monomer segments in the same chain. The reaction is shown in Scheme 7[23]. The cyclic oxonium ion formed by intramolecular stabilization would have electrophilic reactivity at positions 1, 2, and 3, according to the nature of the substituents, but here again reactivity at position 1 would be heavily favored by the alkoxy substituent. Reaction at position 1 leads to propagation and would be expected to dominate; reaction at position 2 constitutes a monomer transfer reaction in which an alkyl group has been transferred; and reaction at position 3 results in propagation with branching. It has also been proposed that a cyclic oxonium ion explains the stereoregular nature of vinyl ether polymerizations with heterogeneous catalysts[389].

In very pure systems true termination reactions are scarce in cationic polymerization. However, a small amount of spontaneous termination occurs as the result of the reaction of the active center with the counterion. In the polymerization initiated by $SbCl_6^-$ salts, termination reactions were reported as the result of combination with chloride[50], the combination with chloride followed by self-initiation reaction of

Scheme 7. A monomer transfer process[23].

the salt[382], or the combination reaction which occurs simultaneously with an elimination reaction[50].

2) Initiation by Iodine: The polymerization of vinyl ethers is considered to proceed by way of a conventional cationic mechanism, however, details concerning initiation are a matter of controversy. Kinetic[390], spectroscopic[305,391], and conductometric[392] studies have not been conclusive in this regard. Careful works by Ledwith and Sherrington[393], and Johnson and Young[394] clarified aspects of the first stage of reaction in iodine-initiated polymerization of ethyl, n-butyl, and isobutyl vinyl ethers in various solvents. According to these workers, an equilibrium is established between vinyl ethers and iodine, and equilibrium constant and enthalpy data indicate that the first product is 1,2-diiodide, and not a charge transfer complex which has been suggested by many investigators[392,395-396]. Rate studies, spectrophotometry, and ethanol substitution experiments seem to confirm these conclusions. The first step of initiation is proposed to involve the following reactions:

.

$$CH_2 = CH\text{-}OR + I_2 \rightleftharpoons CH_2 = CHOR...I_2 \text{ (fast)} \tag{71}$$

$$CH_2 = CH\text{-}OR...I_2 + I_2 \rightarrow ICH_2CH_2(OR)I + I_2 \text{ (slow)} \tag{72}$$

According to Ledwith and Sherrington[393], initiation is complicated by the formation of the ion pair

$$ICH_2\text{-}CH(OR)I + I_2 \rightleftharpoons ICH_2\text{-}CH = O^+\text{-}R \quad I_3^- \tag{73}$$

The iodine initiated polymerization will be reviewed in detail in the *Iodine as a Catalyst/Initiator* section.

3) Mechanisms for Steric Control: Many catalyst systems make stereospecific poly(vinyl ethers) via coordination mechanism. And any mechanism to explain the stereospecific growth of polymer must involve a means by which the configuration of the chain end is fixed in the transition state and a means by which the direction of attack of the monomer on this chain end can be controlled. The way in which these requirements have been met for vinyl ether polymerization is divided into three classes by Ketley[369]; formation of cyclic chain ends, retention of partial sp^3 character in the carbenium ion, and multifunctional catalysts and gegenions. The first two classes include simple homogeneous catalyst systems, and the last class includes heterogeneous catalyst systems and complicated homogeneous systems.

Formation of the cyclic chain end was proposed by Bawn and Ledwith[389](Scheme 8), and the proposed six-membered ring at the growing end is very similar to the one shown in the chain transfer reaction in Scheme 7.

In order to explain the formation of isotactic poly(isobutyl vinyl ether) in the presence of BF₃ coinitiator, Cram and Kopecky[397] suggested the following Scheme 8. In the Scheme, substituents P(polymer chain) and -OR(R = isobutyl) are visualized to occupy the least compressed equatorial positions in the transition state and the carbon carrying the -OR group is inverted during ring opening. The relative configurations of the two asymmetric centers formed determine the overall configurations of the chain. If the configurations are identical an isotactic polymer is formed, whereas if they are opposite a syndiotactic polymer is formed.

Cram's mechanism has also been used by Goodman and Fan[398] to explain the formation of syndiotactic poly(methyl α-methyl vinyl ether). The authors suggest that a growing oxonium ion in the form of a pseudo six-membered ring is formed by the interaction of the terminal carbenium ion with the ether oxygen of the penultimate unit.

Scheme 8. Steric control via cyclic chain end[397].

Perhaps the major objection to this theory is the almost nonexistent role of the catalyst in determining isotacticity. It would seem that any catalyst capable of yielding a carbenium ion on reaction with the vinyl ether would result in stereospecific growth. This objection has been solved somewhat by Bawn and Ledwith[389,399] by the assumption that positive charge resides primarily on carbon and the gegenion is closely associated with the carbenium ion[397].

Retention of partial sp^3 character in the carbenium ion was proposed by Higashimura et al.[400] as an explanation for steric control. A carbenium ion that is not strongly associated with its gegenion should be a true sp^3 hybrid and consequently planar. An attack upon this ion by an incoming monomer should therefore be of the same probability irrespective of which side the monomer approaches from. Consequently, propagation of such a free completely sp^2 carbenium ion should lead to the formation of an atactic polymer unless there is a strong steric interaction between the alkoxide group on the chain end and the alkoxide group on the monomer. In the latter case, a syndiotactic polymer should be formed, and there is some evidence that this in fact occurs[377b]. It is therefore assumed that, for an isotactic polymer to form, the carbenium ion must have a partial sp^3 character.

Higashimura and his coworkers have suggested that the carbenium ion is closely associated with the gegenion. When monomer addition takes place the monomer is oriented with the alkoxide group as far from the polymer end as possible[400] in the transition state. These authors suggest that the direction of tacticity depends on how closely the gegenion is bound[377b].

It is not made clear exactly how the gegenion can effect isotactic placement, however, even though the evidence suggests that it does. One possibility is that in the propagation step, reaction proceeds through a four-center transition state in which the

gegenion is partially bound to both the carbonium ion that is reacting and the one that is being formed.

It has recently been suggested that the extent of association between the growing cation and the counterion is a significant element in the steric control of alkyl vinyl ether polymers[401-402]. The most stable conformation of the last two units of a growing poly(vinyl ether) cation is shown in Scheme 9[403]. The relative ease of front- or back-side attack by the monomer is determined by the tightness of the growing ion pair and the steric hindrance of the approaching monomer with side-chain substituents. Thus, front-side attack leading to the formation of syndiotactic polymers is favored in highly polar solvents where more separated ion pairs are stabilized. However, nonpolar solvents, e.g., toluene, favor tight association between the propagating cation and its counterion, leading to back-side approach and an isotactic polymer. When the growing ion-pair end is crowded by a bulky substituent, such as t-butyl, interference between the bulky side chain and the counterion may result, thereby lowering coulombic attraction between ion-pair components which would favor front-side attack. Figure 5 shows how the fraction of syndiotactic dyads P_m in poly(t-butyl vinyl ether) decreases as the dielectric constant of polymerization solvent increases[404].

Theories concerning the stereospecific polymerization of alkyl vinyl ethers that emphasize the role of the catalyst most strongly are those that consider the catalyst to be a multifunctional entity capable of reacting simultaneously with both the chain end and the attacking monomer molecule. Natta, among others, emphasized this approach.

In the polymerization of cis- and trans-β-chlorovinyl ethers, diisotactic polymers are formed, which indicates a constant mode of presentation of the monomer units. Natta suggested that this may be accomplished by the monomer coordinating by both its double bond and its ether oxygen atom to the dimeric form of the catalyst(in this case, EtAlCl$_2$), which, in turn, is bound to the polymer chain-end(Scheme 10)[369].

Figure 5. The relationship between the structure and the polymerization condition: [404]; Toluene/CH_2Cl_2(vol/vol); A)1/0, B)7/3, C)3/7, D)0/1: Counterions; a)BCl_4^-, b)$GaCl_4^-$ and $InCl_4^-$, c)$TlCl_4^-$, d)$AlCl_4^-$.

Scheme 9. Effect of ion pairing on stereochemistry of propagation for alkyl vinyl ethers[403].

The concept of a multifunctional catalyst is also used by Natta to explain the observation that the catalyst $(C_5H_5)_2TiCl_2AlR_3$ gives a crystalline polymer below 30°C and an amorphous polymer above this temperature[405]. The stereospecific catalyst is assumed to be a complex that is stable only at low temperatures. At high temperatures the complex dissociates to give a fragment or fragments that are still active but cannot influence the steric course of the reaction.

Scheme 10. Monomer unit coordinated by both its olefin bond and ether oxygen to dimeric aluminum alkyl chloride[369].

In heterogeneous catalysts, the heterogeneous nature of the catalysts presumably play a key role in the various stages involved in stereospecific polymerization. Lal and McGrath[349] proposed a coordinated cationic mechanism as in Scheme 11 with the use of sulfuric acid-metal sulfate complexes. Polymerization is initiated by a proton bound to a large heterogeneous counterion derived from the metal sulfate complex. The metal center coordinates with the ether oxygen of the vinyl ether carbonium ion and thereby exercises further steric control for the incoming monomer. The ether oxygen of the incoming monomer is also presumed to coordinate with the metal on the catalyst surface.

The ability of these heterogeneous catalysts to yield high molecular weight polymers at somewhat elevated temperature suggests that the transfer to monomer and termination reactions are suppressed by the heterogeneous complex counterion. Furukawa[406] has suggested that such a complex catalyst should possess at least two coordination centers. As a general trend, an increase in bonding between metal sulfate

Scheme 11. Mechanism of the cationic coordinated polymerization of alkyl vinyl ether with a metal sulfate-sulfuric acid complex catalyst[349].

and sulfuric acid increases the stereoregularity of the polymer and its molecular weight. The strong coordinating ability of the catalyst stabilizes the bisulfate anion by complex formation and leads to the formation of a high molecular weight polymer even at higher temperatures. Furthermore, a high coordinating ability of the catalyst facilitates the coordination of the substituent in the monomer on the catalyst surface thereby producing a polymer of higher stereoregularity even at higher temperatures.

d) Structure, Properties, and Applications

The physical properties of poly(alkyl vinyl ethers) depend on molecular weight, the nature of the alkyl group, and stereoregularity. Homopolymers may appear as viscous liquids, sticky liquids, rubbery solids, or brittle solids. Polyethers with long alkyl chains are very waxy. The glass transition temperatures of the amorphous straight-chain alkyl vinyl ether homopolymers decrease with increasing length of the side chain. Also the melting points of the semicrystalline poly(alkyl vinyl ethers) increase with increasing side-chain branching. On lengthening the side chain by one carbon, specific volume increases by 14%[325,348], and it represents an increase in free volume,i.e., within experimental error the same value was found for poly(n-alkyl methacrylate)[407]. Table 26 shows the glass transition temperatures, melting points, densities, and solubility parameters of poly(alkyl vinyl ethers).

Traditionally, the molecular weight of vinyl ether polymers has been estimated by the so-called K value, a viscosity measurement originated by Fikentscher[368,409]. It is obtained by making use of the relationship shown in equation 74, where η_{rel} is the ratio of the viscosity of the solution to that of the solvent and C is the concentration of polymer, in g/dl.

Table 26. Physical Properties of Poly(Alkyl Vinyl Ethers)[a]

Poly(alkyl vinyl ethers) (Alkyl group)	Tg, °C	Tm, °C [b]	Density, g/cc	Solubility parameter [c] (cal/cc)$^{1/2}$
Methyl	-31	144	-	7.94
Ethyl	-42	86	0.951	7.54
n-Propyl	-49	76	-	-
Isopropyl	-3	190	0.924	-
n-Butyl	-55	64	0.926	7.85
sec-Butyl	-20	-	0.924	-
Isobutyl	-19	165	0.916	7.50
t-Butyl	-	238	-	-
n-Pentyl	-66	-	0.918	7.86
n-Hexyl	-77	-	0.902	7.81
2-Ethylhexyl	-66	-	0.897	-
n-Octyl	-80	-	0.893	7.87

[a] Data from [325].
[b] Data from [327].
[c] Data from [325, 408].

$$\log(\eta_{rel}/C) \;=\; \frac{75k^2}{1 + 1.5kC} \;+\; k \tag{74}$$

The Fikentscher K value equals 10^3k. It has been found that the intrinsic viscosity, $[\eta]$, of methyl and ethyl ether polymers in 2-butanone at 30°C can be related to molecular weight M, by equation 74[410], where $[\eta]$ is in dl/g.

$$[\eta] \;=\; 1.37\text{x}10^{-3}M^{0.54} \tag{75}$$

Natta and his coworkers have shown that the crystalline form favored by poly(α-olefins) with a linear side group is a ternary helix. Such a conformation is in accord with theoretical predictions[411]. However, when the poly(α-olefin) contains a branched side chain, steric hindrance makes the formation of ternary helix too energetic. Therefore conformational modifications occur. The nearer the branching is to the backbone chain, the greater the deviation from the ternary helix, for example, poly(3-methylbutene-1) crystallizes in a quarternary helix[369,412], poly(4-methyl-pentene-1) does in a helix containing seven monomeric units in two turns of the spiral. Poly(5-methylhexene-1), where the branching is distant from the chain, also forms a ternary helix[413].

In poly(vinyl ethers), the ether oxygen functions very much like the methylene group adjacent to the chain in poly(α-olefins). A general similarity in the ways the two sets of polymers crystallize is therefore observed.

Poly(methyl vinyl ether) was found by Bassi to possess a rhombohedric cell with $a = 16.20 \pm 0.10\text{Å}$ and $c = 6.5 \pm 0.05\text{Å}$(chain axis). The polymer forms a ternary helix, and there are 18 monomer units in the unit cell[369,414]. These results are analogous to those obtained for one of the crystalline forms of isotactic polybutene-1[415] and for isotactic 1,2-polybutadiene[416]. Poly(n-butyl vinyl ether) also crystallizes in a

rhombohedric cell with a = 23.7 ± 0.2Å and, as expected, c = 6.5 ± 0.05Å[369,417]. The spectrum is consistent with this polymer also forming a ternary helix.

The degradative effects of γ radiation on diethyl ether solutions of poly(vinyl ethers) have been studied under a variety of conditions[418]. All alkyl vinyl ether polymers, except t-butyl vinyl ether, exhibit similar degradative behavior showing free energy of scission(Gsc) values of 0.3~0.9 scissions per 100 eV at 0°C. Degradation is much more pronounced for poly(t-butyl vinyl ether), which has a Gsc of 3.6 at 0°C.

Poly(vinyl ethers) must be stabilized by the addition of antioxidants or ultraviolet-radiation absorbers. Amorphous homopolymers exhibit outstanding tack characteristics and are, therefore, widely used in pressure-sensitive adhesives, tackifiers, and plasticizers. They are often modified by the additions of many polymers. The homopolymers can be cured by radiation or peroxides to produce interesting vulcanizates[419-423]. Copolymers with small amounts of vulcanizable groups(such as dienes, allyl vinyl ethers, 2-chloroethyl vinyl ethers, etc.) have also been studied[348].

The application of the homo poly(vinyl ethers) includes many interesting areas of polymer science. Some of the recent applications of homopolymers are as follows[309a];

- Poly(methyl vinyl ether)(PVM) is used as pressure-sensitive adhesive composition that adheres to wet surfaces and is removable with water[424]. Remarkably low hygroscopicity(5% water pick up at 90% relative humidity) and compatibility with a wide variety of other polymers make this polymer useful. Another application is the use of in the extention of desalination efficiency of reverse osmosis membranes. Service life of the membranes is extended 70% by treatment of the membranes first with 100 ppm aqueous PVM and then 10 ppm PVM[425]. This polymer is also used for viscosity control and dry-film flexibility in UV photoresist coating solutions.

- Poly(ethyl vinyl ether) is used in adhesives and also in moisture-permeable, non ir-
  ritating surgical casts. Poly(2-chloroethyl vinyl ether) is used in x-ray beam resists.
  The resists are three times more sensitive and give twice the resolution of poly(ethyl
  vinyl ether) based resists[426].

- Lower alkyl vinyl ether homopolymers are used in adhesives and in photoresists.
  They impart dry-film flexibility and build viscosity to a photochemical resist coating
  composition[427].

4. Controlled Polymerization

Almost all initiation systems lead alkyl vinyl ethers to uncontrollable
polymerizations in terms of regulation of molecular weight and molecular weight
distribution(living polymerization).

Bawn et al.[50] reported that the polymerization of isobutyl vinyl ether by stable
carbenium salts($(C_6H_5)_3C^+SbCl_6^-$, $C_7H_7^+SbCl_6^-$, $(C_6H_5)_3C^+BF_4^-$) is one of the
simplest models of cationic polymerization, i.e., it becomes a living polymerization. The
authors assumed rapid and complete initiation, propagation by free ions, and negligible
termination. Chung et al.[428] repeated some of the experiments using more rigorous
purification and drying techniques. Following the usual assumptions, the obtained k_p
values were 2 to 3 times higher than those reported previously and it was concluded that
propagation was essentially due to the free ions since these rate constants agreed with
those measured in radiation-induced polymerizations of the same monomers. However,
no attempts were made to study the process of initiation.

Later, Subira et al.[429] carried out a very detailed and thorough study of the
polymerization of the above polymerization system and found that the oversimplified

reaction scheme previously assumed to hold for the above systems was in fact erroneous. The mistake arose due to insufficient study of initiation process. Also some termination was observed. Using $(C_6H_5)_3C^+SbCl_6^-$ in methylene chloride, the values of k_i was 5.4 l/mol.sec and k_p was 7×10^3 l/mol.sec at 0°C.

Some living polymerization systems have recently been reported by using many initiation systems - iodine containing initiation systems, modified alkyl aluminum chloride initiation system, modified titanium chloride initiation system, and modified boron trifluoride initiation system. The review of all these living systems is given in the previous section *Controlled Ionic Polymerization*.

C. Iodine as a Catalyst/Initiator

1. Equilibrium Reactions with Iodides

Molecular iodine is thought to act like a Lewis acid. It forms many complex ions with iodide[430]. The equilibrium reactions between these complex ions have been studied by many workers and the effects of temperature and solvent were reported. Haddock et al.[431] proposed ions of form of I^-, I_3^-, I_4^{-2}, I_5^-, I_6^{-2} and I_7^- in aqueous solution, and stressed the importance of species I^-, I_3^-, and I_5^-. In the following equilibrium reactions, the value of K_7 is very small compared to those of K_3 and K_5.

$$I^- + I_2 \overset{K_3}{\rightleftharpoons} I_3^- \qquad\qquad (76)$$

$$I_3^- + I_2 \overset{K_5}{\rightleftharpoons} I_5^- \tag{77}$$

$$I_5^- + I_2 \overset{K_7}{\rightleftharpoons} I_7^- \tag{78}$$

As the concentration of iodine decreases the formation of I_3^- increases first then the formation of I_5^- follows. In relatively higher concentrations of iodine and iodide(0.1 M of total iodide and 0.04 M of total iodine), one or more ions form in addition to I_3^- and I_5^-. When the concentration of iodine is less than 7×10^{-4} M, the values of K_3 and K_5 in aqueous solution at 25°C are as follows.

In 2.00 M KNO_3 ; $K_3 = 743.1 \pm 0.6$, $K_5 = 20.2 \pm 0.8$

In 0.1 M KNO_3 ; $K_3 = 769 \pm 5$, $K_5 = 16 \pm 7$

In a solution with a relatively low concentration of iodine, the ratio of $[I_5^-]/[I_3^-]$ is represented by the concentration of iodine and K_5 as in equation 79.

$$[I_5^-]/[I_3^-] = \{K_3 K_5 [I^-][I_2]^2 / K_3 [I_3^-][I_2]\} = K_5[I_2] \tag{79}$$

Only the structure of the triiodide ion, $[I_3^-]$, is of real significance in this case.

Palmer et al.[432-433] reported that the equilibrium constant K_3 has a temperature dependence. They proposed following equation in studies using spectroscopic measurements and distribution experiments in aqueous solutions.

$$\log K_3 = A/T + B + C(\log T) \tag{80}$$

where T is absolute temperature, A is 555.0, B is 7.355, and C is -2.575. This equation correlated well with experimental values. At 3.8°C the observed equilibrium constant K_3 was 1160 whereas the calculated value was 1170. At 50.2°C, the observed equilibrium constant was 409 and the calculated value was 405.

The equilibrium constant K_3 has solvent dependence. Hayakawa et al.[433] found that K_3 increased as the content of alcohol increased in water-alcohol mixed solvents. Benoit et al.[434] also reported that the equilibrium constant became larger in nonpolar aprotic solvents than in polar aprotic solvents, and concluded that non-coulombic contribution must be important from the result of comparison between the free energy, ΔG and the electromotive force value, ΔE, for the equilibrium reaction(equation 76).

The equilibrium reaction in DMF and in acetonitrile are significantly different though the dielectric constants are nearly identical, 36.7 and 38.8 respectively. The change of the free energy of the formation of $I_3{}^-$, $\Delta\Delta G(I_3{}^-)$, becomes dependent on the parameter β as in equation 81, where β is the Kamlet-Taft[436] parameter which expresses basicity in terms of electron donor effects.

$$\Delta\Delta G(I_3{}^-) = -0.81\Delta\Delta G(I^-) + 2.08\beta - 1.22 \tag{81}$$

2. Organic Reaction Systems

In the organic reaction system, molecular iodine has been used especially in the solvolysis of tertiary alkyl halide[437]. Iodine catalyses the solvolysis of t-butyl and t-amyl iodides in aqueous ethanol and in aqueous hexafluoropropan-2-ol. The catalytic effect is also found for t-butyl bromide in aqueous ethanol but to small extent. The

strongest catalysis by iodine was found in the aqueous ethanolysis of 1-adamanthyl iodide.

The catalytic constants for aqueous ethanolysis of t-butyl iodide decrease less steeply than the rate constants of the uncatalyzed reactions as the proportion of ethanol in the medium increases. The proposed reaction mechanism is shown in equation 82 and it involves a pre-association mechanism which is assumed to be rapid[438].

$$RX + I_2 \rightleftharpoons RX.I_2 \rightleftharpoons R^+XI_2^- \rightarrow products \qquad (82)$$

According to this mechanism, catalysis is the consequence of two effects: (1) a favorable equilibrium between covalent alkyl iodide and iodine, and (2) the fact that I_3^- is a better leaving group than I^-.

Another example of iodine catalysis is seen in the methanolysis of 2-iodopropane[393]. When the solution of 2-iodopropane in methanol containing I_2 was allowed to react at 50°C, methyl isopropyl ether was readily formed. The rates of methanolysis was determined by titration of the evolved HI. The existence of iodine catalyzed the solvolysis several orders of magnitude faster.

3. Polymerization Systems

Iodine is an efficient initiator of the polymerization of some reactive monomers, e.g., p-methoxystyrene, alkyl vinyl ethers, N-vinyl carbazole and to a lesser extent styrene and acenaphthylene[123,440]. But alkenes do not polymerize in the presence of iodine, instead they give the corresponding diiodides.

Molecular iodine reacts with double bonds and sometimes polymerizations occur. The addition reaction is complicated due to the apparent occurrence of both a radical and a polar contribution to the mechanism. Fraenkel and Bartlet[441] studied the addition of iodine to styrene and showed that a radical inhibitor reduced the rate of reaction considerably, but did not inhibit it completely. The addition reaction of iodine to alkenes such as propene, butenes, and 1-pentene is rapid, and the diiodides formed tend to decompose in the presence of iodine[442]. Diiodide compounds of pentenes are stable in the absence of iodine, but with traces of iodine they generate hydrogen iodide and tend to polymerize[443].

The polymerizations of aromatic monomers by iodine have been studied by many workers. Okamura et al.[439,444] obtained the propagation rate constants k_p's in the polymerizations of p-methoxystyrene and styrene. They assumed that the total amount of initiator used in the polymerization was distributed among three species; free initiator, initiator complexed to the monomer, and active species, in the early stages of reaction. The determination of the rate constant was in fact erroneous since the iodine bound to the polymer was not taken into account. It was also assumed that stationary-state conditions existed, yet these were not achieved in either system.

Giusti et al.[123b,445] found that the polymerization of styrene by iodine has an induction period which can be eliminated by addition of a cocatalyst, hydrogen iodide. They envisaged the addition of iodine to the olefinic double bond and the slow spontaneous formation of HI in the noncocatalyzed process, that is

$$PhCH = CH_2 + I_2 \rightleftharpoons PhCHI\text{-}CH_2I \tag{83}$$

$$PhCHI\text{-}CH_2I \overset{slow}{\rightleftharpoons} PhCH = CHI + HI \tag{84}$$

$$HI + 2I_2 \rightleftharpoons HI_2{}^+ + I_3{}^-$$

(85)

$$I_3{}^- + HI_2{}^+ + PhCH=CH_2 \rightarrow (PhCHI-CH_3)2I_2$$

(86)

Participation of HI as shown in the scheme results in the formation of 1-phenylethyl iodide which yields an active cationic center by ionization with iodine. Deliberate addition of HI accelerated the establishment of these equilibria, and hence the formation of active centers. But the HI alone does not cause any polymerization. They concluded that the polymerization must be pseudocationic, the active species being both 1-phenyl iodide and styrene diiodide polarized by the specific solvation of iodine molecules. Similar work was carried out on acenaphthylene and the same mechanistic conclusions were reached[123a, 446]. The lack of the effect of high electric fields applied to the polymerizing solutions was an additional element in favor of pseudocationic propagation.

