INVESTIGATIONS UTILIZING MONO- AND DIFUNCTIONAL ORGANO ALKALI
METAL INITIATORS FOR ANIONIC POLYMERIZATION

by

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(ABSTRACT)

This work focused on the formation and the subsequent use of a difunctional organolithium as an