Higashimura et al.[100, 447-450] studied the polymerizations of p-methoxystyrene and p-methylstyrene by molecular iodine, and they observed bimodal molecular weight distributions of the resultant polymers under specific conditions. They concluded that among the active species present in these systems one might be non-ionic. Copolymerization studies with vinyl ethers as second monomer seemed to confirm the presence of more than one type of chain carriers[447]. An interesting but incomplete investigation was also carried out on the possible living character of the polymerization of p-methoxystyrene by iodine in media of low polarity[449-450]. In this situation the active species seem to be long lived and non-ionic, and the molecular weight of the polymers increased with conversion and with second monomer additions after the end of the first polymerization. Unfortunately this study was limited to the measurement of the degree of polymerization(DP).

The polymerizations of many reactive monomers other than those mentioned above have been studied. 2-Vinyl furan[451-452], N-vinylcarbazole and N-vinyl indole[97], anethole[453] are examples. Polymerization phenomena are usually complicated and similar to those of styrene. No definitive polymerization mechanisms have been proposed. In the polymerization of N-vinylcarbazole[366], iodine was found to be incorporated in the polymer probably as C-I bonds in terminal groups.

Among the monomers which can be polymerized by iodine, alkyl vinyl ethers have been studied the most and the polymerization of alkyl vinyl ethers using molecular iodine was reported by Wislicenus in as early as 1878[303]. Eley and Richards[341] demonstrated that ions, not free radicals as proposed earlier[454], are the active intermediates and suggested that a number of equilibria are involved prior to polymerization. They proposed Scheme 12 as the initiation mechanism of the polymerization in ether solvent(ROR).

In Scheme 12, the compound, 15, represents a so-called "inactive π-complex" which does not take part in the polymerization. Later Ledwith and Sherrington re-examined[393] these systems in an attempt to clarify some anomalies in the reported ultra-violet/visible spectra[392], and found that interaction of molecular iodine with alkyl vinyl ethers in methylene chloride leads initially to equilibrium formation of approximately substituted 1,2-diiodoethanes. They proposed Scheme 13 as the initiation mechanism. When the initial ratio of monomer to iodine is sufficiently small for appreciable quantities of free iodine to remain, initiation occurs by iodine catalysis of carbon-iodine bond heterolysis. When the initial ratio is so large that all iodine is consumed rapidly by addition to the monomer double bond, then only comparatively slow initiation results following unimolecular heterolysis of the iodine adduct.

This study of polymerization of alkyl vinyl ethers by iodine was extended by Johnson and his coworkers[394]. In an investigation of the initiation phenomena,

Scheme 12. Proposed initiation mechanism of alkyl vinyl ethers by iodine[341].

Scheme 13. Proposed initiation mechanism of alkyl vinyl ethers by iodine[392].

Johnson and Young demonstrated that the addition of iodine to the vinylic double bond is the key process preceding the formation of active species, based on the large value of heat of reaction of the addition process of double bond and iodine. They also showed that these systems produce polymers containing terminally-bound iodine and that the DP's of these products increase upon further additions of monomer, i.e., these polymerizations possess some degree of living character. No real termination occurs, therefore, and the chains retain their potential for propagation.

Recently Higashimura and his coworkers reported many interesting papers on the polymerization of alkyl vinyl ethers initiated by iodine. They observed an increase in polymer molecular weight with conversion in the iodine-initiated polymerization of isobutyl vinyl ether at low temperatures[388]. But a great improvement in polymerization was attained by employing the hydrogen iodide-iodine catalyst[124]. By using an equimolar mixture of HI and iodine, they observed almost ideal living polymerization of isobutyl vinyl ether in nonpolar solvents at low temperatures. Polymerization by the HI/iodine catalyst is reviewed in the previous section, *Ionic Polymerization via 'Covalent' Propagating Species.*

Chapter III

Experimental

A. Materials and Their Purification

1. Initiators

a) HI Solution

Hydrogen iodide was obtained from the Aldrich Chemical Company as 57% aqueous solution. Dehydration was performed by dropping the solution onto phosphorus pentoxide, and the evolved gas was dried by passing it through a tube filled with phosphorus pentoxide. Then the gas was absorbed into predistilled cold n-hexane or carbon tetrachloride[123b].

The apparatus used in the preparation of the III solution is shown in Figure 6. Typically, about 30 grams of the phosphorus pentoxide was placed into a 250 ml round bottom flask having a small side arm, and purged with a weak stream of dry argon. Approximately 27 ml of 57% aqueous HI was added through a 30 ml dropping funnel mounted atop the flask. The drying tube was more than half-filled with phosphorus pentoxide and the drying agent was evenly distributed along the tube in order to provide a thin channel through which the gas could pass. The solvent was added(210 ml) into the absorption flask via a syringe and the whole apparatus was protected from light using aluminum foil. The target concentration was around ca. 1 M. Time was allowed before the addition of solvent into the absorption flask to purge it of air because hydrogen iodide becomes oxidized in the presence of air and generates iodine. Throughout all experiments, unnecessary contact with air or moisture was avoided.

The solvent was stirred via magnetic stirrer in order to facilitate absorption of the gas, and the rate of gas evolution was regulated by controlling the dropping rate of the aqueous HI solution. When the concentration of the solution was relatively high (such as more than 0.8 N), the solutions were difficult to handle, especially the n-hexane solutions. Therefore, the solutions were sometimes diluted.

b) Iodine

Resublimed iodine was obtained from the Fisher Chemical Company and purified by sublimation from potassium iodide and ignited lime[455]. Typically, 20 g of iodine, 2 g of potassium iodide, and 4 g of ignited lime(CaO) were mixed and sublimed. Crystals were collected and kept in a brown bottle in a dark place.

In order to use the iodine as a catalyst, an n-hexane or carbon tetrachloride solution was prepared just before each polymerization by dissolving the required amount

1. Argon inlet
2. Addition funnel
3. Dehydration flask
4. P_2O_5 tube
5. Bubbler
6. Magnetic bar
7. Ice bath
8. Septum
9. Dry-ice trap
10. NaOH tube

Figure 6. Apparatus for the preparation of HI solution.

of iodine in a certain amount of clean solvent in a septum-capped dry flask protected from light. The solution concentration was controlled to be no more than 1 wt./vol.% due to the solubility restriction at experimental temperatures.

c) Organometallic Compounds

Triethylaluminum(Et_3Al), diethylaluminum chloride (Et_2AlCl), and ethylaluminum dichloride($EtAlCl_2$) were obtained from the Aldrich Chemical Company as 1.0 M hexane solutions. Antimony pentachloride($SbCl_5$) was obtained from the same company as 1.0 M methylene chloride solution. n-Butyllithium was also supplied by Aldrich as a 1.6 M hexane solution. All these organometallic compounds were used as received.

These compounds were always handled under dry, purified nitrogen or argon using clean, dry glass syringes with teflon plungers. All transfers were performed via syringes with stainless steel needles and adaptors. All glassware was cleaned, flamed and purged prior to use. For more detailed information regarding the handling of air sensitive reagents, see Aldrich's " The Safe Handling of Air-Sensitive Reagents " [456].

d) Boron Trifluoride Etherate

Boron trifluoride etherate($BF_3.OEt_2$, molecular weight(mw); 141.93, density(ρ); 1.154[20]) was obtained from the Aldrich Chemical Company and used as received.

e) Methyl p-Toluenesulfonate(MeOTs)

$$CH_3 - \underset{\bigcirc}{\bigcirc} - SO_3CH_3$$

Methyl p-toluenesulfonate was obtained from the Aldrich Chemical Company(mw; 186.23, boiling point(bp); 144~145°C/5 mmHg, melting point(mp); 27.5°C, ρ; 1.22) and distilled under vacuum(7-8 torr). Typically, the first 10 ml of distillate from ~80 ml was discarded, and the next ca 50 ml of distillate was collected(130-135°C) and used. The reported physical properties are[457]: bp; 292°C(760 torr) or 140°C(20 torr); colorless; soluble in alcohol, ether, benzene, etc.; and soluble in water.

f) Benzyl Iodide and Iodomethylstyrene

Benzyl iodide was prepared by the reaction of benzyl chloride with sodium iodide[458].

$$\underset{\bigcirc}{R} \quad -CH_2Cl \quad + \quad NaI \quad \xrightarrow[\text{reflux}]{\text{acetone}} \quad \underset{\bigcirc}{R} \quad -CH_2I \quad + \quad NaCl \quad (87)$$

$$R \equiv H\text{-}, CH_2 = CH\text{-}$$

Typically, 15.1 ml of benzyl chloride(0.13 mole, reagent grade from Fisher) and 30.2 g of sodium iodide(50% excess, reagent grade from Fisher) were added into a 250 ml flask and refluxed with 130 ml of acetone(HPLC grade from Fisher) for one hour. The formed salt was filtered off after the reaction, and the filtrate was evaporated by using a rotary evaporator. The resultant slurry-like material was then dissolved by the addition of 100 ml of water and 100 ml of diethyl ether.

After separation, the ethyl ether layer was washed 3 times with each 50 ml of 5% aqueous sodium thiosulfate($Na_2S_2O_3$) solution in order to remove iodine and benzyl alcohol then dried with anhydrous $MgSO_4$ and filtered. The solvent was evaporated and the resultant material was dissolved in 40 ml of n-hexane and recrystallized in a freezer. Colorless, powdery, needle shaped crystals were obtained by filtration with a glass filter. The crystals and another portion of crystals obtained from the recrystallization of the filtrate were combined and washed with cold n-hexane, yielding 20.5 g(72% of theoretical). The product is a lachrymator, and the melting point agreed well with the literature value. Reported properties of the product and its related compounds are;

Benzyl iodide: mw; 218.04, mp; 24.5°C, bp; 93[10], ρ; 1.7335[25]

Benzyl chloride: mw; 126.6, mp; -43~-48°C, bp; 179°C

Benzyl alcohol: mp; -15.19°C, bp; 204.7, water soluble(4 g/100 ml)

Iodomethylstyrene(mw; 244.07, mp; 9~10°C) was also prepared from chloromethylstyrene(reagent grade from Aldrich, mw; 152.62, para/meta ratio is ca.2) and sodium iodide, according to the procedure described in the above mentioned literature. Crystals of a powdery needle shape were obtained.

2. Monomers

a) Alkyl Vinyl Ethers

$$CH_2 = CH\text{-}O\text{-}R, \qquad R \equiv nBu\text{-}, Et\text{-}$$

n-Butyl vinyl ether(nBVE) was obtained from the Aldrich Chemical Company. It

was washed three times with 5% aqueous sodium hydroxide solution, then washed with distilled water until the pH(hydrogen-ion exponent) became neutral. This monomer was dried over potassium hydroxide pellets(Fisher) and fractionally distilled over finely ground calcium hydride through a 6 inch column packed with glass beads of 5 mm diameter. Then the nBVE was redistilled either by a trap to trap method in the presence of a small amount of n-butyllithium and 1,1-diphenylethylene or by distillation over sodium metal under argon atmosphere before use. No difference was observed in the polymerization using either purification procedure. Distilled nBVE was kept in 50 ml doubly septum-capped bottles in a freezer and used. For detailed information regarding the trap to trap method, see reference 30c. Ethyl vinyl ether(EVE) was obtained from Polysciences(technical grade). It was treated and fractionally distilled using the same procedure described for nBVE, then redistilled over sodium metal under argon atmosphere and kept in septa bottles in a freezer.

b) Oxazolines

R ≡ CH$_3$-, CH$_3$CH$_2$-

2-Methyloxazoline(MeOXZ) was obtained from the Aldrich Chemical Company. It was stirred overnight over finely ground calcium hydride then distilled under nitrogen atmosphere. The middle portion was collected and kept in a septa bottle in a freezer.

2-Ethyloxazoline(EtOXZ) was kindly supplied by the Dow Chemical Company. It was stirred over NaOH pellets for 2 days, distilled under reduced pressure, then redistilled over finely ground calcium hydride after refluxing for one hour. The middle portion was collected and kept in a septa bottle in a freezer. The reported physical properties of these monomers are[166];

2-Methyloxazoline: mw; 85.11, bp; 111°C, ρ; 1.005^{20}, n_D^{20}; 1.434

2-Ethyloxazoline: mw; 99.13, bp; 128.4°C, mp; -62°C, ρ; 0.982^{20}, n_D^{20}; 1.4370

c) Styrenic Monomers

Styrene(from Fisher), p-methylstyrene(p-MeSt, from Aldrich), and α-methylstyrene(from Eastman Kodak) were vacuum distilled after being stirred overnight over finely ground calcium hydride. They were kept in septa bottles in a refrigerator. p-tert-Butylstyrene(p-t-BuSt, from Polysciences) was used after filtration through activated alumina or after distillation from calcium hydride. p-Methoxystyrene(p-MeOSt, from Aldrich) was used as received. The reported physical properties of these monomers are[457];

Styrene: mw; 104.16, bp; 145.2°C, mp; -30.63°C, ρ; 0.906_4^{20}

p-Methylstyrene: mw; 118.18, bp; 173°C, ρ; $0.9261_{15.5}^{15.5}$

α-Methylstyrene: mw; 118.18, bp; 165.4°C, mp; -24.5°C, ρ; 0.9106_4^{20}

p-t-Butylstyrene: mw; 161.27, bp; 219°C, ρ; 0.8818

p-Methoxystyrene: mw; 134.18, bp; $204{\sim}205^{756}$, ρ; 1.0001_4^{13}

d) Propylene Oxide

Propylene oxide(from Aldrich) was used after fractional distillation over finely ground calcium hydride. It was stirred overnight over calcium hydride before distillation(mw; 56.06, bp; 63°C, ρ_4^0; 0.859).

3. Solvents

a) n-Hexane

n-Hexane was obtained from Baker(HPLC grade) Chemical Company or Mallinckrodt(AR HPLC grade). It was first stirred over concentrated sulfuric acid(100 ml of sulfuric acid to 900 ml of n-hexane) for a week to remove olefinic impurities. The yellowish acid layer was washed with distilled water until the pH of the aqueous layer became neutral. After drying with anhydrous sodium sulfate or sodium pellets, the solvent was refluxed over sodium-potassium alloy overnight. The alloy was prepared by addition of chips of potassium metal(mp; 63.6°C) and sodium metal(mp; 97.8°C) into the flask. The solvent was distilled under argon.

n-Hexane was fractionally distilled over calcium hydride and redistilled over sodium metal in the early part of these experiments, but no difference was observed in the polymerization reactions.

b) Carbon Tetrachloride

Carbon tetrachloride was obtained from the Fisher Chemical Company and fractionally distilled over finely ground calcium hydride under argon after being stirred overnight.

c) Acetonitrile

Acetonitrile(HPLC grade) was obtained from Fisher and distilled over finely ground calcium hydride under argon after being stirred overnight.

d) Dimethyl Formamide(DMF)

DMF was obtained from Fisher and distilled over a mixture of BaO and calcium hydride under argon[459].

e) Ethyl Ether

Ethyl ether(anhydrous grade) was obtained from Fisher and used as received.

f) Methylene Chloride

Methylene chloride was obtained from Fisher and treated with concentrated sulfuric acid, then distilled water, and distilled from finely ground CaH_2.

4. Others

n-Butylamine(nBuNH$_2$, mw; 73.14, bp; 77.8°C, ρ; 0.7414$_4^{20}$) was obtained from Fisher and used as received. n-Propylamine(nPrNH$_2$, mw; 59.11, bp; 47.8°C, ρ; 0.7173$_4^{20}$) was obtained from Fisher and used after distillation from CaH_2.

Isopropylamine(iPrNH$_2$, mw; 59.11, bp; 32.4°C, ρ; 0.6891$_4^{20}$) was obtained from Aldrich and used as received. Triethylamine was obtained from Fisher and used with the addition of molecular sieves into the bottle. Dioxane(from Fisher) was used after distillation from calcium hydride. Ethanol and methanol(from Fisher) were used as received.

Other chemicals were obtained from various companies and used without further purifications.

B. Polymer Synthesis

1. Alkyl Vinyl Ether Polymers

$$n \; CH_2 = CH \xrightarrow{\text{initiator}} \text{-(-CH}_2\text{-CH)}_n^- \qquad (88)$$
$$\qquad\qquad | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad O \qquad\qquad\qquad\qquad\qquad\qquad O $$
$$\qquad\qquad | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad R \qquad\qquad\qquad\qquad\qquad\qquad R $$

a) Polymerization by BF$_3$OEt$_2$

To a septum-capped round bottomed flask protected from light with aluminum foil, was added 40 ml of purified n-hexane and 5 ml of purified nBVE. The flask was cooled to -78°C in a dry ice-acetone bath while nitrogen pressure(3~5 psi) was maintained via hypodermic needle. The BF$_3$OEt$_2$ initiator(0.05 ml) was then charged at -78°C. After two hours of reaction(ppt was observed), the reaction was terminated by injecting 3 ml

of NH$_3$-MeOH(1/4 volume/volume of 28% aqueous NH$_3$ solution and methanol) solution[460]. After evaporation of the solvent and unreacted materials, 0.7 g of sticky rubbery material was obtained.

b) Polymerization by Iodine

To a 100 ml septum-capped round bottomed flask, were added 5 ml of purified nBVE and 30 ml of purified n-hexane. The flask was cooled to -15°C in a methanol bath via a Neslab® immersion cooler. Then, 10 ml of iodine initiator solution prepared by dissolving 0.295 g of I$_2$ in 45 ml of purified n-hexane, was charged at -15°C.

The polymerization flask was usually light protected by aluminum foil, but the course of the polymerization was watched in a unprotected flask. The iodine color disappeared immediately after the addition process, and the color of the polymerization mixture was almost clear. Only a slightly pink-yellow tint was observed during the polymerization. At the end of the polymerization, the color turned brown to reddish-black.

After allowing the polymerization to proceed for a given time(e.g., 5 hours), the polymerization was terminated with a triethylamine-methanol solution(1/2 volume/volume). The after-treatment of the polymer was the same as described in *Polymerization by HI/I$_2$*

c) Polymerization by HI/I$_2$

To a 100 ml septum-capped round bottomed flask, were added 10 ml of purified nBVE and 21 ml of purified n-hexane. The flask was cooled to -25°C in a methanol bath.

Into this flask 0.55 ml of HI-hexane solution(0.680 N) was added with a dry syringe. Then 12 ml of iodine solution(0.321 g of purified iodine in 40 ml of purified n-hexane) was charged with a syringe. The reaction time was calculated from the moment the iodine solution was injected.

The reaction mixture was stirred with a teflon coated magnetic bar, and the flask was usually protected from light by aluminum foil. However, the course of the polymerization was watched in an unprotected flask. The addition of hydrogen iodide maintained a colorless solution. In the addition process of the iodine, the iodine color disappeared immediately after addition, and the resultant color of the polymerization mixture was almost clear. A slight pink-yellow tint was observed during the polymerization. At the end of the polymerization, the color turned brown to reddish-black. These observations were very similar to those in the iodine initiated polymerization.

After allowing polymerization to proceed for a given time, the reaction was terminated with 4 ml of triethylamine-methanol(1/2 v/v) solution. Upon injection of the terminator, the color of the reaction mixture turned a deep reddish-brown. Upon stirring ~2 hours, two layers separated. The top layer was colorless and the bottom layer was reddish-black(small volume, 1~2 ml). The solvent and unreacted materials were removed by using a rotary evaporator. The polymer was dried in a vacuum oven(ca. 1 torr) for 2 or 3 days at ~50 °C. Higher drying temperatures yielded undesirable colors in the polymer. The polymer was a viscous liquid, and the polymerization yield was calculated from the weight of the polymer. In this calculation, the initially charged weight of the catalyst was subtracted from the total dried weight.

$$\% \ Yield \ = \ \frac{Dried \ weight \ - \ Weight \ of \ I_3}{Weight \ of \ charged \ monomer(7.70g)} \ x \ 100 \qquad (89)$$

The product was dissolved in n-hexane, washed 3 times with a 5% aqueous sodium thiosulfate solution in order to remove iodine, washed several times with 5% aqueous NaOH and with distilled water, then dried over anhydrous sodium sulfate. A viscous, liquid-like polymer was obtained by the removal of the solvent by using a rotary evaporator, followed by drying under vacuum. The obtained polymer was analyzed by GPC and other techniques.

d) Polymerization by HI/Lewis Acid

1) Polymerization by HI: To a 100 ml, septum-capped round bottomed flask, were added 5 ml of purified nBVE and 40 ml purified n-hexane. The flask was cooled to -20°C in a methanol bath, then 1.90 ml of HI-n-hexane solution(0.210 N) was injected via a dry syringe. After wrapping with aluminum foil, the flask was transferred to a water bath whose temperature was maintained at +20°C. After a given time, the polymerization was quenched with Et$_3$N, and the resultant polymerization mixture was purified using a similar procedure to that described in *Polymerization by HI/I$_2$*.

2) Polymerization by HI/Et$_2$AlCl: To a 100 ml, septum-capped round bottomed flask, were added 10 ml of purified nBVE and 33 ml of purified n-hexane. The flask was cooled to -15°C, then 0.95 ml of n-hexane-HI solution(0.40 N) was injected followed by the injection of 0.5 ml of Et$_2$AlCl solution(15 wt% in hexanes). After 2 hours of reaction, the polymerization was quenched by the injection of 2 ml of Et$_3$N-MeOH(1/2 v/v) solution. For comparison, another reaction was run at the same time in the absence of HI. All reaction conditions were the same. Purification and drying procedures were similar to those described in the preceeding section. Polymerization yields were calculated by measuring the weight of the dried polymer.

3) **Others:** Polymerizations were conducted using the initiation systems HI/Et$_3$Al, Et$_3$Al, HI/SbCl$_5$, and SbCl$_5$. All procedures were approximately the same as those described in the preceeding section.

2. Oxazoline Polymers

a) Polymerization by Methyl p-Tosylate

$$n \quad \underset{O \quad N}{\overset{R}{\triangle}} \quad \xrightarrow{\text{MeOTs}} \quad CH_3 \!\!\left[\!\! \begin{array}{c} N\text{-}CH_2CH_2 \\ | \\ C=O \\ | \\ R \end{array} \!\!\right]_{n-1} \!\!\! N \overset{+}{\underset{O}{\overset{R}{\triangle}}} \quad {}^-OTs \qquad (90)$$

To a 20 ml, septum-capped ampoule, were added 5 ml(49.5 mmole) of purified ethyloxazoline, 7 ml of purified acetonitrile, and 0.38 ml(ca.2.5 mmole) of methyl tosylate.

The contents of the ampoule were frozen in a dry ice-acetone bath and evacuated through a needle by vacuum line. Then, the ampoule was back-filled with argon and thawed. Then again, the ampoule was frozen, evacuated, argon back-filled, and thawed. After this degassing procedure was repeated 2 times, the ampoule was sealed off with a propane-oxygen torch.

Polymerization was conducted in an air convection oven for 21 hours at 80°C. A slightly yellow-red polymerization mixture was obtained. A small portion(ca.20%) of the reaction mixture was precipitated twice into 50 ml of diethyl ether, and a white powder was obtained. The white powdery polymer was dried in a vacuum oven(ca.1 torr). The

yield was almost quantitative(ca.95%). The rest of the polymerization mixture was used in a copolymerization reaction.

b) Polymerization by Benzyl Iodide

$$n \quad \underset{O}{\overset{R}{\bigvee}} N \quad \xrightarrow{\text{BzI}} \quad \bigcirc\text{-CH}_2 \left[\begin{array}{c} \text{N-CH}_2\text{CH}_2 \\ | \\ \text{C}=\text{O} \\ | \\ \text{R} \end{array} \right]_{n-1} \begin{array}{c} \text{N-CH}_2\text{CH}_2\text{I} \\ | \\ \text{C}=\text{O} \\ | \\ \text{R} \end{array} \quad (91)$$

To a 20 ml septum-capped ampoule were added 3.4 ml(34 mmole) of ethyloxazoline and 0.377 g of benzyl iodide dissolved in 2 ml acetonitrile. Then, 5 ml of acetonitrile was added.

Degassing, sealing, polymerization, and after-treatment were almost the same as in the previous section. The reaction product was more reddish than in the preceeding section and the yield was almost quantitative.

A similar polymerization was conducted in a DMF solvent at 98°C. A slightly yellowish, glassy polymer was obtained with 95% conversion.

Methyloxazoline was also polymerized in a 50 ml round bottomed flask equipped with a 3 way stopcock in DMF solvent at 98°C for 1 hour. The polymer was obtained as a white powder or a yellowish gum. The polymer(expected Mn was 850) was so hygroscopic that the white powder became gummy after ca.10 minutes. Conversion was almost quantitative.

3. Amine-Terminated Alkyl Vinyl Ether Oligomers

a) Direct Approach

$$n\ CH_2 = \underset{\underset{R}{\overset{|}{\underset{|}{O}}}}{\overset{|}{CH}} \quad \xrightarrow[\text{2) H}_2\text{N-R}']{\text{1) HI/I}_2} \quad \left[CH_2\text{-}\underset{\underset{R}{\overset{|}{\underset{|}{O}}}}{\overset{|}{CH}} \right]_n \!\!\text{NH-R}' \qquad (92)$$

1) Model Reactions: Into a 25 ml septum-capped round bottomed flask, were added 1 ml of nBVE and 12 ml of HI(0.688 N, ~20% excess) at -25°C. Then the temperature of the bath was raised to -15°C. After 10-20 minutes 6.5 ml of nBuNH$_2$ was injected(730% excess to the HI). The mixture was further reacted for 1 ½ hours at -15°C, then for 1 hour at room temperature. The reaction mixture was washed 4 times with 5% aqueous NaOH solution, 7 times with distilled water, then dried using a rotary evaporator. A small amount(~1.38 g) of product was obtained. This compound was analyzed by ^{1}H NMR, ^{13}C NMR, Fourier transform infrared spectroscopy(FTIR), and thin layer chromatography(TLC).

Synthesis of a model compound from EVE and aniline was tried in another experiment. Into a 50 ml, septum-capped round bottomed flask were added 10 ml of n-hexane and 0.75 ml of purified EVE. Then 10 ml of HI/n-hexane solution(0.688 N, ~5% excess to EVE) was added at room temperature. The mixture was reacted at room temperature for 1 hour with agitation and protection from light. Then 1.3 ml(100% excess) of aniline was added, and the mixture was further reacted for 20 minutes. After a quick washing with aqueous NaOH and distilled water, the solvent(and also hopefully unreacted

aniline) was evaporated using a rotary evaporator, and ca. 0.6 g of hard, black material was obtained. The compound was soluble in acetone.

2) Oligomers: To a 100 ml septum-capped round bottomed flask with a magnetic bar, were added 15 ml of purified n-hexane and 5 ml of purified nBVE. The flask was cooled to -25°C, then 9.5 ml of HI/n-hexane (0.688 N) and 19 ml of iodine/n-hexane solution(0.6732 g of I_2 in 80 ml of n-hexane) were added. The added amount of iodine was 0.1 equivalent per equivalent of HI. After the injection of the iodine solution, the bath temperature was increased to -15°C. Then, the temperature was maintained at -15°C. It took ca. 10 minutes to attain -15°C from -25°C. The polymerization flask was protected from light by aluminum foil from the beginning.

After 30 minutes of reaction, the polymerization was terminated by the injection of 6.5 ml of n-BuNH$_2$(900% excess to the HI), further reacted 2½ hours at -15°C, then reacted at room temperature for 1.5 hours. The resultant polymerization mixture was washed 5 times with 5% aqueous $Na_2S_2O_3$ solution, 4 or 5 times with 5% aqueous NaOH solution, then 7-8 times with distilled water. After the polymer solution was dried with anhydrous Na_2SO_4, the solvent and unreacted materials were evaporated by using a rotary evaporator. The obtained weight of the polymer was 3.89 g(almost quantitative). The amine group was titrated with alcoholic HCl.

b) Indirect Approach

1) Model Reactions: The model reaction is illustrated in Scheme 14. The reaction consists of 3 steps.

1) addition of HI

$$CH_2=CH \xrightarrow[\text{CCl}_4 \, , \, -15\,^\circ C]{\text{equiv. HI}} CH_3\text{-}CHI$$

with O–nBu on the left, and O–nBu on the right.

2) cross addition reaction

i) $CH_2=CH\!\!\bigcirc\!\!CH_3$

ii) I_2

$$CH_3\text{-}CH\text{-}I \xrightarrow[\substack{\text{CCl}_4 \, , \, -15\,^\circ C \\ 2 \text{ hrs}}]{} CH_3\text{-}CH\text{-}CH_2\text{-}CH\text{-}I\text{-}\text{-}\text{-}I_2$$

with O–nBu groups and CH_3 aryl substituent.

3) amination reaction

$$\xrightarrow[\text{Et}_2O, \text{ reflux}]{\text{excess } H_2N\text{-}nBu} CH_3\text{-}CH\text{-}CH_2\text{-}CH\text{-}NH\text{-}nBu$$

with O–nBu and CH_3 aryl substituent.

Scheme 14. Model synthesis of amine terminated alkyl vinyl ether.

In the first step, 0.57 ml of distilled EVE and 2 ml of distilled CCl₄ were added into a 50 ml, septum-capped round bottomed flask. Then the temperature was lowered to -15°C, and 3 ml of HI-CCl₄ solution(0.997 N) was added into the flask.

In the second step, 6 ml of iodine/CCl₄ solution(0.159 g I₂ in 6 ml CCl₄, 0.1 molar equivalent to the amount of HI) and 0.76 ml of p-methylstyrene(1.0 molar equivalent with respect to the amount of HI) were added. Reaction time was 2 hours.

In the third step, 5 ml of n-butylamine and 20 ml of diethyl ether were added and refluxed for 10 hours. The reaction mixture was washed 5 times with 5% aqueous NaOH solution, then 5 times with distilled water. The organic phase was dried with anhydrous sodium sulfate, and the solvent was removed by rotary evaporator. The weight of the product was 1.69 g(theoretical, 1.58 g).

In another experiment, nBVE was used instead of EVE. 0.380 ml of nBVE in 1 ml of CCl₄ was reacted with 3 ml of CCl₄-HI solution, followed by reaction with 0.382 ml of p-methylstyrene in the presence of iodine. The reaction mixture was refluxed with 2 ml of n-butylamine and 15 ml of diethyl ether for a total of 10 hours.

2) Oligomers: Into a 100 ml, septum-capped round bottomed flask, were added 4 ml of nBVE and 32 ml of n-hexane, followed by the addition of 3.10 ml of n-hexane-HI solution(0.680 N) at -20°C. After 5 minutes 10 ml of iodine solution(0.0533 g I₂ in 10 ml n-hexane) was added and the temperature was increased to -15°C. It took ~5 minutes to increase the temperature from -20 to -15°C. As the reaction proceeded, the color of the polymerization mixture changed from slightly pink to a dark color.

After 40 minutes 1 ml of EVE was injected, and the color of the reaction mixture again became almost colorless, but a thin layer of a dark precipitate was observed around the bottom of the flask. This precipitated layer(probably formed during the polymerization of nBVE) dissolved after agitation and the color of the mixture became

brownish but homogeneous and transparent. After 5 minutes the color of the system darkened, then after another 5 minutes the system was shaken and the color of the system became an opaque dark brown.

Into this reaction system 0.55 ml of p-methylstyrene(100% excess) was injected and reacted for 5 hours. The color and the opacity remained unchanged.

Upon addition of 4 ml of n-propylamine(ca. 2100% excess), the color of the reaction mixture became reddish and then changed to a transparent yellow with a small amount of a reddish-black precipitate on the bottom of the flask(~1 ml). The reaction mixture was refluxed with 25 ml of diethyl ether for 10 hours, then washed 4 times with 5% aqueous NaOH solution(25 ml each) and 5 times with distilled water. The collected aqueous layer was extracted with 50 ml of hexanes, washed with aqueous NaOH solution and distilled water, then combined with the main portion of organic layer. The combined organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated using a rotary evaporator. The polymer was dried under vacuum for two days at room temperature, and the obtained weight of the polymer was 4.08 g(theoretical, 4.28 g) with a viscous, liquid-like property(theoretical $Mn = 2040$). The amine functional group was titrated with alcoholic HCl.

4. Block Copolymers

a) Sequential Polymerization

1) Alkyl Vinyl Ethers: Poly(nBVE)-block-poly(EVE) was synthesized as an intermediate in the preparation process for amine-terminated poly(alkyl vinyl ethers). In that case, 5 monomeric units of EVE were incorporated after the polymerization of nBVE. The

number of the monomeric units in the first poly(nBVE) block were 5, 15, and 45 depending on the molecular weights of the desired oligomers. The purpose of this block copolymerization was to reduce the steric hindrance which could possibly present during the crossover addition reaction (the reaction step 2 in the model reaction). Experimental procedures are included in the previous section entitled *Indirect Approach.*

2) Alkyl Vinyl Ether-Oxazoline: The nominal structure of the block copolymer described in the following procedure is 5 units of nBVE - 5 units of EVE - 1 unit of p-MeSt - 10 units of EtOXZ.

Into a 20 ml septum-capped ampoule with a magnetic bar in it, was added 0.64 ml of nBVE in 1 ml CCl_4, and 1 ml of HI-CCl_4 solution(0.997 N) at -15°C. 2 ml of I_2-CCl_4 solution(0.1295 g I_2 in 10 ml CCl_4) was then added. The reaction mixture became heterogeneous. After 5 minutes, 0.475 ml of EVE in 1 ml of CCl_4 was added and reacted for 5 minutes. Each reaction time was more than twice the time required for 100% conversion based on the results of the kinetic study.

In the next step 0.153 ml(20% excess) of p-methylstyrene was injected and reacted for two hours, then 1 ml of ethyloxazoline was added with 7 ml of acetonitrile. The ampoule was degassed and sealed, then put in an oven at 80°C.

After 24 hours, the reaction mixture became a transparent reddish color. After another 24 hours, the reaction mixture turned black, and a small amount of a precipitate formed. The reaction mixture could not be precipitated into diethyl ether. The solvent was evaporated, and the product was dried in a vacuum oven for 2 days at 40~50°C. A brownish-black hard material weighing 1.80 g(theoretical yield, 1.89 g) was obtained. Decolorizing carbon did not remove the color from the product.

b) Coupling Reaction

A living poly(ethyloxazoline) of molecular weight ca. 1000 was terminated with an amine-terminated alkyl vinyl ether oligomer($Mn = 2140$) for the preparation of A-B type block copolymers.

Poly(EtOXZ)-N$\overset{\text{Et}}{\underset{+}{\bigcirc}}$O $^-$OTs + Pr-NH-Poly(alkyl vinyl ether) $\longrightarrow$

$$\text{Poly(EtOXZ)} - \underset{\underset{\text{Et}}{\overset{|}{\underset{|}{C=O}}}}{N} - CH_2CH_2 - \overset{\overset{^-OTs}{\overset{+}{|}}}{\underset{\underset{\text{Pr}}{|}}{NH}} - \text{Poly(alkyl vinyl ether)} \qquad (93)$$

First, poly(ethyloxazoline) was prepared by following the procedure described in *Oxazoline Polymers*. Then, 3.43 ml(34 mmole) of EtOXZ, 0.50 ml(3.28 mmole) of MeOTS and 5 ml of acetonitrile were reacted for 20 hours at 80°C after degassing 3 times. From the total 7.95 g of polymerization mixture, one portion(3.07 g) was quickly transferred into a nitrogen filled, clean, round bottomed flask(25 ml) and the rest of the mixture was precipitated into diethyl ether.

The precipitated portion of the polymerization mixture was filtered and dried in a vacuum oven for 2 days at ca. 50°C, yielding 2.42 g(theoretical, 2.45 g) of a white, powdery material was obtained.

The contents of the round bottomed flask were quickly equipped with a 3-way stopcock, then 2.685 g of amine-terminated oligomer in 4 ml methylene chloride was

injected. The dissolution beaker was rinsed with 2 ml of methylene chloride, and this solution was injected into the round bottomed flask also.

The contents of the flask were degassed with dry nitrogen three times by a freeze-thaw technique, then reacted at room temperature with agitation. Small portions of the reaction mixture were sampled after 12 and 24 hours then mixed with Et_3N-MeOH solution and dried for GPC analysis. The total reaction time was two days.

Following the reaction, the solvent was removed by rotary evaporation and dried in a vacuum oven for 1 day. The polymer obtained was jelly-like, non-sticky, insoluble in water but soluble in methanol.

C. Kinetic Studies

1. HI/I₂ System

Time versus conversion was investigated in the kinetic studies. Experimental procedures were almost the same as described in the section entitled *Polymerization by HI/I₂*. A series of reactions at each temperature were carried out using 3~6 round bottomed flasks(100 ml). Reaction times were calculated from the moment the iodine solution was injected into an individual flask. The temperature of the bath was kept homogeneous by stirring with a magnetic bar. After given reaction times, the polymerizations were quenched via injection of a triethylamine/methanol solution. For one series of polymerizations performed at -15°C, diethylamine/methanol was used. Experimental temperatures were -5, -15, -25, -35, and -45°C. In order to study the effects

of initial iodine concentration on the polymerization, only the initial concentrations of the iodine were varied. Other reaction parameters such as the initial concentration of HI, nBVE, reaction temperature, or reaction time remained identical.

2. HI System

Experimental procedures for these reactions were similar to those described for the kinetic study with the HI/I_2 system. Here also 5 ml of nBVE and 40 ml of n-hexane were used, the solution was cooled to -20°C, then 1.90 ml of HI/n-hexane solution(0.21 N) was injected. Polymerization was conducted in a water bath whose temperature was regulated within ±0.1°C. All the flasks were protected from light with aluminum foil, and the temperatures investigated were 20, 30, and 40°C.

D. Structural Analysis

1. Nuclear Magnetic Resonance Spectroscopy(NMR)

a) Proton NMR

^{1}H NMR analysis was performed using either a Bruker WP-270SY superconducting multinuclear NMR or a Bruker WP-200SY superconducting multinuclear NMR. ^{1}H NMR spectra were obtained on the monomers, reaction intermediates, oligomers, and

polymers. The solvent used was usually deuterated chloroform with tetramethylsilane(TMS) as the internal standard. In some cases, the solvent was n-hexane or CCl₄, and a deuterated solvent was put into a small capillary tube inside a NMR tube to function as the lock solvent.

b) Carbon-13 NMR

^{13}C NMR analysis was performed using a Bruker WP-270, Bruker WP-200SY, or Bruker NR-80. Proton decoupled ^{13}C NMR spectra were usually obtained with nuclear overhauser enhancement(NOE). For quantitative analysis, ^{13}C NMR spectra were obtained without NOE.

Low temperature ^{13}C NMR spectra(50.3 MHz) were recorded on the Bruker WP-200SY spectrometer in CCl₄ at -20°C with deuterated acetonitrile as a locking solvent in a 5 mm(outside diameter) sealed inner tube. All solutions(nBVE, HI/CCl₄, and iodine/CCl₄ solution) were transferred under dry nitrogen via dry syringes in a septum-capped NMR sample tube(10 mm outside diameter) which was placed in a low temperature bath(-20°C). Then, the NMR sample tube was cooled in a dry-ice acetone bath in order to avoid undesirable temperature build-up during transfer to the NMR probe. Proton decoupled ^{13}C NMR spectra were recorded with NOE when the temperature of the probe equilibrated at -20°C.

For the spectra of α-alkoxy alkyl iodide, 127 μl of nBVE(1 mmole) in 1 ml CCl₄ and 1 ml of CCl₄/HI solution(1 mmole) were used. For the spectra of α-alkoxy alkyl iodide/iodine, 64 μl of nBVE(0.5 mmole) in 0.5 ml of CCl₄, 0.5 ml of HI/CCl₄ solution(0.5 mmol), and 65.0 mg of I₂(0.25 mmol) in 3 ml CCl₄ were used. Higher concentrations of iodine, such as 130 mg in 3 ml CCl₄, could not be used due to solubility

considerations. NMR spectra were obtained up to 300 ppm from TMS. The INEPT microprogram[461] was run for the assignment of each carbon atoms.

For tacticity determination, proton decoupled ^{13}C NMR spectra of poly(nBVE) and poly(EVE) were obtained with NOE in deuterated chloroform at room temperature at a polymer concentration of 5~20 w/v%.

2. Fourier Transform Infrared Spectroscopy(FTIR)

All FTIR spectra were obtained using a Nicolet MX-1 FTIR spectrometer. Samples were generally run as thin cast liquid films on salt plates.

3. Ultraviolet/Visible Spectroscopy(UV/vis)

UV/visible spectra were recorded on a Perkin-Elmer 552 Spectrophotometer. Solutions were injected via dry syringes into a septum-stoppered quartz cell which was placed in a methanol bath(-21°C). Enough time was allowed to attain temperature equilibrium, then the methanol on the cell walls was quickly wiped off and the cell was quickly inserted into the cell chamber of the spectrophotometer. The cell chamber was purged with dry argon throughout this experiment to prevent possible moisture condensation on the cell walls. A fast scan speed, (480 nm/min), was used in order to minimize the temperature change of the cell during the measurement.

UV/visible spectra of HI, I$_2$, α-alkoxyalkyl iodide, and α-alkoxyalkyl iodide/iodine were obtained in n-hexane solution.

4. Titration

Titrations were carried out using a Fisher Scientific Titrimeter II automatic titrator. Titrations were performed using a 10 ml buret filled with standardized alcoholic solutions of acid.

Amine-terminated oligomers were titrated with isopropyl alcohol-HCl solution. Thus, 0.1641 g of amine-terminated oligomer(expected molecular weight, 2040) was dissolved in 80 ml of isopropyl alcohol and titrated with 0.09991N isopropyl alcohol-HCl. The starting pH was ~9.05 and 0.76 ml of standard HCl solution was consumed to reach the endpoint(the calculated molecular weight was 2161). In a repetitive titration, 0.2039 g of oligomer consumed 0.98 ml of standard HCl solution(calculated molecular weight was 2082). On the average, the titrated molecular weight was 2120 g/mole. Other oligomers and model compounds were titrated similarly.

The normality of the HI solution was also determined by titration. Usually 5.0 ml of HI solution was sampled by a syringe and injected into distilled water(~50 ml) inside a 125 ml separatory funnel. HI was extracted by shaking and separated. The total amount of aqueous HI solution became ~100 ml after two more extractions, and this acid was titrated with standard methanolic KOH solution.

For some titrations, 1 drop of methanolic phenolphthalein solution was added to the sample solution to confirm the endpoint by the appearance of the distinctive red color.

5. Separation

Effort was made to separate model compounds by thin layer chromatography(TLC) or by column chromatography. Plastic backed TLC plates(silica gel GF254) were obtained from Kodak, and used after being cut to a proper size. Developing solvents used were CHCl$_3$/hexanes(2/8 v/v), ethylacetate /n-hexane(1/40 v/v), and other combinations of solvents. After the selection of a suitable solvent system for the separation of a certain mixture, column chromatography or dry column chromatography[462] was performed. For dry column chromatography, 230 mesh silica gel containing material which fluoresced at 254 nm, in ca.10 inch long(packed length) and a one inch wide nylon tube, was used. The tube was obtained from the Fisher Chemical Company. The structure of the column was very similar to that for column chromatography except that the bottom was clamped and a couple of vent holes were made at the bottom.

Dry column chromatography used was just an extension of the TLC technique with large volumes of separation materials. The solvents and sample handling procedures were the same as for the TLC except that the solvent was developed from top to bottom.

6. Molecular Weight and Distribution

a) Gel Permeation Chromatography(GPC)

Molecular weights and their distributions were determined by size exclusion chromatography(GPC) with a Waters 244 instrument or Waters 150C variable temper-

ature instrument typically equipped with a a 5-column set(500, 10^3, 10^4, 10^5, and 10^6Å) of microstyragel columns. A differential refractive index(RI) detector was used. Usually a 0.1 wt/vol. percent solution in THF was used with a flow rate of 1.0 ml/min.

For analysis of amine-terminated oligomers and coupling reaction products, a 4-column set(500, 10^3, 10^4, and 10^5Å) of ultrastyragel columns was used in THF.

GPC columns were calibrated with polystyrene standards. Data were analyzed by a linear least square method(linear fit) or by a cubic fit. Most of the time the linear fit method was used.

b) Vapor Phase Osmometry(VPO)

Number averaged molecular weights(Mn) of a series of poly(nBVE)s were determined by VPO with toluene as the solvent.

c) Viscosity Determination

Intrinsic viscosities of oligomers were measured using a Cannon-Ubbelohde dilution viscometer in a thermostatically controlled water bath. Four concentrations of an oligomer in chloroform were used for the measurements. For each concentration, specific viscosity η_{sp} was calculated by using the solution flow time,t, and pure solvent flow time, t_0, as in equation 94.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \cong \frac{t - t_0}{t_0} \tag{94}$$

The intrinsic viscosity value in deciliters/gram was determined using a computer program which determines the intercept of the specific viscosity versus concentration relationship as in equation 95(as the concentration C → 0).

$$\frac{\eta_{sp}}{C} = [\eta] + K_H[\eta]^2 C \tag{95}$$

where K_H is the Huggins constant.

7. Thermal Analysis

Thermal properties of the polymers were determined by differential scanning calorimetry(DSC) and thermogravimetric analysis(TGA) using a Perkin-Elmer Model-2 thermal analyzer. Glass transition temperature(Tg) and decomposition temperatures were measured. A typical heating rate was 10°C/min.

Chapter IV

Results and Discussion

A. Polymerization of Alkyl Vinyl Ethers by HI/I₂ Initiation System

The original objective of this research was to investigate the possibility of the preparation of a functionally-terminated poly(alkyl vinyl ether), especially an amine-terminated one via the newly developed HI/I$_2$ initiation system. Preliminary synthetic attempts of amine-terminated prepolymers ended in failure due to unknown factors in the polymerization and the instability of the final product. Therefore this research effort has been directed along two paths - one investigates the polymerization behavior via kinetic study, the other investigates the possibility of increasing the stability of an amine-terminated prepolymer.

Many interesting and useful results were obtained in the kinetic studies, which have significance of their own in the investigation of the nature of the propagating chain end. Also the kinetic data aided in the preparation of amine-terminated prepolymers by facilitating the prediction of necessary reaction times for a given polymerization system under a certain condition via the known rate constants of polymerization. In general, kinetic data are related with a reaction mechanism which governs every reactions in that system. A correct reaction mechanism makes modification and improvement of a given reaction system possible.

1. Kinetic Studies

Iodine has been used as a catalyst in the polymerization of alkyl vinyl ethers for a long time. Hydrogen iodide, however, has been used as a component of initiation systems since 1960's[123].

Recently Higashimura et al.[10,26] reported the living polymerization of a series of alkyl vinyl ethers initiated by a mixture of hydrogen iodide and iodine. The degree of polymerization of the poly(alkyl vinyl ethers) was inversely proportional to the initial amount of hydrogen iodide and the molecular weight distributions(MWD) were quite narrow. They propose that the propagating chain end has a relatively stable covalent-like structure, such as 15, activated for polymerization by iodine.

$$\sim CH_2 - CH\text{-}I$$
$$|$$
$$O$$
$$|$$
$$R$$

15

There are relatively few kinetic measurements of the polymerization of alkyl vinyl ethers initiated by the hydrogen iodide-iodine system, which is in marked contrast to the wealth of data available for iodine-initiated polymerizations. A kinetic investigation appeared necessary in order to establish reliable data to generate mechanistic reaction schemes. In this work, rates of polymerizations of nBVE and EVE were measured and the effects of hydrogen iodide, iodine, and monomer concentrations on the rates of polymerizations were determined and expressed in a rate equation. The observed rate equation has been analyzed in conjunction with spectroscopic measurements in an attempt to gain information about the polymerization reaction.

a) Addition of HI to Double Bond

The addition of HI to the double bond of an alkyl vinyl ether monomer(M) is very rapid. This fact was confirmed by using NMR with the addition of a stoichiometric amount of hydrogen iodide to the monomer in carbon tetrachloride solution. The reaction took place inside a septum-capped 5 mm NMR tube at -15°C. The tube was quickly inserted into an NMR probe, and NMR was run at room temperature. The resultant compound is the addition product $CH_3CHI-O-Alkyl(RI)$. This is shown in Figure 7.

This observation was very similar to that of Higashimura et al.[26], however, the RI seems to be unstable at room temperature. Proton NMR spectra of the compound in $CCl_4/CDCl_3$ solution(3/1 v/v) changes and the NMR peaks become quite different after about two hours.

Figure 7. 270 MHz proton NMR spectra of addition reaction of HI with nBVE at room temperature: A) nBVE, B) addition product, C) after 2 hrs.; CCl₄/CDCl₃(3/1) solvent.

b) Time versus Conversion

Polymerization initiates by an addition of the hydrogen iodide solution into the monomer solution followed by the injection of the iodine solution. Reaction times are taken from the moment when the iodine solution is injected.

When the polymerization is quenched with $Et_3N/MeOH$, the following reactions are possible.

$$\sim CH_2\text{-}CH\text{-}I...I_2 \quad + \quad Et_3N \quad \longrightarrow \quad \sim CH_2\text{-}CH\text{---}N^+\text{-}Et \ I_3^-$$

with substituents O, R on the left structure and O, R, Et, Et on the right structure.

$$\xrightarrow{MeOH} \quad \sim CH_2\text{-}CH\text{-}OMe \quad + \quad Et_3NH^+ \ I_3^- \qquad (96)$$

with substituents O, R.

A dried polymerization mixture contains salt. The weight of the salt and -OMe has to be subtracted from the gross weight in order to calculate the yield. Only the weight of I_2 + HI is subtracted in the real calculation because it constitutes the major weight fraction(74% of the salt and -OMe). Table 27 shows the conversion data, calculated by equation 89.

Initial amounts of monomer were all 10.0 ml and weighed around 7.70 g. Throughout this experiment the concentrations of iodine, hydrogen iodide, and the initial monomer concentrations in all flasks were constant in n-hexane. Only the reaction temperatures differed. At -5°C, 2 more data points were tried with reaction times of 90 minutes and 150 minutes, but the conversion had already reached ~100%.

Table 27. Time-Conversion of the Polymerization of nBVE at Various Temperatures[a]

Reaction temp., °C	Reaction time(min.) % Conversion (g yield) [b]				
-5	30 38.8 (2.98)				
-16	30 15.8 (1.22)	60 25.8 (1.99)	90 32.3 (2.49)	120 43.3 (3.31)	240 78.4 (6.04)
-25	92 17.0 (1.30)	120 30.4 (2.34)	180 43.2 (3.33)	270 58.1 (4.48)	
-35	90 10.5 (0.81)	180 18.9 (1.45)	270 26.5 (2.04)		
-45	122 5.8 (0.45)	212 9.0 (0.69)	300 11.7 (0.90)		

[a] $[M]_o = 1.77$ mole/l, $[HI]_o = 8.73$ mM, $[I_2]_o = 8.49$ mM, Total reaction volume = 43.4 ml.

[b] Total dried weight - I_3.

Figure 8 presents plots of the kinetic data. The plots of percent conversion versus time show straight lines with decreasing slopes as the polymerization temperature decreases. The rate of polymerization(Rp) shows a zeroth order dependence on monomer concentration. The lines do not fall on the zero point of the time axis at any temperature probably because the temperature of a polymerization mixture was slightly higher than the specified temperature at the beginning stage of polymerization. The iodine solution used was at room temperature, and also heat may have evolved from the complexation between iodine and the monomer.

The initial concentration of the monomer was reduced to 0.173 mole/l from 1.77 mole/l for further confirmation of the effects of monomer concentration on the polymerization. Time versus conversion data are included in Table 27. The time versus conversion plot still shows a linear relationship(Figure 9). In this case, the nBVE employed was 1 ml (~0.772 g), so the experimental data is more scattered. The observed rate constant(116 l/mole.min) is similar to that calculated(85 l/mole.min) from the previous time-conversion experiment as plotted in Figure 8.

When carbon tetrachloride(ε = 2.238 at 20°C) is used as the reaction medium instead of hexane(ε = 1.890 at 20°C), the rate of polymerization increases. EVE shows a more rapid polymerization than nBVE as indicated in Figure 10. One data point in Figure 10 deviates from the straight line because of the inaccurate temperature controls of the polymerization bath. The order of reactivity(ethyl > n-butyl) is very similar to one observed with a metal sulfate-sulfuric acid complex catalyst in heptane[349], but different from one observed with a boron trifluoride etherate catalyst[326,350].

Figure 11 shows the dependence of the number averaged molecular weight of poly(nBVE) on the conversion. The molecular weight is directly proportional to the polymerization conversion for a given condition. The molecular weight distributions shown in Figure 12 are also quite narrow as predicted in living polymerizations.

Figure 8. Time-conversion plots of nBVE polymerization at various temperatures in n-hexane: $[M]_0$ = 1.77 M, $[HI]_0$ = 8.73 mM, $[I_2]_0$ = 8.49 mM; A) -5°C, B) -16°C, C) -25°C, D) -35°C, E) -45°C.

Figure 9. Time-conversion plot of nBVE polymerization at low monomer concentration in n-hexane: $[M]_0 = 0.173$ M, $[HI]_0 = 2.42$ mM, $[I_2]_0 = 2.31$ mM; temperature, -15.5°C.

Figure 10. Time-conversion plots of nBVE and EVE polymerization in CCl_4: $[M]_0$ = 1.77 M, $[HI]_0$ = 8.7 mM, $[I_2]_0$ = 8.5 mM; temperature, -16°C.; A) EVE, B) nBVE.

Figure 11. Conversion-Mn plot of poly(nBVE) obtained at -16°C in n-hexane: $[M]_0$ = 1.77 mM, $[HI]_0$ = 8.73 mM, $[I_2]_0$ = 8.49 mM; A) GPC with polystyrene standard, B) VPO.

Figure 12. MWD of poly(nBVE) obtained at various temperatures in n-hexane: Temperature(%
conversion); A) -5°C(39), B) -15.5°C(100), C) -25°C(58), D) -35°C(27), E) -45°C(12).

Interestingly, the molecular weight distribution is altered by changing the quenching solution in a polymerization. All the GPC traces in Figure 12 are from those polymers quenched with an $Et_3N/MeOH$ solution. All showed narrow molecular weight distributions. When the polymerization was quenched with an $Et_2NH/MeOH$ solution(-16°C), however, the molecular weight distribution tended to be broader with longer storage times. The polymers in Figure 11 were all quenched by a diethylamine/MeOH solution, and dried in a vacuum oven at ca. 60°C for one day to estimate the yields. When the polymers are quenched, the following reaction takes place:

$$\underset{\substack{| \\ O \\ | \\ R}}{\sim CH_2\text{-}CH}\text{-}I...I_2 \quad + \quad Et_2NH \quad \xrightarrow{\quad MeOH \quad} \quad \underset{\substack{| \\ O \\ | \\ R}}{\sim CH_2\text{-}CH}\text{-}\underset{\substack{| \\ H}}{\overset{I_3^-}{N^+}}\overset{Et}{\underset{Et}{\diagdown}} \qquad (97)$$

$$\underset{\sim}{16}$$

Here, the further substitution of the quarternary amine group of compound 16 with methanol is more difficult than is the case in equation 96 where the quarternary amine is tetra-substituted. Therefore, during the drying process, compound 16 could undergo some kinds of reactions to broaden the molecular weight distributions.

Table 28 shows the raw data Figure 11. Though conversion versus molecular weight shows a linear relationship, the molecular weight distributions are broad and the obtained molecular weights are higher than the expected values calculated based on the initial charge ratio of monomer to HI. Undesirable reactions during the drying process would be the major reasons for those differences when the sample is treated with diethylamine/methanol.

Another interesting example of MWD broadening is the polymerization which is quenched by ammoniacal methanol or $n\text{-}BuNH_2$ under the same reaction conditions.

Table 28. Molecular Weights of Polymers Quenched by Et₂NH/MeOH

Reaction time (hrs.)	0.5	1	1.5	2	4
Initial nBVE, g	7.72	7.61	7.64	7.67	7.72
Dried weight [a]	1.37	2.14	2.64	3.46	6.19
% Conversion [b]	15.8	26.1	32.6	43.2	78.2
Mn, GPC [c]	7,800	12,600	15,000	20,800	33,600
MWD	1.74	1.60	1.51	1.49	1.46
Mn, VPO	4,480	10,310	9,900	14,750	24,740
Mn, Theor.	3,210	5,310	6,630	8,780	15,900

[a] Dried weight in vacuum(~1 torr) for 24 hours at ca. 60 °C. This contains salts.

[b] {(Dried weight - I_3)/ 7.7 } x 100.

[c] Polystyrene standard.

Quenching with ammoniacal methanol gave Mn ~3700(GPC) with MWD ~1.40(at quantitative conversion), and quenching with n-BuNH$_2$ gave Mn ~3600 with MWD ~1.34. On the other hand, the polymerization with a I$_2$ catalyst gave Mn ~17,000 with MWD ~1.65(at 77% conversion) when quenched with n-BuNH$_2$. Especially when a polymer was dried at high temperature and for long time, the obtained polymer was brown colored and hard to wash. In those cases, front tailing(high molecular weight) was usually observed in the GPC trace. On the other hand, Japanese workers[10,26] have not reported a broadening of the molecular weight distributions of polymers quenched by ammoniacal methanol because they did not treat the samples in the same way as in this research. Recently, they have briefly mentioned that the quenching of the polymerization with ammoniacal methanol brought a little bit broader molecular weight distribution than was the case where the quenching was done with aniline derivatives[295]. They now agree that the chain end quenched with primary alkyl amine is unstable. This phenomenon of molecular weight distribution broadening is directly related to the stability of the terminal group of a polymer. Thus, the compound 16 is less stable than the acetal in equation 96. The stabilities of the related compounds are discussed in detail in the *Synthesis of Amine-Terminated Oligomers* section.

c) Influence of Iodine Concentration

In order to determine the effects of iodine concentration on the polymerization, the concentrations of hydrogen iodine and monomer were fixed and the ratio of iodine/hydrogen iodide was varied. Figure 13 shows the dependence of the polymerization conversion of nBVE on the initial ratio of iodine/hydrogen iodide for a given polymerization time. The conversion or the number averaged molecular weight of the polymer is linearly proportional to the initial concentration of iodine. When the

iodine is absent, polymerization does not occur. The concentration of active species calculated from the conversion/number averaged molecular weight is essentially equal to the initial hydrogen iodide concentrations. One data point was omitted due to its large deviation from the line.

In a kinetic investigation a separate time versus conversion curve is usually obtained for each concentration of iodine[341]. That is, several time versus conversion curves have to be obtained for varied iodine concentrations. However, only one time versus conversion data was obtained in this experiment because the polymerization system is known from previous experiments to be very simple.

The polymerization system is a living system where the concentration of active center becomes initial HI concentration, and has zeroth order dependence on [M]. When the zeroth order dependence on [M] holds for all ratio of iodine/hydrogen iodide, the rate of polymerization Rp, becomes

$$Rp = \frac{-d[M]}{dt} = k[HI]_0[I_2]_0^x \tag{98}$$

where $[HI]_0$ is the initial concentration of hydrogen iodide, $[I_2]_0$ is the initial concentration of iodine, k is the rate constant, and x is the unknown constant. The equation 98 can be integrated for a reaction time t, and both sides are divided by $[M]_0$ which is the initial concentration of monomer. It then becomes

$$\frac{[M]_0 - [M]}{[M]_0} = \frac{k[HI]_0[I_2]_0^x}{[M]_0}t \tag{99}$$

When the values of $[HI]_0$, $[M]_0$, and k(i.e., reaction temperature) are fixed, the conversion(left side expression) is directly proportional to $[I_2]_0^x$ at any reaction time t. Therefore the log-log plot of conversion versus $[I_2]_0$ makes it possible to obtain the un-

Figure 13. Effect of initial ratio of $[I_2]/[HI]$ on the conversion of poly(nBVE), and concentration of active center.: $[M]_0 = 0.773$ M, $[HI]_0 = 5.13$ mM; reaction temperature, -15.5°C; reaction time, 5 hrs; solvent, n-hexane.

known constant x. When the constant x is 1, the conversion is directly proportional to $[I_2]_0$ when other values are fixed. In this experiment $x = 1$, and this observation is tested by plotting conversion versus initial iodine concentration.

d) Observed Rate of Polymerization

In these experiments the following were observed:

- Living polymerization.
- Zeroth order dependence of Rp on monomer concentration.
- First order dependence of Rp on the initial iodine concentration.
- First order dependence of Rp on the initial hydrogen iodide concentration.

Therefore, the observed rate of polymerization can be expressed as

$$Rp = k_p^{app}[I_2]_0[HI]_0 \tag{100}$$

where $[I_2]_0$ is the initial concentration of iodine and $[HI]_0$ is the initial concentration of hydrogen iodide. The apparent rate constant of the polymerization, k_p^{app}, and the experimentally determined rate constants of the polymerization are shown in Table 29.

The overall activation energy of the polymerization of nBVE in n-hexane was calculated from an Arrhenius plot(Figure 14) and found to be about 9.1 kcal/mole(38 kJ/mole). This value is very similar to the value of 9.7 kcal/mole obtained earlier from the polymerization of nBVE in heptane using a metal sulfate-sulfuric acid complex catalyst[349] and to the value of 10.0 kcal/mole obtained from the polymerization of 2-ethylhexyl vinyl ether in petroleum ether using an iodine catalyst[341]. However, it

Table 29. Apparent Propagation Rate Constant of nBVE and EVE in the Polymerization Initiated by HI/I$_2$ Catalyst

Temperature (°C)	k_p^{app} (l/mol.min)		
	nBVE		EVE
	n-hexane	CCl$_4$	CCl$_4$
-16	71	137	271
-25	52		
-35	21		
-45	7.8		

is higher than the values(ca.6~7 kcal/mole) reported for polymerizations initiated with free ion salts[50,429,463].

e) Possible Elementary Reactions

1) Addition of HI: This polymerization systemn clearly involves several elementary reactions. One simple reaction is the addition of HI to the double bond of an alkyl vinyl ether monomer, where the resultant addition product becomes the main source of the active chain ends. This reaction is seen in Figure 7.

2) Monomer-Iodine Complexation: Among the many possible elementary reactions, one possible major reaction is a reversible equilibrium between iodine and a monomer. This equilibrium has been studied by many workers[395], and the majority of the reports[392,396,439] conclude that a charge transfer complex is formed.

$$M(monomer) + I_2 \underset{}{\overset{K_{1eq.}}{\rightleftharpoons}} C(complex) \tag{101}$$

Other researchers suggest that the reversible equilibrium may not actually be a charge transfer complexation, but rather may involve reversible diiodide formation[123b,393,394]. Ledwith and Sherrington[393] suggest that the reversible equilibrium involves reversible adduct formation as in equation 102.

$$I_2 + CH_2 = CHOR \overset{K}{\rightleftharpoons} ICH_2\text{-}CHI\text{-}OR \tag{102}$$

$$\ln k_p{}^{app} \ = -4.580/T + 22.236$$

Figure 14.   Arrhenius plot of polymerization rate constants of nBVE: Apparent rate constants.

They propose that a free iodine molecule catalyzes the dissociation of the adduct to the corresponding carboxonium and triiodide ions, and polymerization takes place by a further reaction between the carboxonium ion and a monomer.

Later Johnson and Young[394] studied the initiation reaction of molecular iodine induced polymerization of alkyl vinyl ethers and suggested that the initiation reaction involves fast complexation, as in equation 101, followed by the slower adduct formation.

$$C + I_2 \rightarrow ICH_2CH(OR)I + I_2 \quad \text{slow} \tag{103}$$

In proposing these equations, they argue that the observed rate equation of the *disappearance of the iodine*, $R_p = k[M][I_2]^2$, has three obvious interpretations: (a) the rate-determining step is the simultaneous collision of one monomer and two I_2 molecules, (b) I_2 molecules react pairwise to form an equilibrium concentration of an intermediate which reacts slowly with a monomer, or (c) one monomer and one I_2 molecule form an equilibrium concentration of, for example, a charge-transfer complex which reacts with a second I_2 in a rate determining step. Of these possibilities, they state that (a) seems impossible, but either (b) or (c) are plausible, with (c) the more likely. Also they mention that the rate dependence of the disappearance of iodine on the dielectric constant of a solvent is understandable with interpretation(c). After obtaining a series of equilibrium constants, they obtain the heat of reaction of -33 kJ/mole from the Van't Hoff plot of the equilibrium constants for the addition of I_2 to the double bond of nBVE in cyclohexane. The value is similar to that predicted for the formation of 1,2-diiodides(ca. 40 kJ/mole) using standard tables of bond strengths.

One cannot decide conclusively which opinion among these is most reasonable. Depending on the relative reactivity of the diiodide compared to the reactivity of a propagating active species, any of these opinions could be reasonable.

If the reactivity of the diiodide is similar to that of the iodide, the diiodide forma-
tion will increase the total concentration of iodides and should lead to broader molecular
weight distributions. However, this has not been observed in these HI/I_2 initiated
polymerization systems. To comply with the observed living nature of the
polymerization, under the given polymerization conditions, the possible diiodide forma-
tion reaction[394,439] between iodine and the complex has to be slow enough to be ig-
nored. The reaction only becomes significant if the amount of iodine is large compared
to that of hydrogen iodide. Slow diiodide formation could explain the induction periods,
observed by many workers, in the polymerization of alkyl vinyl ethers initiated with
iodine only. On the other hand, the reaction in equation 102 is not plausible under this
assumption.

If the reactivity of the diiodide is very low compared to that of the iodide[26],
reversible diiodide formation would not significantly increase the number of propagating
chain ends, and the observed living behavior is explainable. Also, the initiation reaction
for a simple iodine-initiated polymerization can involve the dimeric iodide formed by the
reaction between a diiodide and an iodine molecule in the presence of a monomer, but
this initiation reaction is probably not the reaction in equation 103.

In the current study the disappearance of the iodine color seems to be consistent
with the formation of a **charge transfer complex, C,** whose identity is somewhat different
from a normal charge transfer complex because it has an exceptionally strong interaction
and reversible equilibrium(equilibrium constant 24.5 l/mole and $\triangle H^0$ = -33 kJ/mole,
compared to a typical benzene-I_2 complex which has equilibrium constant 1.72 l/mole
at 25°C and $\triangle H^0$ = -14.7 kJ/mole)[394]. The structure of the complex may be similar
to that of the diiodide structure in a classical reaction coordinate but in any event, an
iodine atom must be in close contact with the other iodine atom in order to attain

equilibrium rapidly. The **charge transfer complex, C,** *is defined as a species whose identity and reactivity are unknown* in this research.

The equilibrium constant of the complexation at a certain temperature can be calculated from the Van't Hoff plot by using a literature value of $K_{1eq.}$ and the corresponding ΔH. By using $\Delta H = -33$ kJ/mole, $K_{1eq.}$ becomes 24.5 l/mole. at 23°C in cyclohexane. The calculated values, from equation 104, are,

$$\ln K_{1eq.} = -(\Delta H/R)/T + constant(4.539) \tag{104}$$

76 at 0°C, 176 at -15°C, and 239 at -20°C. Therefore complexation increases as the temperature decreases."

3) RI...I₂ Complexation: In addition to the complexation between a monomer and iodine, iodide can also form another charge transfer complex R-I...I₂ with an iodide compound, RI, in the reaction system.

$$RI + I_2 \overset{K_{2eq.}}{\rightleftharpoons} RI...I_2 \tag{105}$$

This equilibrium(equilibrium constant $K_{2eq.}$) can be reasonably assumed from the fact that iodine acts as a Lewis acid and can attract an iodide ion to make a triiodide ion as in the equilibrium in equation 76. The equilibrium constant toward the I_3^- formation has been reported to be ca. 740 in an aqueous medium at room temperature[431]. Likewise, the iodine molecule attracts iodine atom in the carbon-iodine bond, but the extent of the attraction depends on the nature of the carbon-iodine bond. This complexation is discussed later in later sections.

4) Chain Growth: At least two propagation reactions can be proposed, and identifying the correct reaction mechanism depends on how the propagation reactions are defined.

One possible propagation mode is (A), the reaction between charge transfer complex, C, and iodide compound, RI. Another possibility is (B), the insertion of a monomer into the activated carbon-iodine bond in the complex. The former reaction (A) can be assumed due to the nature of the charge transfer complex. The exceptionally strong interaction and reversible equilibrium between iodine and monomer suggest that the complex has the possibility of being somewhat *activated*, which is different from the idea of an *inactive*[392] complex.

$$RI + C \xrightarrow{k_p} RI + I_2 \tag{106}$$

where k_p is the rate constant of propagation reaction.

On the other hand, the latter reaction (B) is very similar to a conventional ionic propagation or propagation where the propagating chain end is activated by a catalyst[7,11]. Scheme 4 represents this reaction[26].

$$RI...I_2 + M \xrightarrow{k'_p} RI...I_2 \tag{107}$$

where k'_p is the rate constant of propagation reaction.

f) Kinetic Reaction Schemes

The combinations of the major elementary reactions appear to fit the observed rate of polymerization. Here the reaction schemes are divided into two from the previous two chain growth modes.

Fast addition of hydrogen iodide(HI) to a monomer(M) leads to an iodide compound(RI) whose reactivity is assumed to be equal to that of polymeric iodide. Any iodide compound is designated as RI and the total concentration of iodide compounds is represented as $[RI]_0$, and $[RI]_0 = [HI]_0$ from the living nature of this polymerization. Both propagation modes mentioned above fit the observed pseudozeroth order dependence of Rp on the monomer concentration. Also, the combination of these two leads to the same result. In both schemes fast equilibria of complexations are assumed. Followings are the possible two reaction schemes.

1) Reaction Scheme A: The chain grows via interaction between the monomer-iodine charge transfer complex and the iodide compound.

Iodide formation

$$M + HI \rightarrow RI \tag{108}$$

Complexation of I_2

$$M + I_2 \overset{K_{1eq.}}{\rightleftharpoons} C \tag{101}$$

Chain growth

$$RI + C \xrightarrow{k_p} RI + I_2 \qquad (106)$$

Then the rate of polymerization becomes

$$Rp = k_p[RI][C] = k_p[HI]_0[C] \qquad (109)$$

From the equilibrium constant, [C] becomes

$$[C] = K_{1eq.}[M][I_2] \qquad (110)$$

And the total concentration of iodine becomes the initial concentration of iodide, then

$$[I_2]_0 = [C] + [I_2] \qquad (111)$$

From equation (110) and (111),

$$[C] = \frac{K_{1eq.}[I_2]_0[M]}{1 + K_{1eq.}[M]} \qquad (112)$$

Then, by the substitution of equation 112 into equation 109, the rate of polymerization becomes

$$Rp = \frac{k_p K_{1eq.}[HI]_0[I_2]_0[M]}{1 + K_{1eq.}[M]} \qquad (113)$$

$$\cong k_p[HI]_0[I_2]_0 \qquad (114)$$

$$\text{for} \quad K_{1eq.}[M] >> 1$$

Under a typical polymerization conditions $K_{1eq.}$ is on the order of 10^2 and [M] is on the order of $10^0 \sim 10^{-1}$, therefore the assumption holds until the polymerization conversion reaches a very high percentage.

2) Reaction Scheme B: The chain grows via insertion of a monomer into the activated carbon-iodine bond.

Iodide formation

$$M \ + \ HI \ \rightarrow \ RI \qquad\qquad (108)$$

Complexation of I_2

$$M + I_2 \ \overset{K_{1eq.}}{\rightleftharpoons} \ C \qquad\qquad (101)$$

$$RI + I_2 \ \overset{K_{2eq.}}{\rightleftharpoons} \ RI...I_2 \qquad\qquad (105)$$

Chain growth

$$RI...I_2 \ + \ M \ \overset{k'_p}{\longrightarrow} \ RI...I_2 \qquad\qquad (107)$$

Then the rate of polymerization becomes

$$Rp \ = \ k'_p[M][RI...I_2] \qquad\qquad (115)$$

From the equilibrium constants,

$$[C] \ = \ K_{1eq.}[M][I_2] \qquad\qquad (110)$$

$$[RI...I_2] = K_{2eq.}[RI][I_2] \tag{116}$$

And from the mass balance of $[I_2]_0$ and $[RI]_0$,

$$[I_2]_0 = [I_2] + [C] + [RI...I_2] \tag{117}$$

$$[RI]_0 = [RI] + [RI...I_2] \tag{118}$$

It then becomes

$$[RI...I_2] = \frac{K_{2eq.}[RI]_0[C]}{K_{2eq.}[C] + K_{1eq.}[M]} \tag{119}$$

$$\cong \frac{K_{2eq.}[RI]_0[C]}{K_{1eq.}[M]} \tag{120}$$

$$\text{for} \quad K_{1eq.}[M] >> K_{2eq.}[C]$$

and becomes

$$[I_2] = [C] + [RI...I_2] + \frac{[C]}{K_{1eq.}[M]} \tag{121}$$

Then, from equations (120) and (121),

$$[RI...I_2] \cong \frac{K_{2eq.}[RI]_0[I_2]_0}{1 + K_{2eq.}[RI]_0 + K_{1eq.}[M]} \tag{122}$$

By substitution of equation (122) into the equation (115),

$$\text{Rp} \cong \frac{k'_p K_{2\text{eq.}}[\text{RI}]_0[\text{I}_2]_0[\text{M}]}{1 + K_{2\text{eq.}}[\text{HI}]_0 + K_{1\text{eq.}}[\text{M}]} \tag{123}$$

$$\cong \frac{k'_p K_{2\text{eq.}}[\text{HI}]_0[\text{I}_2]_0}{K_{1\text{eq.}}} \tag{124}$$

for $K_{1\text{eq.}}[\text{M}] >> (1 + K_{2\text{eq.}}[\text{HI}]_0)$

Under a typical polymerization conditions, the initial $[\text{M}]/[\text{HI}]_0$ is on the order of $10^2 \sim 10^1$, $[\text{C}] \cong [\text{I}_2] \cong [\text{HI}]_0$, $K_{1\text{eq.}}$ is on the order of 10^2, and $[\text{M}]$ is on the order of $10^0 \sim 10^{-1}$. Therefore both of the above assumptions hold well until the conversion reaches a very high percentage for similar values of $K_{1\text{eq.}}$ and $K_{2\text{eq.}}$, and hold better for the smaller value of $K_{2\text{eq.}}$ than that of $K_{1\text{eq.}}$.

The two rate equations above are obtained by using equilibrium constants, and no steady state approximation is made. With steady state approximations, similar equations are obtained with proper assumptions, though the steady state approximations are less reasonable than using equilibrium constants because these approximations assume constant concentration of an intermediate.

When equation 101 is represented as,

$$\text{M} + \text{I}_2 \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} \text{C} \tag{125}$$

where k_c and k_{-c} are the rate constants for forward and reverse reactions respectively, steady state approximation can be set for [C], and a similar rate expression as in equation 114 can be obtained when $k_c[\text{M}] >> k_p[\text{RI}] + k_{-c}$. Also, for the scheme (B),

steady state approximation can be set for [RI...I$_2$], but the derivations of equations become more difficult.

The existence of the monomer-iodine complexation is indispensable in the derivation of the final rate expression in the reaction scheme (B). If the complexation between I$_2$ and RI (equation 105) is predominant compared to the complexation between I$_2$ and M (equation 101), then equation 101 can be omitted in the reaction scheme. And if equation 101 is omitted, the final rate expression will not have the form of pseudozeroth order dependence on [M]. Neither derivation via an equilibrium constant nor derivation via steady state approximation generates a desirable rate expression.

The primary difference between the above schemes (A) and (B) is in the rate constant expressions. In case (A), the k_p value is equal to the observed rate constant, but in case (B), the k'_p value is determined by the relative magnitude of the values of $K_{1eq.}$ and $K_{2eq.}$ for an observed rate constant. If the ratio of $K_{2eq.}/K_{1eq.}$ is small, the value of k'_p has to be large. For a conventional anionic[5] or cationic[464] polymerization, rate of polymerization becomes larger as charge separation increases. Similarly, the more the carbon-iodine bond is activated by the iodine molecule, the closer the structure of the iodide will be to I$_3^-$, and the value of k'_p will be larger.

2. Spectroscopic Characterization of RI...I$_2$

a) UV/Visible Spectroscopy

A series of UV/visible spectroscopic measurements were performed in order to estimate the value of $K_{2eq.}$. The measurements and interpretations of the UV/visible

spectra of the all elements of the polymerization are rather complicated and difficult, so this measurement was limited to the complexation between RI and I_2(equation 105).

Available data on λ_{max}(absorption maximum) and ε_{max}(molar absorption coefficient) of iodide compounds in nonpolar solvents are very limited in the literature. However, in aqueous solutions the λ_{max} and ε_{max} are well documented. Table 30 shows the molar absorptivities of I_2, I^-, and I_3^- in an aqueous solution[432]. In Table, ε_{max} of iodine is on the order of 10^2, but that of I_3^- is on the order of 10^4.

In Figure 15, the absorption bands of $CH_3CHI-O-nBu(RI)$ and iodine appear at 270 and 510 nm respectively in n-hexane solvent. Calculated ε_{max} values from the following Beer-Lambert equation are ca. 924 for RI, and ca. 797 for iodine.

$$A = \varepsilon bc \qquad (126)$$

where A is absorbance, ε is molar absorption coefficient(l/mol.cm), b is path length of the cell(cm), and c is the concentration of the solution(mol/l). The value of ε_{max} of RI is close to the reported value of 1.13×10^3[4], and can be compared to data in the literature for the $n{\rightarrow}\sigma^*$ transition of alkyl iodides(e.g., $RCH(CH_3)I$; $\lambda_{max} = 260\,nm, \varepsilon = 5.8 x 10^2$ in ethanol[465]). The small bump around the 300~400 nm region of the iodine spectra is due to some noise and is not the absorption band.

Figure 16 shows the UV/visible spectra of the mixture of RI and iodine. As the ratio of RI/I_2 changes, the extent of absorption of RI and I_2 changes as expected. As the ratio of I_2/RI increases the absorption peaks at 300-400 nm where the triiodide ion absorption peak is reported to occur [392-393] increases, but only slightly. The iodine band and the RI band do not show any distinctive change after they were mixing, except for a slight shift of λ_{max} of RI. The absorption peak at 300-400 nm may originate from a structure similar to the triiodide compound. If the structure of the complex is similar to that of the triiodide ion, the molar absorptivity would be expected to be large because that of

Table 30. Molar Absorptivities of Iodine and Iodides in Aqueous Solution[a]

Species	Molar absorptivity [b]			
	460 nm	370 nm	350 nm	288 nm
I_2	730.9	31.7	16.1	83.5
			18	95
I^-		0.009	0.011	0.057
I_3^-		18,980	25,750	38,790
			26,400	40,000

[a] 25 °C, ionic strength 0.02 [432].
[b] l/mol.cm.

Figure 15. UV/vis spectra of iodine and CH₃CHI-O-nBu in n-hexane at -21°C: A) iodine, 1.5 mM; B) CH₃CH-O-nBu, 1.0 mM.

the triiodide ion is on the order of 10^4 in an aqueous solution. In that case, the equilibrium constant, $K_{2eq.}$, should be very small. However, more than one charge transfer complex could exist in this system, so that only a qualitative estimate is possible with the given experimental data.

b) NMR Spectroscopy

Complex formation between RI and I_2 leads to the activation of the carbon-iodine bond where charge separation of the bond occurs. The resultant ionic character of the bond can be studied by using the NMR chemical shift difference between the iodide compound and its corresponding complex.

NMR is a powerful technique to elucidate the ionic nature of a bond. Many workers[466-468] have discussed the use of ^{13}C NMR in the determination of the ionic character of a carbon. The ionic character of a carbonium ion correlates with the ^{13}C NMR chemical shift[467] as in the following equation.

$$d_z = 160z \qquad (127)$$

where d_z is ^{13}C NMR chemical shift(ppm), after the elimination of the ring current portion, z is the charge on carbon. Also Musher[469] reported that the chemical shift in proton NMR would be approximately

$$d_z = 10z \qquad (128)$$

where d_z is the proton NMR chemical shift(ppm) after the elimination of the ring current portion, and z is the charge on the carbon attached to the proton. For example, in $(CH_3)_2CH^+$, $d_{CH_3} = 5.04$ ppm and $d_{CH} = 13.50$ ppm.

Figure 16. UV/visible spectra of the mixture of CH_3CHI-O-nBu in n-hexane at -21°C: $[CH_3CHI$-O-nBu$]/[I_2]$, mM/mM: A) 0.80/0.31, B) 0.67/0.51, C) 0.57/0.65.

In certain cases for single bonds ^{13}C-H coupling constants, J, are correlated to the *s character*, α^2, associated with the C-H bond orbital.

$$J(^{13}C, H) = 500\alpha^2 \tag{129}$$

By using any of the above equations cationic character or anionic character of the carbon can be predicted(e.g., as in alkyl vinyl lithium compounds[57,466]). In this research equation 127 was used with obtained ^{13}C NMR spectra.

In Figure 17, the chemical shift of the carbon attached to the iodine atom(peak f) shifted 0.83 ppm downfield by the addition of 0.5 equivalents of iodine. No other peaks were observed up to 300 ppm from TMS. From the above equation 127, the calculated degree of overall activation clearly becomes very small.

If complexation of iodine compound(RI) consists of only one equilibrium such as in equation 105, two interpretations are possible. One is the case where almost all of the iodide compound is inactive and only a quite small portion of the iodide compound is activated, like a free ion pair. The other is the case where a large portion of the iodide compound forms a complex with only weak interaction. In the complexation, however, the strength of the complexation as well as the equilibrium constant $K_{2eq.}$, would be determined by the negative charge density of the iodine atom of the carbon-iodine bond. The small shift in the carbon-13 NMR spectra suggests that the strength and the equilibrium constant are small values. By contrast, if the complexation consists of multistep equilibria, then the interpretation becomes more complicated. For all cases, however, the interaction between iodide compound and iodine molecule appears to be very weak, compared to the interaction between monomer and the iodine molecule.

Thus, in the polymerization, almost all of the iodine should form a charge transfer complex with monomer and only a very small amount of the iodine could produce a

Figure 17. Carbon-13 NMR spectra of CH₃CHI-O-nBu and its mixture with iodine in CCl₄ at -20°C: A) [RI], 0.47 M; B) [RI]/[I₂], 0.12 M/0.06 M.

charge transfer complex with the iodide compound. Then, the rate constant k'_p in scheme (B) has to be large, enough to be compared to that of conventional cationic polymerization, to comply with the observed rate constant.

3. Tacticity

a) Carbon-13 NMR

Proton decoupled ^{13}C NMR spectra of poly(ethyl vinyl ether) were obtained without NOE as shown in Figure 18.

The side group methyl carbon($-CH_3$) and main chain methine carbon($-CH-$) are insensitive to the stereochemical configuration, and the microstructures of the main chain methylene carbon ($-CH_2-$) and side group methylene carbon($-CH_2O-$) were assigned according to the Hatada's paper[470]. Their assignment was based on the microstructure of poly(methyl vinyl ether), in the order of rrr, mrr, mrm, rmr, mmr, mmm, from low to high field. Here the individual integrations of the tetrads of main chain methylene carbon were not tried due to the poor resolution, instead they were summed up and integrated as r and m. The integration result of the main chain carbon and the result of the side chain methylene carbon showed very similar tacticity result as in Table 31. Thus the assignments were internally consistent as pointed out by Matsuzaki et al.[471].

The reported spin-lattice relaxation time T_1 values of side chain $-OCH_2-$ are 0.29 sec. at 22°C(68 MHz) for poly(allyl vinyl ether)[472], and 1.19 sec., 1.15 sec. at 110°C(25 MHz) for poly(ethyl vinyl ether) mm, mr diads, respectively. So the relaxation delay 5 sec. between each pulse was assumed to be enough from the following equation[473].

Figure 18. 50.3 MHz carbon-13 NMR spectra of poly(EVE) in CDCl₃ at room temperature: *Mn*, 14000; Polymerization temperature, -16°C; A) expanded plot of side chain methylene, B) expanded plot of main chain methylene.

Table 31. Tacticities of Alkyl Vinyl Ethers

Polymer	Polymerization system	Triads observed [a] %			Diads calculated [b] (%)		Diads observed [c] (%)	
		rr	rm	mm	r	m	r	m
Poly(EVE)	HI-I_2 / CCl_4 / -16°C	7.8	63	29.2	39.3	60.7	38 [d]	62 [d]
Poly(EVE) [e]	BF_3OEt_2 / toluene / -78°C	8	37	55	26	74	-	-
Poly(EVE) [f]	BF_3OEt_2 / toluene / -78°C	8	36	56	26	74	25	75
Poly(EVE) [f]	BF_3OEt_2 / CH_2Cl_2 / 0°C	12	50	38	37	63	35	65
Poly(EVE) [f]	PF_5 / CH_2Cl_2 / 0°C	12	54	34	39	61	36	64
Poly(nBVE)	HI-I_2 / n-hexane / -5°C	16.2	38.7	45	35.6	64.4	-	-
Poly(nBVE)	HI-I_2/ n-hexane/ -15.5°C	13.9	33.9	52.1	30.9	69.1	-	-
Poly(nBVE)	HI-I_2/ n-hexane/ -45°C	12	30	58	27	73	-	-

a Triads were determined from the resonance peaks of the side group -OCH_2-.

b These diads were calculated from the triads, m = mm + (1/2)mr,
  r = rr + (1/2)mr.

c Determined from the resonance peaks of the main chain -CH_2-.

d Determined by the weights of paper cuts of the spectrum.

e Data from [470].

f Data from [471].

$$\frac{1}{T_1} \propto \frac{\eta}{kT} \tag{130}$$

where η is viscosity of the solution, k is Boltzmann constant, and T is temperature in Kelvin. At lower temperature the T_1 value decreases because the viscosity of a polymer solution increases and the value of T becomes less. The expected T_1 value is less than 1 sec. Relaxation delay of $5T_1$ allows 99% recovery toward equilibrium nuclear spin population.

Also the decoupled C-13 NMR spectra of poly(nBVE) were obtained with and without NOE. For a specific carbon in poly(nBVE), the spectra with NOE and the spectra without NOE, did not show any difference. For the tacticity measurement, decoupled spectra with NOE were used. As shown in Figure 19, only the main chain methylene carbon and the side chain methylene carbon are sensitive to the stereoconfiguration. The shapes of these two resonance peaks are very similar to that of poly(EVE), and the side chain methylene peak reveals fine microstructure. But the assignment was tried only for triads, rr, mr, mm, due to the difficulty of the assignment of the peaks more than triads. Better resolution is also needed for the assignment of tetrads or finer microstructure.

The integration values are already shown in Table 31. Interestingly isotacticity increases as the polymerization temperature decreases. This observation is the reverse of the one observed in the polymerization of methyl methacrylate with free radical or group transfer catalysts[474], or with alkyllithium catalysts in toluene[475]. This observation is similar to the one observed in the polymerization of (-)mentyl vinyl ether or (S)-1-methyl propyl vinyl ether with $C_7H_7SbCl_6$ in CH_2Cl_2[476]. As the polymerization temperature decreases, the optical activities of both polymers increases in the direction of the optical activities of the monomers. But a direct comparison cannot be made be-
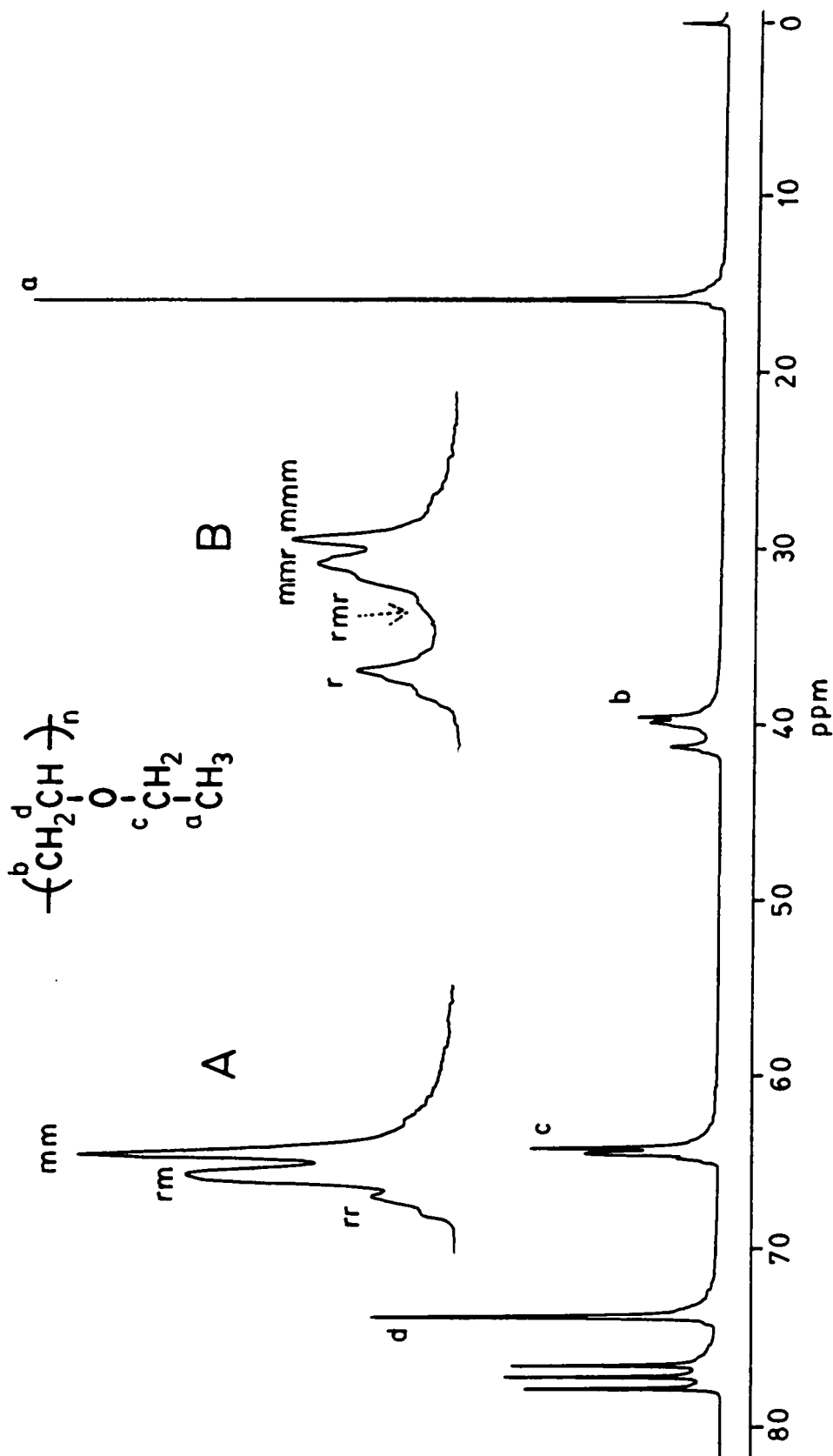
Figure 19. 50.3 MHz carbon-13 NMR spectra of poly(nBVE) in CDCl₃ at room temperature: Mn, 15000; polymerization temperature, -15.5°C; A) expanded plot of side chain methylene.

cause of the differences in technique and monomers. On the other hand, available data on this subject in cationic polymerization is quite scarce.

From the data in Table 31, the persistence ratio, ρ, which is a criterion for Bernoullian statistics, was calculated by

$$\rho = \frac{2(m)(r)}{(mr)} \tag{131}$$

Also the first order Markov conditional probabilities $P(m/r)$ and $P(r/m)$ were calculated by

$$P(m/r) = \frac{0.5(mr)}{(m)} \tag{132}$$

$$P(r/m) = \frac{0.5(mr)}{(r)} \tag{133}$$

The calculated results are shown in Table 32. The data deviate noticeably from the Bernoullian statistics. On the other hand, the reported values for the polymers prepared with BF_3OEt_2, showed close resemblance to the Bernoullian statistics. Therefore the polymerization system with HI/I_2 should be different from the polymerization system(homogeneous) with a BF_3OEt_2 catalyst. The attempts to establish a higher order stereopolymerization model needs finer tacticity data.

b) Proton NMR

The 270 MHz spectrum of poly(ethyl vinyl ether) exhibits two components for the β-proton resonance(backbone methylene) in $CDCl_3$ at room temperature. The α-proton(methine) overlaps with side group methylene protons and is very difficult to

Table 32. Tacticity Analysis of Poly(Alkyl Vinyl Ethers)

Polymer	Polymerization temp.(°C)	Mn	Triads observed			persistence ratio(ρ)	P(m/r) + P(r/m)
			rr	rm	mm		
Poly(EVE)	-16	14,000	0.078	0.63	0.292	0.757	1.32
Poly(nBVE)	-5	8,000	0.162	0.387	0.45	1.185	0.844
Poly(nBVE)	-15.5	15,000	0.139	0.339	0.521	1.260	0.794
Poly(nBVE)	-45	2,400	0.12	0.30	0.58	1.314	0.761
Poly(EVE) [a]	-78	-	0.08	0.36	0.56	1.069	0.936
Poly(EVE) [a]	0	-	0.12	0.50	0.38	0.932	1.073

[a] Data from [471].

resolve. When the β-protons are decoupled from α-proton, they show multiplet splittings very similar to the typical AB quartet of isotactic diads, mixed with other peaks(Figure 20).

In a typical case, e.g., in poly(methyl methacrylate) [473,478] or in poly(vinyl formal) [473], syndiotactic diads exhibit a singlet peak at the middle of the AB quartet. Therefore 1 or 2 peaks in the middle have to be assigned to the syndiotactic diads in the spectra, but the assignment of the peaks was not attempted. It seems as if the spectra reveal fine structure, such as tetrads, so the assignment cannot be straightforward.

On the other hand, a similar but broader spectrum was obtained by Ramey et al.[479] with a sample prepared with BF_3 etherate in toluene at -78°C. They obtained coupling constant J_{AB} = 15 cycles/sec., but no attempt was made to integrate the peaks. Another similar spectrum can be seen in reference 472 with poly(allyl vinyl ether). In this experiment, no attempt was made to optimize the splittings of NMR spectra by changing either NMR solvent or temperature. Some of the reported solvents are CH_2Cl_2(at 80°C)[471], C_6H_6[479], and CS_2[479].

Resonance peaks overlapped so much in the spectrum of poly(n-butyl vinyl ether) that neither α-proton nor β-proton could be resolved(Figure 21).

4. Thermal Analysis

The DSC and TGA results of the representative samples of poly(EVE) and poly(nBVE) are summarized in Table 33.

The DSC traces(2nd run) of both polymers are shown in Figure 22. For both polymers first run and second run traces are almost same. For poly(EVE), observed glass

Figure 20. 270 MHz proton NMR spectra of poly(EVE) in CDCl$_3$ at room temperature: *Mn*, 14000; polymerization temperature, -16°C; A) decoupled spectrum.

Figure 21. 270 MHz proton NMR spectra of poly(nBVE) in CDCl₃ at room temperature: *Mn,* 8000; polymerization temperature, -5°C.

transition temperatures(Tg) are -34°C for the first run and -32.4°C for the second run. For poly(nBVE), Tgs are -57.5°C for the first run and -59.5°C for the second run.

The Tg values of poly(EVE) are slightly higher than the data(-42°C) shown in Table 26, in Chapter II, but are within a range similar to the reported value of poly(EVE)(-31°C) prepared a with BF_3OEt_2 catalyst in toluene at -78°C[470]. On the other hand, the Tgs of poly(nBVE) are very close to the reported value(-55°C) in Table 26.

The thermogravimetric analyses of the samples are shown in Figure 23. The first 5% weight loss in air occurred at 230°C for both samples, and the first 5% weight loss under the nitrogen atmosphere occurred at 350°C for poly(EVE) and 310°C for poly(nBVE). The existence of the ether linkage probably enhances the decomposition in air.

5. Nature of the Active Chain End

The kinetic studies suggest that the active chain end has less ionic character during polymerization, and the UV/visible study and NMR spectroscopy support this point of view.

A similar polymerization system(i.e., iodine catalyzed polymerization) has been studied by many workers[123b,341,392] through conductivity measurement, and they point out that little or no conductivity is detectable during the polymerization. Johnson and Young[394] observe that there is very little conductivity during the polymerization, but it increases rapidly at high conversion. Low conductivity during the polymerization implies that either the solvent-separated ion pair or the free ions are almost absent in

Table 33. Thermal Data of Poly(Alkyl Vinyl Ethers)

	Poly(EVE)	Poly(nBVE)
Polymerization condition	HI-I$_2$ / CCl$_4$ /-16 °C	HI-I$_2$ / CCl$_4$ /-15.5 °C
Mn	14,000	15,000
% Isotactic triad (mm)	29.2	52.1
Tg, °C	-32.4	-59.5
5% Weight loss, °C (under air)	230	230
(under N$_2$)	350	310

Figure 22.   DSC scans of poly(alkyl vinyl ethers):   A) poly(EVE); B) poly(nBVE)

Figure 23. TGA scans of poly(alkyl vinyl ethers): Air; A) poly(EVE), B) poly(nBVE); N₂; C) poly(nBVE), D) poly(EVE).

this polymerization system because the conductivity measurement is highly sensitive to these species[467].

The polymerization, therefore, proceeds through an almost covalent carbon-iodine bond in the Winstein spectrum, but still the biggest question is *how the carbon-iodine bond is activated ?*

As seen in Table 29, the rate constant of the polymerization doubles as the polymerization solvent changes from n-hexane to CCl_4. Therefore, the polymerization mechanism probably involves an ionic transition state as pointed out by Eley and Richards[341]. This sensitivity of the polymerization to the polarity can be seen even in the polymerization in a fixed nonpolar solvent. A higher concentration of monomer can change the polarity of the system and therefore change the rate of polymerization. A slightly different kinetic equation recently report[480] probably results from this fact.

Interestingly, a similar polymerization phenomena is observed in the polymerization of styrene with a perchloric acid catalyst[481]. When the polymerization is conducted in CCl_4 at 30°C, the time versus conversion plot shows the zeroth order rate dependence on the monomer concentration. But when the polymerization is conducted in CCl_4/CH_2Cl_2 mixed solvent(65/35, v/v) at 0°C, the plot deviates from the zeroth order. The authors envisage the polymerization reaction as a process in which: 1) the monomers make reversible complexation with $HClO_4$ attached or unattached to a growing chain end; 2) the complex slowly undergoes ionization to an ion-pair state; 3) in that form attacks a styrene molecule in solution or one already associated with the complex by first or zeroth order kinetics, respectively. After analyzing similar results with Laidler and Eyring's theory[482], they propose that the transition state is a fully developed ion-pair. Therefore, their concept of the transition state is different from the concept of pseudocationic polymerization[9] because they hypothesize an additional ionic character.

A similar behavior is also observed in the polymerization of styrene by trifluoroacetic acid[102]. The polymerization cannot be represented by a single, simple equation, so the importance of complexation is implied, but there is no interpretation of the polymerization reaction in terms of reaction mechanism.

Another interesting phenomena can also be found in the coordination polymerization. The polymerization of styrene with $VCl_3/Al(iBu)_3$ catalyst[483a], or the polymerization of propylene with $AlEt_2Cl/V(acac)_3$ (where acac $\equiv$ acetylacetonate) catalyst[483b] shows zeroth order kinetics. Coordination polymerization studies cast light on the area of cationic polymerization. For example, the use of an acetate/BCl_3 complex catalyst[11] is very similar to the use of benzoate in a coordination polymerization [483 c,d,e].

In the polymerization of alkyl vinyl ethers with an HI/I_2 initiation system, the complexation between monomer and iodine plays the biggest role in the observed reaction kinetics. In reaction scheme B, the complexation regulates the amount of iodine which can activate the RI compounds. Here the complex, C, exists as a reservoir of iodine. But in reaction scheme A, the complex takes part in the polymerization reaction as an activated complex. So, the difference between both mechanism lies in the reactivity of the complex. However the reactivity and identity of the complex have not been studied systematically, though many people [26,392,394] conjecture that the complex is not a real complex but an adduct(based on the UV/visible spectra of the monomer-iodine mixture).

Whether the complex is an adduct or not, there is no doubt about the reversibility of the process. The route to the complex from the simple mixture of monomer and iodine has to be activated in some manner in order to form the product, so the complex will have a certain moment during its formation process when it can be considered as an active species. A similar example is the formation of a halonium ion intermediate in

Scheme 15. Proposed polymerization mechanism in Scheme A.

the addition process of a halogen to a double bond[484]. The reversible complexation process can therefore be considered as a preliminary process for the polymerization reaction, and the *imaginary* transition state can be proposed as in Scheme 15.

Scheme 15 is closely related to the concept of pseudocationic polymerization, but it may involve an ionic transition state in the carbon-iodine bond. The role of the oxygen atoms in the ether linkages remains as unknown in this scheme, and the position of the iodine in the complex is difficult to be compromised and therefore remains tentative. The reported average bond distance of the $C=C$ double bond is 1.34Å, and the I-I bond is 2.67Å[457]. Therefore two iodine atoms can make a close contact with each other while they maintain their contacts with both carbons and oxygen. Perhaps only one iodine atom can make contacts with two carbons and oxygen.

On the other hand, the polymerization scheme B will be similar to the mechanism in Scheme 4, which is similar to the Schemes 3 or 5. In the scheme B, a carbon-iodine bond is activated by iodine, and a monomer is inserted into the activated carbon-iodine bond. However, the insertion step is still not clear, especially in its ionic character. As mentioned before, the carbon-iodine bond has to be fully dissociated in order to explain the observed rate of polymerization. If the mechanism involves coordination type chemistry, however, the mechanism is very complicated, and the in situ C-13 NMR technique[483f] which was utilized in the coordination polymerization of olefines, probably can help the elucidation of the mechanism. Interestingly, the group transfer polymerization is reported to proceed with Bernoullian statistics[474] which is different from the propagation statistics in this HI/I_2 polymerization system.

Unfortunately analysis of the polymer microstructure cannot help the proposal of a reliable mechanism much, due to the lack of detailed information. But the data does show that the polymerization system of $HI-I_2$/n-hexane at low temperatures is not governed by Bernoullian random statistics, whereas the reported polymerization systems of

SbCl$_5$/pentane/-72°C[472,485], BF$_3$OEt$_2$/toluene/-78°C[470,471], or

BF$_3$OEt$_2$/CH$_2$Cl$_2$/0°C[471] are governed by Bernoullian random statistics.

In the polymerization of vinyl ethers, it has been reported that the steric structure of the polymer remarkably dependent on the size of counter ions and the polarity of the medium. For α-substituted vinyl ethers, isotacticity generally increases as the size of the counter ion increases, or as the polarity of the medium decreases[486]. This trend is very similar in the polymerization of α-methylstyrene[402b]. But in the polymerization of α,β-disubstituted vinyl ethers, the steric hindrance between the substituents of the incoming monomer and of the growing chain end plays a more important role in determining the steric structure of the polymer than the steric interaction between the growing chain end and the counter ion[487]. But all these findings are for cationic polymerization with traditional ionic catalysts, where the positive active chain ends make close or loose association with the counter ions. Therefore the mechanism of stereocontrol in the polymerization of the HI/I$_2$ initiation system differs from the one proposed[403,485] in Scheme 9 because the polymerization proceeds via quite nonionic propagating species. The development of a reliable stereocontrol mechanism requires more reliable data.

B. Polymerization of n-Butyl Vinyl Ether by HI Catalysts

1. Polymerization by HI

The polymerization of nBVE was conducted at 20°C, 30°C, and 40°C in the presence of HI only. Measurements of time versus conversion data are summarized in Table 34 and plotted in Figure 24.

At 20°C one of the polymerization flasks was checked after 10 hours of reaction time, and no color was observed. When the polymerization mixture was quenched with 5 ml of the $Et_3N/MeOH(1/2$ v/v) solution, neither precipitation nor a color was observed.

After ~40 hours of reaction time the conversion reached ~30%, but the conversion did not increase by further reaction during the remainder of the total reaction time of 94 hours. The active chain end appeared to be dead. However, when 1% of iodine relative to the initial amount of HI was added to the reaction system, the polymerization reaction resumed and quantitative conversion was reached. Interestingly, the observed rate of polymerization of 790 l/mole.min(calculated from the conversion for the first 9 hours after the addition of iodine) was very similar to the value of 740 l/mole.min calculated from equation 100 and the Arrhenius equation with the activation energy of 38 kJ/mole.

At 30°C the rate of polymerization was fast, and the polymerization reached almost quantitative conversion without any addition of I_2, but the molecular weights deviated markedly from the predicted, and the distributions were rather broad. The polymerization mixture was reddish color for the polymerization flask with the 95.3%

Table 34. Time-Conversion of the Polymerization of nBVE with HI[a]

20 °C

Reaction time (hrs)	5	10	20	42	69	94	94 +9 [b]	94 +18 [b]
%Conversion	8.9	10.1	10.1	29.7	33.5	32.7	69.7	97.1
Mn (GPC) [c]	800	900	800	-	1800	1400	4000	-
Mn (Theor.) [d]	900	1000	1000	2900	3300	3200	6900	9600
MWD	1.2	1.21	1.23	-	1.44	1.42	1.28	-

30 °C

Reaction time (hrs)	5.7	24.4	40	60
%Conversion	13.2	59.3	95.1	95.3
Mn (GPC) [c]	1100	3300	4000	
Mn (Theor.) [d]	1300	5800	9400	
MWD	1.21	1.34	1.43	

40 °C

Reaction time (hrs)	0.5	1	3	5.3	7
%Conversion	15.6	22.7	29.4	62.7	68.9
Mn (GPC) [c]	700	700	2500	1500	3100
Mn (Theor.) [d]	1500	2200	3000	6200	6800
MWD	1.42	1.57	1.16	1.76	1.43

[a] $[nBVE]_0$ = 0.84 M, $[HI]_0$ = 8.53 mM, n-hexane solvent.
[b] Reaction time after addition of 1% iodine.
[c] Linear fit with polystyrene standard.
[d] Based on the assumption of living polymerization.

Figure 24. Time-conversion of the polymerization of nBVE with III: $[M]_0 = 0.84$ M, $[III]_0 = 8.53$ mM, n-hexane; A) 20°C, B) 30°C, C) 40°C, D) after addition of iodine.

conversion when the aluminum foil was opened before the quenching of the solution. At 40°C the observed polymerization phenomena were very similar to those at 30°C, but the molecular weights deviated more than those obtained at 30°C.

2. Polymerization by HI/Lewis Acids

Polymerization of nBVE was conducted with HI/Lewis acid initiation systems. The polymerization was also conducted with each Lewis acid without any added HI for the purpose of comparison. Lewis acids used were Et_3Al, Et_2AlCl, and $SbCl_5$. Table 35 summarizes the reaction conditions and the conversion data.

The polymerization did not occur in the temperature range of -78 ~ 25°C with Et_3Al only, and polymerization occurred when HI was present in a 1/1 ratio, the polymerization occurred. With HI/Et_3Al initiation system at 25°C, the polymerization conversion reached 30.1% after 10 hours of reaction. This value can be compared to 10.1% conversion without Et_3Al at 20°C with a reaction time of 10 hours, or to 59.3% conversion without Et_3Al at 30°C with a reaction time of 24.4 hours recorded in Table 34. This indicates that the existence of Et_3Al did not contribute much to the polymerization conversion of nBVE. Qualitatively speaking, the acceleration effect(or catalytic effect) of Et_3Al approached zero in this polymerization system. This observation is very similar to the one reported on the polymerization of isobutyl vinyl ether in toluene[405]. No polymerization was observed in that system either. Et_3Al appears insufficiently active to ionize the carbon-iodine bond.

With Et_2AlCl, polymerization was observed for both cases. The rate of polymerization was faster with Et_2AlCl only, than was the case where HI/Et_2AlCl was used. The obtained polymer was sticky and flowed with standing for a day or two. The

Table 35. Experimental Result of the Polymerization with HI/Lewis Acid[a]

Catalyst	Reaction temp. (°C)	Reaction time (hrs)	% Conversion	
			Without HI	With HI(1/1 ratio)
Et_3Al	-78	2	0.2	1.5
	-34	2	0.3	1.4
	-5	2	0.3	3.1
	25	2	0.5	18.2
	25	10	-	30.1
Et_2AlCl	-15	2	98.2 (very high mw)	70.0 (low mw)
$SbCl_5$	-15	7	99.1 (low mw)	99.1 (low mw)

[a] $[nBVE]_0$ = 1.76 M, $[Lewis acid]_0$ = 8.5 mM, $[HI]_0$ = 8.5 mM.

molecular weight of the polymer appeared to be very high. In contrast, the polymer obtained with the HI/Et$_2$AlCl initiation system was a free flowing viscous liquid.

In the polymerization initiated with Et$_2$AlCl, the polymerization takes place via an Et$_2$AlClOH$^-$ counterion[15,28] generated by the reaction of Et$_2$AlCl with water present in the polymerization system(H$_2$O in n-hexane was $\sim$10 ppm by Karl-Fisher titration).

$$H_2O + Et_2AlCl \rightarrow H^+Et_2AlClOH^- \tag{134}$$

But in the polymerization initiated with HI/Et$_2$AlCl, polymerization takes place via an Et$_2$AlClI$^-$ counterion[28] generated by the reaction of Et$_2$AlCl with RI. RI is instantaneously produced when HI is added into the monomer solution.

$$RI + Et_2AlCl \rightarrow R^+(IEt_2AlCl)^- \tag{135}$$

Although the concentration of the active chain end of the system with Et$_2$AlClOH$^-$ is less than that of the other system, this system shows a faster rate of polymerization probably due to the greater stability[78] of the Et$_2$AlClOH$^-$ counterion compared to that of Et$_2$AlClI$^-$. This observation can be interpreted as a similar trend as in Table 6. However, "nucleophilicity" seems to be misdefined in reference 8. "Nucleophilicity" usually refers to basicity although nucleophilicity is a kinetic term, whereas basicity is thermodynamic term)[488]. A more stable anion is less nucleophilic toward a carbocation.

From Drago's empirical constant(Table 7) OH$^-$ is more reactive than I$^-$, so the -ΔH of OH$^-$ in equation 16 is greater than that of I$^-$ for a fixed Lewis acid(Et$_2$AlCl). That means the stability of Et$_2$AlClOH$^-$ is greater than the stability of Et$_2$AlClI$^-$. Therefore in the polymerization reaction the Et$_2$AlClI$^-$ will be more associated with

propagating carbocations and will promote a slower reaction as observed in this experiment.

On the other hand, properties important in influencing nucleophilicity are[489]: 1) the solvation energy of the base; 2) the strength of its bond to a carbon *2p*-orbital; 3) its effective size; 4) the electronegativity of the attacking atom; and 5) the polarizability of the attacking atom.

With $SbCl_5$, however, polymerization behavior for both cases was very similar and the viscosity of the polymers appeared to be very similar. One of the possible reasons is the self-ionization of $SbCl_5$ molecule into $SbCl_4^-$ and Cl^+[8,490] for the polymerization system with $SbCl_5$ only. But other possibilities can not be ruled out. When the initiator solution(CH_2Cl_2) was injected into the n-hexane reaction solution, dark precipitation was observed, probably due to the poor solubility of the catalyst in n-hexane.

3. Nature of the Active Chain End

The polymerization of nBVE with HI was expected to proceed as an ionic propagating species for both HI only and HI/Lewis acid, but the polymerization with HI only was not as simple as expected. At 20°C the polymerization stopped after ~30% conversion, and the polymerization became sluggish, However, the active chain end, RI, remained as a dormant species which could resume polymerization by the addition of iodine. Therefore, the carbon-iodine bond in RI is thought to be insufficiently active to polymerize at 20°C in n-hexane. At 30°C the polymerization mixture showed reddish color after 60 hours of reaction(almost a quantitative conversion). The appearance of the iodine color is a typical phenomenon of the HI/I_2 or I_2 polymerization system at the end of polymerization. If the polymerization at 30°C is hypothesized to proceed via a

HI/I$_2$ polymerization system, then the observed straight time versus conversion curve can be understood, and the amount of iodine present in the system can be back-calculated from the observed rate of polymerization. The amount of iodine calculated by the expected reaction rate constant 1250 l/mole.sec(from Arrhenius equation and activation energy) and equation 100 is ~0.38% as compared to the initial HI concentration. Similarly, the amount of iodine calculated at 40°C from the estimated reaction rate constant 2020 l/mole.sec is 0.95%.

Therefore the polymerization in these systems seems to take place mostly via the RI/iodine initiation system. The iodine can be formed from the oxidation of HI with the adventitious oxygen in the system. At standard temperature and pressure 0.45 ml of air contains 4 x10^{-6} mole of oxygen, equivalent to the 1% of initial HI in the system. Though precautions were taken against the involvement of oxygen in this system, the existence of adventitious oxygen still cannot be ruled out considerg the equipment used. But other possible sources of oxidation cannot be ruled out either. At higher reaction temperatures the RI can generate HI, as in equation 136, and the HI can be oxidized[455].

$$\sim CH_2\text{-}CHI\text{-}OR \quad \rightarrow \quad \sim CH = CH\text{-}O\text{-}R \ + \ HI \tag{136}$$

$$4I^- \ + \ 4H^+ \ + \ O_2 \quad \rightarrow \quad 2I_2 \ + \ 2H_2O \tag{137}$$

On the other hand, equation 136 can explain the broad molecular weight distributions noted in Table 34. The reactivity of the carbon-iodine bond toward polymerization and dehydroiodination determines the rate of polymerization and the molecular weight distribution. The reason for the leveling off of the polymerization at 20°C(Table 34) is uncertain, but one explanation might be the existence of a reaction which involves the true consumption of iodine, similar to the reaction in equation 103.

Then the activation energies of the reactions in equations 103, 136, 137, and the polymerization can make the polymerization reactions different at different reaction temperatures.

The polymerization of nBVE with a HI/Lewis acid proceeds via an almost ionized carbon-iodine bond, which differs from the HI only initiation system. But here, the cocatalysts(Lewis acids) used were unable to promote a synergistic effect, i.e., no specific acceleration of the reaction was observed. No calculation of molecular weight distributions was tried, however, so other effects cannot be commented upon.

Recently Sawamoto et al.[491] reported a new initiation system. Instead of using I_2, they used ZnI_2, which itself alone is inactive in the polymerization of iBVE. When ZnI_2 was used with HI, the rate of polymerization became faster than that of the HI/I_2 system, and a narrower molecular weight distribution was observed. Though the exact nature of the active chain end is still unknown, this kind of synergistic effect is required for a cocatalyst. Interestingly, ZnI_2, which is thought to make complexation with MMA monomer, is one of the catalysts used in the group transfer polymerization of MMA[117] as an electrophilic catalyst.

C. Polymerization of Oxazoline

The polymerizations of oxazolines were attempted with methyl tosylate, benzyl iodide, benzyl iodide/iodine, and iodine. When 2-methyloxazoline was reacted with benzyl iodide, benzyl iodide/iodine, or iodine in DMF at ~98°C for ~10 hours, all three reactions showed almost quantitative conversion, but the best result was obtained with benzyl iodide. The obtained polymer (expected Mn ~1000, from the initial charge ratio

of monomer/initiator) with benzyl iodide is a hygroscopic white powdery material which becomes a yellowish gum upon absorption of moisture, but the obtained polymer with benzyl iodide/iodine or iodine is a reddish black gummy material. When the polymerization temperature is changed to 60°C, the polymerizations show 55%, 63%, and 64% conversions for benzyl iodide, iodine, and benzyl iodide/iodine respectively. The appearances of the obtained polymers were almost the same as those obtained at 98°C. The powdery poly(2-methyloxazoline) is soluble in water, methanol, ethanol, CHCl₃, acetone, acetonitrile, and DMF, but insoluble in THF, dioxane, and toluene.

Polymerization of 2-ethyloxazoline was conducted in DMF at 98°C for 1 hour, and a slightly yellowish glassy polymer was obtained with 95% conversion(expected Mn ~1200). The polymer is soluble in water methanol, ethanol, CHCl₃, THF, dioxane, CH₂Cl₂, acetone, acetonitrile, and DMF, but insoluble in toluene. The polymerization of 2-ethyloxazoline was also conducted with methyl tosylate in acetonitrile at 80°C for 22 hours. White powdery material is obtained with almost quantitative conversion(expected Mn ~1200). A better result is usually obtained with a methyl tosylate catalyst in an acetonitrile solvent. Poly(2-ethyloxazoline) of Mn ~2200 was also synthesized.

The physical properties of oxazoline polymers and their polymerization behaviors were not studied in this research because this area is not a major concern of this research. They were only synthesized in order to be incorporated into the A-B type block copolymers. The nature of their active chain ends and their polymerization behaviors are relatively well-known in the literature. Some of these discussions are plotted in *Review of Literature.*

D. Synthesis of Amine-Terminated Oligomer

1. Direct Approach

a) Oligomer

The preparation of a functionally-terminated oligomer was originally the primary objective of this research. Therefore, the polymerization of nBVE(theoretical $Mn \sim$ 10K at 100% conversion) was quenched by MeOH, MeOH/NaOH, and diethylamine, in order to prepare -OH and amine-terminated prepolymers.

When the polymerization is quenched by large quantity of methanol, the IR spectra of the obtained polymers show strong O-H stretching bands. And when the polymerization is quenched with a NaOH-MeOH solution, the IR spectra show some absorption peaks of -OH functional groups. When the polymerization is also quenched by diethylamine(neat), absorption peaks are observed in the -C-N- stretching band region(1260 cm^{-1}). These IR spectra are shown in Figure 25.

The GPC trace of the polymer quenched with NaOH-MeOH shows front tailing very similar to imbedded bimodal distribution with $Mn \sim$63K and $Mn \sim$12.6K(area ratio, 1/5). A similar GPC curve was obtained for the polymer quenched with diethylamine. These GPC curves are similar to those obtained in the kinetic study with quenching other than Et$_3$N/MeOH.

From the IR spectra, the synthesis of a functionally terminated prepolymer appeared to be promising. The hydroxyl absorption peak of the polymer quenched with MeOH-NaOH is rather small compared to that of polymer quenched with MeOH. The

Figure 25. FTIR Spectra of functionally terminated poly(nBVE): Terminated with; A)MeOH, B)MeOH-NaOH, C)Et₂NH.

reason for the -OH absorption peak of the polymer quenched with MeOH, is still uncertain. H_2O contamination of the MeOH or other chemical reactions are suspected. However, trouble resulted from the titration of the polymer quenched with Et_2NH. The polymer was titratable, but the titration result was not reproducible.

The molecular weight of the polymer was decreased to ~600 in order to better observe the functional group. This polymerization was quenched with n-BuNH$_2$, and its IR spectrum is shown in Figure 26. Compared to the IR spectrum of the high poly(nBVE)(synthesized with BF_3OEt_2, Mn ~15 x10^6, outside of exclusion limit of GPC), the polymer shows 3 different absorption peaks at 3330, 1669, and 1635cm^{-1}. The absorption peak at 3330cm^{-1} can be interpreted as N-H stretching vibration, but the absorption was too weak, and the peaks at 1669 and 1635cm^{-1} cannot be rationalized because the expected secondary amine usually does not show any absorption peak at this region[492]. The possibility of N-H bending vibration of an *amine salt* was ruled out because the sample was washed several times with an ~5% aqueous NaOH solution. On the other hand, the C-N stretching band was missing at ~1260cm^{-1}. Therefore, the IR spectra do not support the existence of a secondary amine. Neither the proton NMR nor the titration support the existence of an amine functional group.

b) Model Compound

A model reaction was performed in order to confirm the structure of the amine. The desired reaction was the reaction in equation 138.

The obtained yield was 1.35 g(theoretical 1.38 g) after evaporation of solvents by rotary evaporator, but further evaporation with a rotary evaporator(~30 min. more in a warm water bath) yielded 1.21 g. The product develops into more than 2 spots in TLC in hexane/acetone(7/3 v/v) solvent and shows more than 3 spots in acetone. The proton

Figure 26. FTIR Spectra of poly(nBVE): A) $Mn \sim 600$, terminated with nBuNH$_2$, B) BF$_3$ catalyzed.

NMR spectrum of the product is very complicated. Many strong peaks at 1.85 and 2.0 ppm, many small peaks at 1-3 ppm, strong 3 to 5 mixed resonance peaks of triplets and quartets at 3.1-3.7 ppm, a strong quartet at 4.7 ppm(probably CH_3-CH(OR)N-), and a small triplet at 7.7 ppm were observed. Existence of -NH- was difficult to confirm.

$$CH_3\text{-}CH\text{-}I \quad + \quad excess\ H_2N\text{-}nBu \quad \longrightarrow$$
$$| $$
$$O$$
$$\backslash$$
$$nBu$$

$$CH_3\text{-}CH\ NH\text{-}nBu \quad + \quad salt \qquad (138)$$
$$|$$
$$O$$
$$\backslash$$
$$nBu$$

$$\underset{\sim}{17}$$

In carbon-13 NMR, a CH peak was observed at ~100 ppm(probably -CH(OR)-NHR), and a quarternary carbon peak was observed at ~167 ppm(probably C=O in amide). The intensity of the peak at 167 ppm indicates that the compound is one of the major compounds in the product.

In Figure 27, the IR spectrum of the model reaction product was compared with that of N,N-dibutylacetamide[493]. The absorption bands at 1716, 1666 cm^{-1} of the model reaction product show similar patterns to those of the acetamide. In addition, the model reaction product contains an -NH- absorption band.

Not much information can therefore be drawn from either the NMR results or from the IR spectra. The model reaction must involve more than one reaction product because of the instability of the desired reaction product. A low temperature separation technique, such as room temperature gas chromatography, may help the identification of the product and the reaction itself.

Figure 27. FTIR spectra of model reaction product via direct route: A) model reaction product, B) N,N-dibutylacetamide.

c) Stability of Chain End

The instability of the amine chain end contributes to the failure of the amine-terminated poly(nBVE) synthesis. The structure of the desired reaction product, 17, is very similar to that of an acetal, 18, known to be stable in a basic condition and unstable in an acidic condition(R, R′ = alkyl).

$$CH_3\text{-}CH\text{-}O\text{-}R'$$
$$|$$
$$O$$
$$|$$
$$R$$

18

At a different pH, the stability of an acetal is so distinctive that this property is used in the protection of a hydroxyl group in organic synthesis[494]. If the -OR in 18 is -OH, then the structure is known as a hemiacetal formed by the addition of water to an aldehyde. In a basic condition a hemiacetal is in an equilibrium with its starting material. It can be converted into acetal in the presence of large amount of alcohol when in an acidic condition. The structure of the chain end obtained by the quenching with MeOH or MeOH/NaOH is thought to have the hemiacetal structure. The existence of an aldehyde is predicted because the hemiacetal forms an equilibrium with aldehyde.

The structure of the compound, 17, is known as 1,1-amino ether(α-amino ether) or carbinolamine ether[495a]. Low molecular weighted 1,1-amino ethers derived from secondary amines are liquids that can be distilled without decomposition, often at atmospheric pressure. They are readily soluble in organic solvents but not in water. They are rapidly hydrolyzed by aqueous media. The compounds are useful aminomethylating agents[495b].

Compounds similar to 1,1-amino ethers are 1,1-amino alcohols(carbinolamines), which are readily dehydrated to imines, or enamines with base or acid catalysis[488]. The chemistry of these compounds is quite well known compared to that of amino ethers. General base catalysis of dehydration of the tetrahedral intermediate is usually formulated as involving nitrogen deprotonation concerted with elimination of a hydroxide ion.

$$B \quad H-\underset{R'}{\overset{R}{N}}-\underset{R}{\overset{R}{C}}-OH \longrightarrow B^+H \quad + R'N=CR_2 \quad + OH^- \qquad (139)$$

General acid catalysis of carbinolamine intermediate breakdown occurs with the assistance of the expulsion of water.

$$H-\underset{R'}{\overset{R}{N}}-\underset{R}{\overset{R}{C}}-OH \quad H-A \longrightarrow R'\underset{H}{N^+}=CR_2 \quad + H_2O \quad + A^- \qquad (140)$$

The formed imine compounds are so extremely unstable that separation is usually impossible except with aromatic imines.

On the other hand, disubstituted amines cannot form imines, and dehydration proceeds to give carbon-carbon double bonds bearing amino substituents(enamine).

$$R_2'N-\underset{OH}{\overset{R}{C}}-CH_2R \longrightarrow R_2'N-\overset{R}{C}=CHR \quad + H_2O \qquad (141)$$

The enamines have better stability than the similar imines due to the possible resonance structure involving nitrogen. Enamines are still hydrolyzed in basic or acidic media, however, and the resonance structure makes the β-carbon nucleophilic.

Therefore, as seen in the dehydration mechanisms in equations 139 and 140, the chemistry of 1,1-amino ethers is expected to be very similar[495a] to that of carbinolamines though 1,1-amino ethers have been reported to be more stable.

The observed result of this research, therefore, seems to coincide with the stabilities of the chain ends. Oligomers end-capped with a primary amine did not show the existence of any amine by either titration or IR, probably because the amine chain end was decomposed during the work-up and drying procedures. The oligomers end-capped with a secondary amine were titratable because the amine could exist as enamines or 1,1-amino ethers due to the superior stability of the more highly substituted structure. However, the metastable nature of this structure could lead to irreproducible titration results. Also, the N-H stretching band of the model compound can be rationalized as indicating the existence of a small amount of 1,1-amino ether structure because this product was dried with a rotary evaporator at moderate temperatures, and the time allowed between preparation and the IR measurement was relatively short.

Still, the biggest puzzle remains the interpretation of the absorption band at $\sim 1670 cm^{-1}$ in the IR spectra of Figure 26-A and Figure 27-B. As mentioned above, one possible interpretation is the existence of a disubstituted amide formed via an unknown rearrangement reaction. But the compound itself has not been identified, therefore this is a just conjecture. Proper separation of the reaction product in the model reaction may help the identification of the components and further the establishment of a reliable rearrangement scheme.

Similarly, not much information can be drawn from a model reaction of ethyl vinyl ether with aniline(EVE + HI + aniline) except that the obtained hard brownish black product may be a C-N polymer or a hexahydrotriazine derivative.

Therefore, for the sake of the stability of the functional chain end, a less electronegative atom is desirable in the geminal position, Y, of the functional hetero atom, X, perhaps the proton or carbon in alkyl or aryl groups.

$$\sim CH_2 - \underset{\underset{Y}{|}}{\overset{\overset{H}{|}}{C}} - X - R \qquad (X = NH, O)$$

$$(Y = H, C)$$

$$\underset{\sim}{19}$$

2. Indirect Approach

a) Model Reaction

The possibility of a stable amine-terminated poly(alkyl vinyl ethers) synthesis was checked by model reactions with ethyl vinyl ether or n-butyl vinyl ether. As mentioned earlier in *Experimental* part, a model reaction consists of 3 steps: addition of HI; cross addition reaction; and amination reaction as in Scheme 14.

1) Addition of HI: The addition of HI to the double bond of an alkyl vinyl ether monomer is believed to be very fast. Addition of HI to ethyl vinyl ether produces an adduct α-iodoether in CCl₄ solution at -20°C. Figure 28 shows the proton NMR spectrum of the adduct. The sample was prepared in an NMR tube in CCl₄ and kept for 2 days in a freezer(-20°C), then the spectrum was obtained at room temperature using an internal capillary tube containing CDCl₃ and TMS. This spectrum clearly shows the structure of the expected adduct. Small peaks at 1 ~ 2 ppm are believed to originate

from unknown impurities probably formed by the decomposition of the product at room temperature. On the other hand, this spectra can be compared to the one in Figure 6, which is derived from n-butyl vinyl ether. The observed multiplet of n-butyl vinyl ether adduct at ~6 ppm can be interpreted as a result of the presence of decomposition products because this spectrum was obtained with a $CDCl_3/CCl_4$ mixed solvent at room temperature. Obtaining a good proton NMR spectrum of the nBVE/HI adduct requires a lower temperature NMR technique similar to the combination in Figure 9.

2) Cross Addition Reaction: The 1/1 addition product of HI and alkyl vinyl ethers was reacted with an equivalent amount of styrenic monomer in the presence of iodine in the cross addition reaction.

$$CH_3\text{-}\underset{\underset{R}{\overset{|}{O}}}{\overset{|}{CH}}\text{-}I...I_2 \quad + \quad CH_2 = \underset{\underset{R_2}{\overset{|}{\bigcirc}}}{C}\text{-}R_1 \quad \longrightarrow$$

$$CH_3\text{-}\underset{\underset{R}{\overset{|}{O}}}{\overset{|}{CH}}\text{-}CH_2\text{-}\underset{\underset{R_2}{\overset{|}{\bigcirc}}}{\overset{\overset{R_1}{|}}{C}}\text{-}I...I_2 \quad\quad\quad (142)$$

where R = Et, nBu; R_1 = -H, -CH$_3$; and R_2 = -H, p-CH$_3$, p-OCH$_3$, p-t-Bu.

In this reaction the reaction rate is dependent on the nucleophilicity of the double bond of the styrenic monomer, which is a function of the substituent groups R_1, and R_2. These groups affect the reaction in at least three ways: polar effects; steric effects; and side reactions such as aromatic substitution or reaction with the substituent groups. The side reactions which have been reported in strong acid initiated systems should be less important, however, in this reaction(indanyl structure in the polymerization of the

Figure 28. 270 MHz proton NMR spectrum of the addition product of EVE and III

$$CH_3^b - CHI^d$$
$$-O - CH_2^c$$
$$- CH_3^a$$

styrene[13] initiated by ionic catalysts is one of the well-known examples of an aromatic substitution reaction). The σ value in the Hammett equation[496] and the Es value in the Taft equation[497] determine the effect of the substituent R_2. For both substituents R_1 and R_2, however, the Q-e scheme usually used in a *random* copolymerization can be used as the criteria for the selection of substituent groups.

The Hammett equation is represented as

$$\log k/k_0 = \sigma \rho \tag{143}$$

where k is the rate constant of a reaction, k_0 is the rate constant of the standard reaction(e.g. when $R_2 = H$), ρ is the proportional constant which determines the charge density of the transition state of a reaction(a ($+$) signifies a negatively charged transition state, whereas a (-) signifies a positively charged transition state), and σ is the polarity constant of a substituent(a positive value indicates an electron withdrawing group, whereas a negative value indicates an electron donating group). The σ is further divided into inductive factor σ_I, and resonance factor σ_R as in the following equation.

$$\sigma(=\sigma_P) = \sigma_I + \sigma_R \tag{144}$$

For this cross addition reaction, ρ becomes negative because the transition state is positive(cationic reaction), and therefore a substituent with a more negative σ value makes the double bond more nucleophilic.

The Taft equation is represented as

$$\log k/k_0 = Es \tag{145}$$

where k, k_0 are the same as before, and Es denotes the extent of bulkiness(a positive sign means less bulky, whereas a negative sign means bulkier). A bulkier group will prevent

both the aromatic substitution and the cross addition reaction. But because the β-carbon of the double bond is located in slightly remote from the substituent, the effect of steric hindrance is expected to be less for the cross addition reaction.

Q and e values in a Q-e scheme are determined by the reactivity ratios r_1 and r_2 in a binary copolymerization. Q is the resonance stabilization factor, and e is the polar factor. A more positive Q and a more negative e mean a more nucleophilic double bond. The stability usually considered in the Q-e scheme is the radical stability, but the stability of the cationic species in this research is similar.

Table 36 shows the reported values of σ, Es, e, and Q[499]. As shown in Table 36, the σ value generally parallels the value of e or Q. Many workers[500-502] have tried to correlate the reactivity of a monomer with Hammett reaction parameters. Sometimes the relative reactivity of a homologous series of monomers is related[500] with the Pavelich-Taft equation[503] as in equation 146.

$$\log(1/r_1) \;=\; \log(k_{12}/k_{11}) \;=\; \rho_I\sigma_I \;+\; \delta Es \tag{146}$$

where r_1 is the reactivity ratio, k_{12} and k_{11} are the rate constants in copolymerization(equation 62, 63), δ is the proportional constant, and the other parameters are defined as before. This equation takes into account the effects of both the polar and steric factors of a homologous series of monomers. On the other hand, the Q-e scheme can be applied more widely for different kinds of monomers, and the reactivities of different monomers can be related with this scheme. One example is the correlation between the anionic polymerizability of unsaturated monomers and the polar factor e[28b,33]. The e value is a more sensitive measure than the Q value for similar monomer structures[500,502].

Table 36. Values of e, Q, σ, and Es of Some Monomers[a]

	e	Q	σ	Es
Styrene	-0.800	1.000	0	1.24
p-Methyl-	-0.980	1.270	-0.15	0
p-MeO-	-	-	-0.15	-
p-t-Bu-	-0.900	1.370	-0.24	-1.54
α-Me-	-1.270	0.980	-	-
EVE	-.1.170	0.032		
nBVE	-1.200	0.087		
nPrVE	-1.520	0.014		
iBVE	-1.770	0.023		

[a] Data from [494a, 499].

The cross addition reaction and the subsequent amination reaction have to be considered simultaneously, since the α-substituent(R_1) promotes the former as well as possible side reactions(e.g. the elimination reaction in the latter).

Several styrenic monomers were tried in the cross addition reaction. A styrenic monomer was allowed to react with an EVE/HI adduct in the presence of iodine, and after reacting, the carbon-iodine bond was replaced by carbon-oxygen-methyl by alcoholysis with methanol. The cross addition reaction was so sluggish for styrene that only small fraction of the styrene was reacted in a given reaction time. The cross addition reaction were faster for other monomers like p-methylstyrene, p-methoxystyrene, and p-t-butylstyrene. For p-methoxystyrene, the yield recovered after the rotary evaporation of the benzyl ether structure was 65% and TLC was too complicated. For t-butylstyrene, the yield recovered was 98% and the TLC was not good either. Among these monomers, p-methylstyrene showed the best result under this reaction condition. Its yield was 92% and FTIR, NMR, and TLC showed promising results. The product(for the case of p-methylstyrene) was separated with high performance liquid chromatography(HPLC) and the observed results are discussed in the next section, *Stereochemistry of the Chain End.*

The exact sequence of the reaction rates of the styrenic monomers can be obtained by monitoring the cross addition reactions with a proton NMR at low temperature. Other information such as side reactions and the thermal stabilities of the reaction products may also be obtained, but these were not gathered in this experiment.

Figure 29 shows the proton NMR spectra of the cross addition reaction product for nBVE and p-methylstyrene. The spectrum of the product for EVE and p-methylstyrene is almost identical in the region of 3 ~ 8 ppm. The multiplet in the region of 5.3 ppm is believed to have originated from the stereo-isomers of this compound. These are all -CH-I peaks.

Figure 29. 270 MHz proton NMR spectra of cross addition reaction

The cross addition reaction is catalyzed by the iodine as in the homopolymerization of alkyl vinyl ethers. Under reaction conditions, the rate of further propagation of the carbon-iodine bond in the p-methylstyrene unit is predicted to be very small compared to that of the cross addition reaction because the nature of the carbon-iodine bond is quite different from that of the carbon-iodine bond in an alkyl vinyl ether/HI adduct. Usually no polymerization takes place for styrene or p-methylstyrene under these reaction conditions. Therefore, the expected structure of the cross addition reaction product will be a 1/1 addition product. A relative reactivity sequence can be seen in the rate constant of polymerization initiated by I_2 at 30°C in ethylene chloride solvent as shown in Table 37[504].

3) Stereochemistry of the Chain End: When the cross addition reaction product of EVE/HI/p-methylstyrene is refluxed in methanol with Et_3N, the NMR spectrum of the obtained product shows complicated resonance peaks. The p-methyl proton shows two peaks overlapped at 2.3 ppm, and the benzylic proton shows splitting into a quartet and a triplet(Figure 30). The carbon-13 NMR spectrum also shows very complicated peaks, but these peaks can be considered as a group of two sets of peaks having similar intensity. All these derivatives are thought to have originated from the different configurations of the reaction product.

When the cross addition reaction product(iodo compound) is reacted with methanol in the presence of Et_3N, the reaction occurs as in equation 147. Therefore, the configuration is expected to be retained, due to the two consecutive backside attacks. The configuration of the product can be treated as same as the cross addition reaction product(iodo compound).

Table 37. Propagation Rate Constant of Vinyl Monomers in the Polymerization Initiated by Iodine[a]

Monomer	k_p (l/mol.min)
p-Chlorostyrene	0.071
Styrene	0.22
p-Methylstyrene	5.7
p-Methoxystyrene	350
2-Chloroethyl vinyl ether	290
Isobutyl vinyl ether	390

[a] In ethylene chloride at 30 °C[504].

CH₃–CH–CH₂–CH–OMe

Figure 30. 270 MHz proton NMR spectrum of an ether model compound

$$\sim CHI \quad + NEt_3 \quad \xrightarrow{S_{N2}} \quad \sim CH-N^+Et_3 \quad I^-$$

with Me-substituted benzene rings.

$$\xrightarrow[S_{N2}]{MeOH} \quad \sim CH-O-Me \quad + \quad Et_3NH^+I^- \qquad (147)$$

When Cahn-Ingold-Prelog notation[488] is employed, the product has four possible isomers because the model compound has two asymmetric carbons. The four possible iodo compounds are represented in Figure 31, and their relationship is shown in Scheme 16.

| 3R, 1R (RR) | ⟷ | 3S, 1R (SR) | | ↕ enantiomers |
| 3S, 1S (SS) | ⟷ | 3R, 1S (RS) | | ⟷ diastereomers |

Scheme 16. Relationship of stereo isomers.

If intramolecular hydrogen bonding is assumed between oxygen and the benzylic proton, then through the internal hydrogen bondings, the five-membered ring structures are subjected to strains from the bulky substituents. The chemical shift difference of the benzylic proton in the NMR spectra can then be explained. Each enantiomeric pair is expected to have the same chemical shift values for -CHI-, but the diastereomers is expected to have different values. From Figure 31 and from molecular models, the RR and

3R,1R

3S,1R

3S,1S

3R,1S

Figure 31. Possible 4 stereo isomers of a model compound.

SS structures are thought to have less steric hindrance for the closer O...H interaction. Therefore the NMR chemical shift of *RR* and *SS* compounds appears more down field.

For the methanol substituted compounds, *RR* and *SS* are expected to have more intramolecular hydrogen bonding and thus be less polar toward intermolecular interaction. The assignment of the HPLC chromatogram might then resemble Figure 32 because the HPLC column used was reverse phase(C_{18} column) and the eluent used was polar(acetonitrile). But this assignment is tentative, so further verification is needed. Separation of the isomers followed by NMR spectroscopy will be one method of verification.

TLC was used in an attempt to separate the methanol substituted model compound, but the compound could not be separated. On the other hand, an ethanol substituted model compound was separated by TLC in $CHCl_3$/hexanes(2/8 v/v). The compound was separated by using column chromatography, and then the main portion was separated again in order to obtain one of the major isomers. Figure 33 shows the carbon-13 NMR of one of the separated compounds. The resonance peaks correlate well with the structure of the expected model compound. And in the proton NMR spectrum, only one resonance peak of the methyl(2.35 ppm) in the p-methylstyrenic unit and only quartet(4.45 ppm) from the benzylic proton, were observed. The separation of other isomers was unsuccessful.

When the p-methylstyrene was changed to p-methoxystyrene or p-t-butylstyrene, the TLC of the obtained methanolysis product showed many spots believed to have originated from side products. During the alcoholysis reaction model compounds can accompany possible side reactions because the benzylic carbons have an electron rich environment due to the inductive effect of the substituents. The styrenic monomer with the more negative *e* value in the *Q-e* scheme will have more side reactions under a given reaction condition. Side reactions with the substituent are also expected under severe

Figure 32. HPLC chromatogram of a model compound.

Figure 33. Carbon-13 NMR spectrum of an isomer of a model compound.

reaction conditions. A mild reaction condition is required for the iodo compound which has a polar styrenic unit.

The configuration of the iodo compound is quite important in the final step of the model reaction because major steric interaction is believed to occur between the incoming nucleophile and the C_4 methyl group of the iodo compound. Thus, the less hindered configuration toward the backside attack of the incoming nucleophile - *RR, SS* - will have the faster rate of reaction. If the methyl group is replaced by a polymer backbone, steric hindrance will be increased. Also a nucleophile of smaller size will have a faster rate of reaction.

4) Amination Reaction: In the amination reaction, the desirable reaction is the substitution reaction and the side reaction is elimination (Scheme 17)[494a]. The ratio of substitution/elimination is determined by R_1, R_2, R_3, and solvent polarity. The effects of R_1 and R_2 will be similar to those in cross addition reactions. Electron donating R_1 and R_2 promote both reactions but drive the reaction toward the S_{N1} side from S_{N2}. For a fixed R_1 and R_2(R_1 = H, R_2 = Me in this experiment), the reaction parameters can be narrowed down to the bulkiness of the R_3 in the amine and to the solvent polarity.

The size and the basicity of a nucleophile are very important in a bimolecular nucleophilic substitution(S_{N2}) reaction. For a selected base, R_3 has to be small in size and linear in shape in order to suppress possible elimination reactions. Solvent polarity also may be very important. More polar solvents favor an unimolecular reaction and the substitution/elimination ratio is then determined by the nature of the carbon-iodide bond. For this situation, the choice of the amine contributes little to the substitution reaction. Therefore, in order to suppress possible unimolecular reactions, the solvent should be less polar. In this experiment Et_2O was used.

Figure 34. Monitoring of amination reaction by proton NMR: A) before reflux, B) 30 min. reflux, C) 90 min. reflux, D) reflux for 6 hours.

Scheme 17. Amination reaction.

Amination reaction was monitored by proton NMR as shown in Figure 34. With gentle refluxing, the left side of the peaks(5.42 ppm) of -CHI- disappear first, then the peaks corresponding to the -CHI- (5.42, 5.33 ppm) disappear almost completely. A small amount of elimination product is also formed. The shape of the peaks(doublet, quartet) agrees well with the predicted peak shape of the -CH=CH- double bond. Here, the amount of the elimination product is less than 5% based on the integration of the NMR peaks. More elimination is observed with a longer reflux. The proton NMR spectrum of the model compound is shown in Figure 35.

The small side peak at $\sim$7.2 ppm originates from the unreacted iodo compound. No splitting is observed in the -CH_3 of p-methylstyrenic unit for this model compound. The existence of the amine functional group is confirmed by FTIR as in Figure 36 by the N-H stretching band around 3350 cm^{-1}.

The model compound with EVE shows almost same result. Both proton NMR spectra are almost identical in the region of 10 $\sim$ 4 ppm, and FTIR spectra are almost same. In the FTIR spectra the presence of the C-I bond can be confirmed by the weak but sharp absorption band at 625 cm^{-1}. No absorption band is observed at this region for either model compound. The existence of an amine functional group can usually be confirmed also by the disappearance of the broad NMR resonance peaks of -NH- when the proton is exchanged with deuterium. The proton NMR spectrum changed(disappeared) in the region of $\sim$3.7 ppm for the model compound with EVE when the proton was exchanged with deuterium by shaking with D_2O. But for the model compound with nBVE, no noticeable change was observed. This technique seems insensitive to the existence of -NH- in these model compounds compared to the FTIR technique.

Other amines besides $nBuNH_2$ such as $nPrNH_2$, $iPrNH_2$, and CH_3NH_2 were tried in the amination reaction. With $iPrNH_2$ a longer reaction time(more than 10 hours) was

Figure 35. 270 MHz proton NMR spectrum of amine terminated model compound.

Figure 36. FTIR spectrum of amine terminated model compound.

needed and more elimination was observed. CH_3NH_2 used was in a 40% aqueous solution, and isopropanol was used in the amination reaction as a solvent in order to make a homogeneous reaction mixture. The mixture was reacted by stirring for 14 hours at room temperature.

The final products were titrated with 0.1 N standard alcoholic HCl in isopropanol and the percent amine functionality of a sample was calculated by using equation 148.

$$\% \text{ Amine} = \frac{\text{Titrated molar quantity x Theoretical MW}}{\text{Weight of the sample}} x \ 100 \qquad (148)$$

Double inflection points were usually observed in the titration curve(mV versus ml or time). The second inflection point was taken as the equivalent point of the titration. Only a single inflection point was observed for the model compound with CH_3NH_2. Several inflection points were observed for the model compound with $nBVE-nBuNH_2$, but these could be grouped into two large inflection points. Four titrations were performed with this sample, and the results showed scattered values from 60% to 80%. The average amine content value was ~70%. The reason for the double inflection points in the titration curves is still unknown.

The results of the titrations are summarized in Table 38.

b) Oligomer Synthesis

A series of oligomers were synthesized by employing the synthetic strategies as shown in the model reaction in combination with the previous kinetic result of the homopolymerization. For oligomers, 5 units of EVE were incorporated in order to facilitate the cross addition reaction because the steric hindrance of EVE is expected to

Table 38. Titration Results of Amine Compounds

Structure[a]	Yield (g)	Yield (Theor., g)	Mn (Titrated)	Mn (Theor.)	%Amine
EVE - nBu	1.69	1.580	310	263	85
EVE - Me	1.25	1.328	295	221	75
EVE - iPr	-	1.496	361	249	69
nBVE - nBu	-	0.874	415	291	70
5nBVE - 5EVE - nBu	1.040	1.050	1460 (900: 1.86)[c]	1053	72
15nBVE - 5EVE - nPr[b]	4.081	4.284	2080 (1800: 1.71)[c]	2040	98
45nBVE - 5EVE - nPr[b]	10.632	10.595	9800 (6900: 1.17)[c]	5045	51

[a] EVE - nBu means 1 unit of EVE - 1 unit of p-methylstyrene - $nBuNH_2$,
5nBVE - 5EVE -nBu means 5 units of nBVE - 5 units of EVE - 1 unit of
p-methylstyrene - $nBuNH_2$.

[b] Prepared in n-hexane solvent, others were prepared in CCl_4.

[c] Mn by GPC and the MWD in linear fit with polystyrene standard.

be less than that of nBVE, especially when the polymer backbone has a tendency to make a 3/1 helix with high isotacticity as mentioned in *Review of Literature.* The AB blocks need not be separated strictly in the structure of the block copolymers, but the higher probability of an EVE unit at the chain end will be enough to reduce steric hindrance in the cross addition reaction.

The 5 units of EVE were incorporated into oligomers by sequential addition polymerization. For example, for the oligomer of molecular weight ~2,000, 15 units of nBVE and 5 units of EVE were used. Based on the reaction rate constant k_p^{app} ~74 l/mol.min at -15°C and the initial concentrations of the reactants, the expected reaction time for the 100% conversion of nBVE is ~48 minutes using equation 99. The expected reaction time for the 100% conversion of EVE is ~8 minutes using k_{EVE} ~$2k_{nBVE}$. The rest of the reaction was very similar to the model reaction. Thus oligomers of different molecular weights were synthesized and their expected molecular structure was

$$\sim \left(CH_2\text{-}CH \atop \underset{nBu}{\overset{|}{O}} \right)_n \left(CH_2\text{-}CH \atop \underset{Et}{\overset{|}{O}} \right)_5 CH_2\text{-}\underset{\underset{CH_3}{\bigcirc}}{CH}\text{-NH} \longrightarrow nPr \quad nBu$$
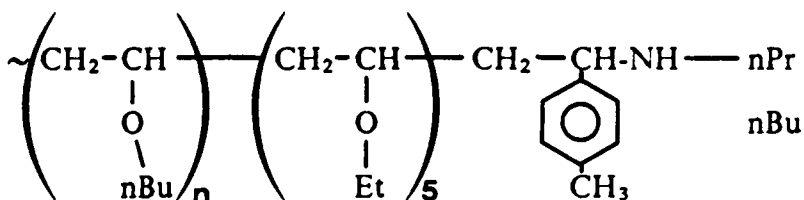
The synthesized oligomers were titrated with alcoholic HCl in isopropyl alcohol and the percent amine was calculated using equation 148. The results are summarized in Table 38. As seen in the Table the titration results range from 69 to 85% except for the oligomers of Mn~ 2040, 5045(theoretical).

For the Mn of 5045 the titration shows quite low percent amine, probably due to the lower concentrations of the functional group and the p-methylstyrene in the reaction mixture(dilution effect). As the molecular weight of the oligomer increases, the percent amine under this reaction condition is expected to decrease(charged mole ratio of oligomer/p-methylstyrene was usually 1/1).

On the other hand, quite a good result was obtained for the oligomer of theoretical molecular weight of 2040 probably due to the different charge ratio of oligomer/p-methylstyrene. Unlike the other experiments, a 100% excess amount of p-methylstyrene was used here. Therefore, the α-iodo ether compound has enough available p-methylstyrene molecules in the cross addition reaction though the addition reaction goes toward completion. As shown in Table 37, the cross addition product(iodo compound) is almost impossible to propagate with p-methylstyrene monomer. Therefore, at the end of the cross addition reaction, the cross addition reaction product and an excess amount of p-methylstyrene are expected to be present. Even in the case where self-propagation takes place, an excess amount of p-methylstyrene is beneficial.

The unreacted p-methylstyrene can react with an amine via a Michael type addition reaction[494a] as in equation 44. But the presence of this reaction product in the final product is unlikely because: 1) a catalyst is usually employed in the addition reaction for the less reactive styrenic double bond; 2) the product was vacuumed for two days at room temperature so the absence of small molecules is expected; 3) the titration value is quite exact - more than 100% is expected in the presence of low molecular weighted amine compounds. Molecular weight determinations by NMR and VPO will show indirect evidence in support of this conjecture.

Spectroscopic identification of amine functional groups was quite difficult as the molecular weight of the oligomers increased. Figure 37 shows the FTIR spectrum of the oligomer of theoretical $Mn \sim$ 1053. The weak absorption peak of the N-H stretching band was observed at ~3,350 cm⁻¹. On the other hand, for the oligomer of theoretical $Mn \sim$ 2040, only a very weak bump was observed.

The molecular weights of the oligomers were determined by GPC and the data are summarized in Table 38. Because the molecular weights are located close to the exclu-
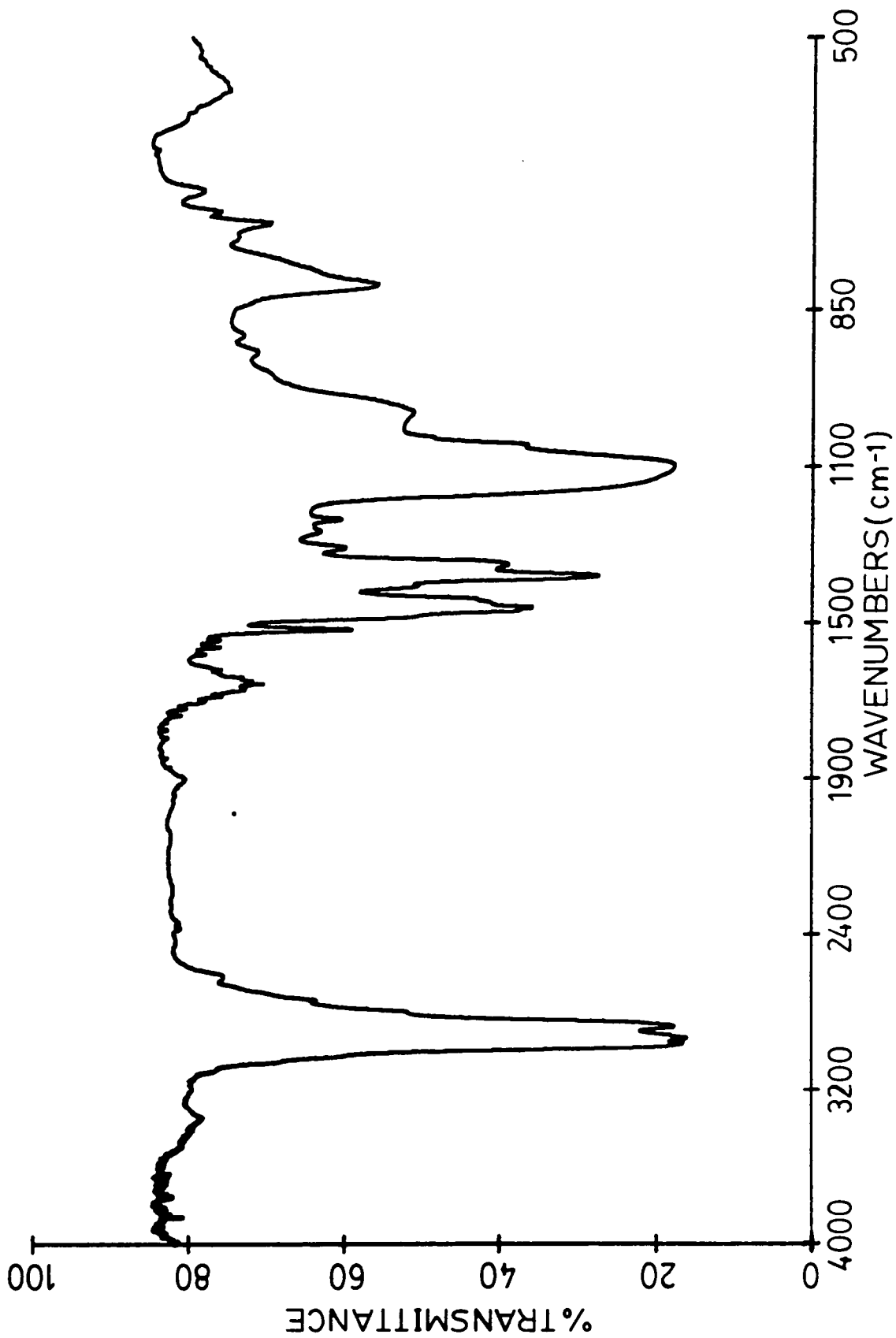
Figure 37. FTIR spectrum of amine terminated oligomer: *Mn* ∼1,053.

sion limit of the GPC column, the calculated molecular weights are expected to deviate considerably from the real values. The GPC traces are shown in Figure 38.

E. Block Copolymerization

1. Sequential Polymerization

In this research, several sequential polymerizations were attempted as follows:

- Poly(nBVE) - poly(EVE)

- Poly(nBVE) - poly(propylene oxide)

- Poly(alkyl vinyl ethers) - p-methylstyrene - poly(EtOXZ)

- Poly(EtOXZ) - poly(nBVE)

- Poly(EtOXZ) - poly(propylene oxide)

Among these trials only poly(nBVE) - poly(EVE) and poly(alkyl vinyl ethers) - p-methylstyrene - poly(EtOXZ) showed positive results. No block copolymerization was observed for other cases.

The middle monomeric unit(or units) acts as a junction unit in the preparation of a A-B type block copolymer, and the stability of the junction unit is very important in the final stability of the block copolymer. The importance of this unit is similar to that in amine terminated prepolymers. The stability of a block copolymer formed by the reverse addition sequence of monomers is predicted to be different from the one formed by forward addition sequence. The 5, 15, and 45 units of nBVE and each 5 units of EVE
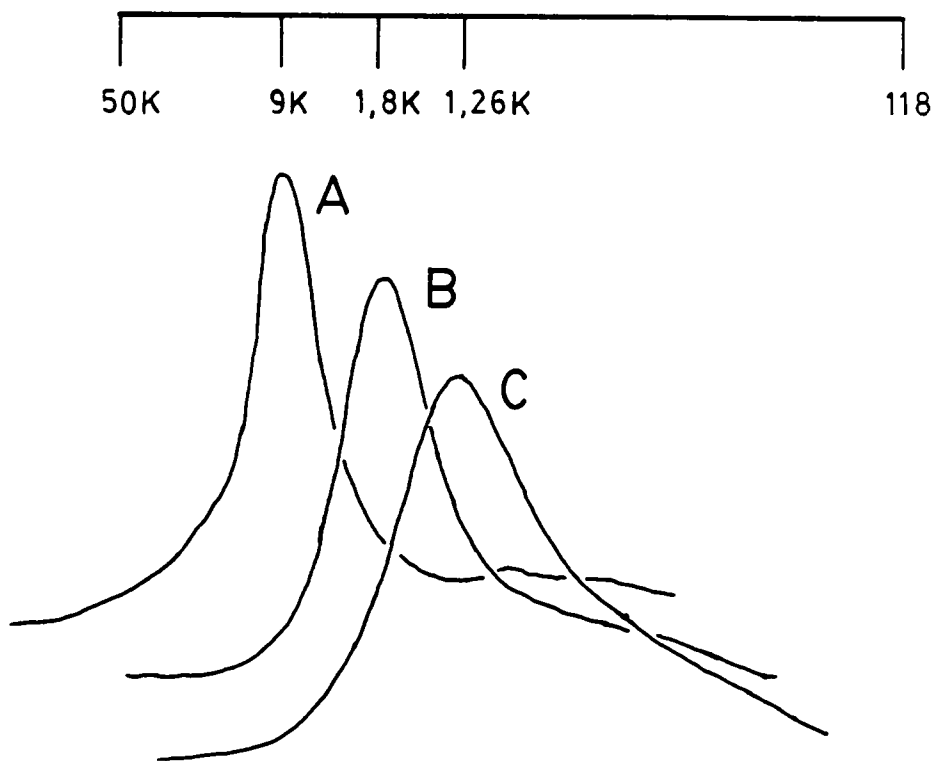
Figure 38. GPC chromatograms of amine terminated oligomers in THF: RI detector, polystyrene standard; the theoretical MWs of oligomers are A)5045, B)2040, C)1053.

were polymerized in the synthesis of poly(nBVE) - poly(EVE). As previously mentioned, this structure was introduced as an intermediate to the cross addition reaction in order to facilitate the cross addition reaction by rendering less bulky EVE units. This polymerization is relatively easy and the structure of the block copolymer can be well regulated as reported by other workers[10,505].

In the attempt of the synthesis of poly(nBVE) - poly(propylene oxide), the possibility of cross propagation with HI/I_2 initiation system was checked. When propylene oxide monomer was introduced into the reaction flask of one unit of nBVE/HI in the presence of iodine, no polymerization was observed. The inability of the cross propagation seems to have two possible origins. One is that propylene oxide does not have a double bond with which the activated complex mechanism(Scheme 15 in the kinetic study) can work. The other is that the reaction condition is not sufficient to activate cross propagation(if one assumes reaction mechanism B as in Scheme 4), due to the different reactivities of these monomers. But it is interesting to note that the oxygen atom in the propylene oxide has the possibility of forming an oxonium ion during polymerization(as proposed in equation 41) if the propagation reaction proceeds via dissociated ionic species[15]. Therefore it will be very interesting to find out what will happen if a polymerization reaction of nBVE or other monomers with double bonds is tried in the presence of propylene oxide at higher reaction temperature with an I_2 or a ZnI_2 catalyst. The HI/ZnI_2 initiation system is reported to yield living polymerization of vinyl ethers at temperatures up to 40°C in toluene. This reaction may generate a critical clue to the selection of polymerization mechanisms.

For the synthesis of poly(alkyl vinyl ethers) - p-methylstyrene - poly(EtOXZ), an oligomeric iodo compound(5 units of nBVE - 5 units of EVE - 1 unit of p-methylstyrene) was synthesized first by employing a HI/I_2(10/1 molar ratio) initiation system in CCl_4. Then the block copolymerization of EtOXZ was attempted(10 units of EtOXZ) at 80°C

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for 48 hours. In this block copolymer the styrenic unit acts as a junction point to stabilize the block copolymer. The chain end of the oligomeric iodo compound has a benzylic -CH-I bond very similar to the structure of the benzylic iodide used as an initiator in the polymerization of EtOXZ. The reactivity of oligomeric -CH-I is predicted to be larger than that of benzyl iodide because in a sense the carbon is secondary. The polymerizability of EtOXZ by this oligomeric iodo compound is doubtlessly seen in the yields of the products(1.8 g / 1.83 g theoretical for the p-methylstyrene junction unit and 2.05 g for the p-methoxystyrene junction unit). The formed polymers were brittle and foamy due to vacuum drying for the one with p-methylstyrene junction and slightly sticky with less foam for the one with p-methoxystyrene junction unit.

It seems better to stop the polymerization reaction before the polymerization reaction mixtures turn dark. The iodine is thought to intervene in the polymerization reaction by self initiation as seen in the homopolymerization of oxazolines by benzyl iodide/I_2 or I_2. In the polymerization, the iodine molecule is expected to form I_3^- by the presence of I^- in a polar solvent, and the expected color of I_3^- is usually a brownish dark color. But in this research, a clear reddish color was observed for both polymerizations(for p-methylstyrene junction or p-methoxystyrene junction) after a 24 hours reaction time. Therefore, this observation suggests that the iodine in the polymerization may have other identity other than I_3^-, such as a complex with the EtOXZ monomers.

In any case, however, the amount of iodine has to be reduced in order to suppress possible self initiation of the iodine molecule. The rate of cross addition reaction is traded off in this case because the iodine catalyzes the cross addition reaction. By selecting a reactive monomer such as p-methoxystyrene as the junction unit, this drawback can be compensated for. But the stability problem of the junction point and the possible elimination of HI from the iodo compound before cross propagation toward EtOXZ,

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still remain for this situation. A milder reaction condition is desirable in the reaction in order to suppress the possible decomposition(or side reactions) of alkyl vinyl ether units by active ions.

In order to suppress self initiation of iodine, the iodine was removed from the iodo compound after the cross addition reaction by washing with aqueous $Na_2S_2O_3$ followed by washing with water and drying in vacuum oven, but the copolymerization result was worse than in the reaction done without removal of iodine. Another method of I_2 removal seems desirable.

In the attempt to synthesize poly(EtOXZ) - poly(nBVE), and poly(EtOXZ) - poly(propylene oxide), living poly(EtOXZ) was prepared first, and then nBVE or propylene oxide was added(reaction temperature, 35°C). No polymerization was observed in either case with living poly(EtOXZ) prepared either by benzyl iodide or by methyl tosylate. The reason has to do with the reactivity of the monomers. In the polymerization of oxazolines, propagation is explained by the nucleophilic attack of a monomer on the oxazolinium ion[184-185]. The basicity of a monomer can thus be considered as the reactivity of the monomer in this reaction. The basicities for both nBVE and propylene oxide are believed too low to open the oxazolinium ring.

2. Coupling Reaction

Block copolymerizations were tried by using a coupling reaction of living poly(EtOXZ) with an amine terminated oligomer, Jeffamine(*amine terminated poly(propylene oxide) from Texaco*), and poly(propylene oxide).

When poly(propylene oxide) of *Mn* ~2,000 was refluxed for two days with living poly(EtOXZ) of *Mn* ~2,000 in acetonitrile, the obtained product was heterogeneous.

Also, when a similar mixture was refluxed in the presence of Et_3N as a possible acid acceptor, the reaction mixture separated into two phases. Therefore, with alcoholic -OH groups the coupling reactions were unsuccessful.

On the other hand, when the living poly(EtOXZ) of Mn ~2,000 was reacted for two days with Jaffamine of Mn ~2,000 in CH_2Cl_2 at room temperature, the reaction mixture became homogeneous.

The best results are obtained by the reaction of the amine terminated oligomer of Mn ~2,040 with living poly(EtOXZ) of Mn ~1,210. This reaction scheme is represented in equation 93. During the reaction, a small amount of reaction mixture was sampled for GPC analysis. Figure 39 shows the GPC chromatograms of oligomers, poly(EtOXZ), and the reaction products. As the reaction times increase, the bimodal distribution changes to a monomodal distribution, but the chromatogram of the final reaction product did not move to a higher Mn, probably as a result of the negligible contribution of the poly(EtOXZ) block to the total hydrodynamic volume of the final block copolymer in THF solvent.

The hydrodynamic volume of poly(EtOXZ) in THF is thought to be very small. The reported surface tension of the poly(EtOXZ) of Mn ~1,300 is 52.6 dyn/cm[506] and the reported GPC solvent is usually $CHCl_3$. In this solvent, reported MWDs of living polyoxazolines are quite narrow(1.1 ~ 1.3). The poly(EtOXZ) of theoretical Mn ~1,210 shows Mn ~300 in THF with MWD of 1.54. For the poly(EtOXZ) of Mn ~2,000, the peak height of the chromatogram was too small and the shape was quite irregular. The discrepancy of Mn may be partly caused by the exclusion limit of the column, but the small hydrodynamic volume is probably the major reason.

Intrinsic viscosities were measured in $CHCl_3$ for the starting materials and the product. Poly(EtOXZ) of Mn ~1,210 shows $[\eta]_{CHCl_3}^{23}$ = 0.03 dl/g, the amine terminated oligomer of Mn ~2,040 shows $[\eta]_{CHCl_3}^{23}$ = 0.06 dl/g, and the block copolymer shows
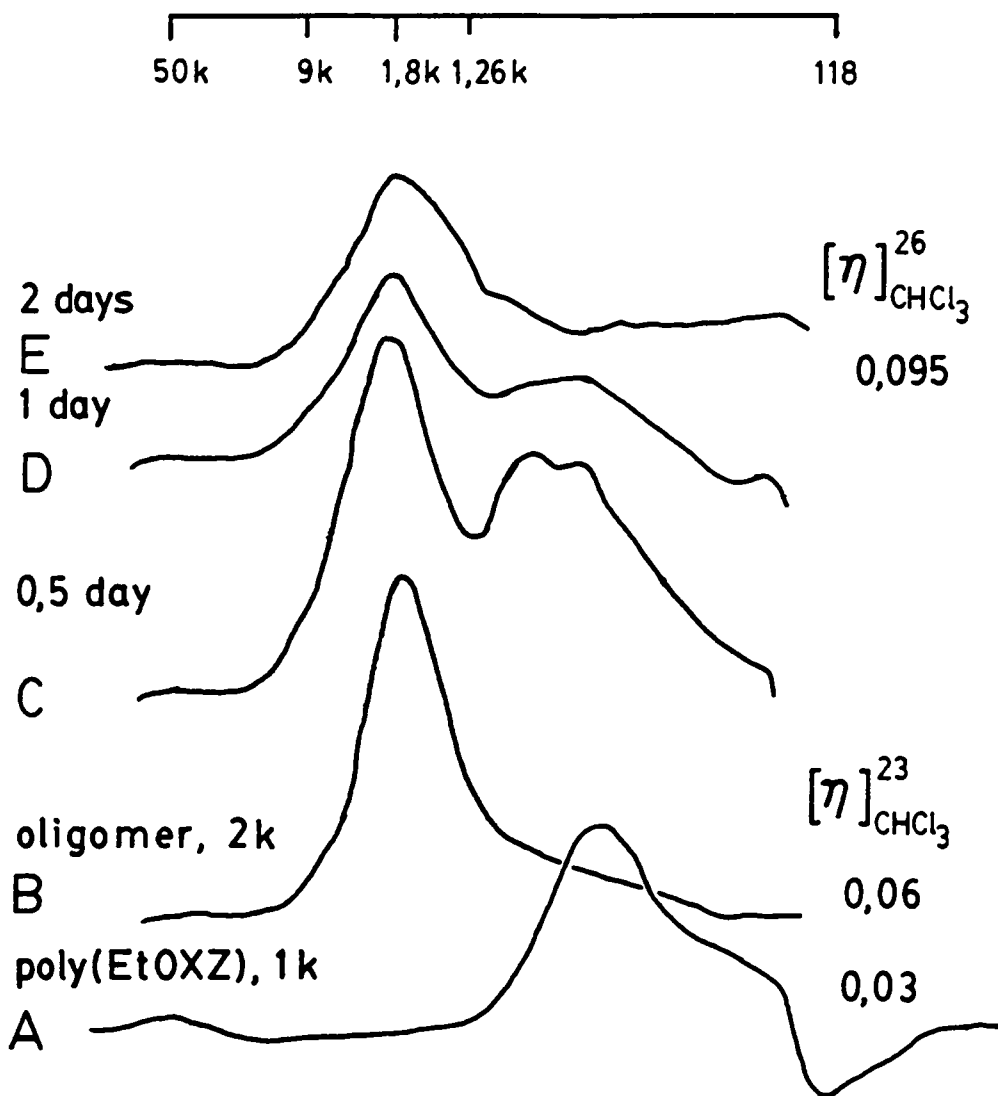
Figure 39. GPC chromatograms of coupling reaction in THF: A) poly(EtOXZ) of Mn ~1210, B) -NH- terminated oligomer of Mn ~2040, C) after reaction of 0.5 day, D) after reaction of 1 day, E) after reaction of 2 days.

$[\eta]_{CHCl_3}^{26}$ = 0.095 dl/g. The intrinsic viscosity data suggest that this coupling reaction is a good way to make a block copolymer. This kind of coupling reaction for a small molecule in the preparation of a functionally terminated prepolymer was reported in the literature with a quantitative conversion[272].

The formed block copolymer is soluble in methanol but insoluble in water, whereas the poly(EtOXZ) is soluble in both solvents, and the amine terminated oligomer is insoluble in water. The block copolymer is expected to exist as an amine salt and can be changed to the corresponding tertiary amine by passage through an anion exchange resin[182].

Chapter V

Conclusions

This research has generally focused on cationic polymerization where polymerization proceeds via covalent-like propagating species. The polymerization system of poly(alkyl vinyl ethers) initiated by HI/I_2 initiation system was chosen as a system of current interest, and the research was directed toward the investigation of the nature of the active propagating species and the preparation of a functionalized prepolymer.

Some conclusions about the nature of the active propagating chain end of the chosen system have been reached by kinetic study with spectroscopic measurements.

- The introduction of charge transfer complexation between monomer and iodine can explain the observed rate of polymerization of alkyl vinyl ethers initiated by an HI/I_2 initiation system well, regardless of the specific identity of the complex. At least two propagating modes are proposed. The identity, reactivity, and role of the monomer-iodine charge transfer complex are thought to be important in this

polymerization process. In one of the proposed modes, the complex participates in the propagating reaction. However in the other proposed mode, the complex becomes inactive, and only a small portion of the iodide chain end is activated by iodine. At present there is no strong evidence for eliminating either of the proposed propagation modes. More systematic investigation of the propagating chain end will perhaps reveal the real polymerization pathway in these interesting polymerization systems.

- A HI catalyst alone seems to be insufficient for the polymerization of alkyl vinyl ethers. Another cocatalyst component is needed.

- Tacticity measurement shows that the association between propagating chain end and the possible counterion seems to be very intimate, as evidenced by non-random polymerization behavior. The tacticity results support both proposed modes of propagation, but they eliminate the possibility of propagation via a fully dissociated ion pair in one of the propagation modes. Instead, close association of the counterion is the more likely pathway in that mode of propagation.

A synthetic strategy was developed in the synthesis of amine-terminated poly(alkyl vinyl ethers). Incorporation of a styrenic monomer at the propagating chain end of living poly(alkyl vinyl ethers) provides a convenient intermediate synthesis of a relatively stable amine-functionalized prepolymer. The cross addition and amination reactions are optimized by proper selection of substituent groups at the styrenic monomer. This approach to prepolymer synthesis is quite successful as evidenced by the block copolymerization of the resultant amine-terminated prepolymer with living poly(ethyloxazoline).

Chapter VI

Future Work

The findings from this research have generated many unanswered questions. Throughout this research, an attempt has continually been made to identify potential research areas. These are described in this chapter.

The polymerization system of alkyl vinyl ethers by a HI/catalyst initiation system is sufficiently notable and promising to merit further study. It appears that this system is closely related to group transfer polymerization or coordination polymerization in which many initiation systems are employed. A selected initiation system can be modified by changing the initiator or catalyst, or by the addition of an ether or carbonyl compound. This research indicates that polymerization with a different catalyst, those used in GTP or coordination polymerization are potentially useful.

Kinetic and spectroscopic investigation of HI/ZnI_2 or $ZnBr_2$ initiation systems will help refine our understanding of polymerization mechanisms. More refined tacticity measurements of poly(alkyl vinyl ethers) initiated by HI/I_2 or HI/ZnI_2 at various temperatures may give a clue to a more reliable polymerization scheme. More detailed

kinetic investigation of the polymerization of an alkyl vinyl ether with low initial ratios of $[M]/[I_2]$ may also give a range of limits where pseudozeroth order kinetics can be applied.

Utilization of the living polymerization technique in the synthesis of well-defined poly(vinyl ethers) will be rewarding. For example, polymers with specific pendant groups such as mesogens can be synthesized by using a selected initiation system. These polymers are very useful for the study of structure-property relationships.

The preparation of AB or ABA type block copolymers with poly(alkyl vinyl ether) units and the investigation of the properties of the block copolymers are beneficial to polymer science for the preparation of new materials. The following studies are needed for the successful synthesis of block copolymers by using amine-terminated prepolymers: a) quantitative kinetic investigation of the cross addition reaction with various styrenic monomers probably by using low temperature NMR; b) functionality dependence of the amine-terminated oligo-(alkyl vinyl ethers) as the molecular weight of the oligomer increases(good yield is expected up to Mn ~5,000 with excess amount of p-methylstyrene); c) checking the stability of the resultant block copolymer(by using GPC) after a treatment of the sample with heat or reflux in a solvent, when a reactive styrenic monomer other than p-methylstyrene is used as a junction unit of the block copolymer of poly(alkyl vinyl ether)-poly(EtOXZ).

Unsaturated prepolymers can be prepared by the reaction of the cross addition reaction product with a proper salt of an unsaturated carboxylic acid, such as sodium methacrylate. Selection of a proper solvent will be the key factor in the reaction. The stability of the prepolymer will depend upon the structure of the chain end. Telechelics are also possible by the initiation with a bifunctional alkyl vinyl ether/HI adduct.

Finally, this study confirms that the living polymerization of oxazolines is quite simple and the formed living oxazolinium ion is quite stable for a long time under inert

atmosphere. After living polymerizations, block copolymers can be prepared by coupling reactions with an amine-terminated prepolymer such as amine-terminated polysiloxane or some other prepolymer. The properties of the polyoxazoline block can be changed by changing the substituent.

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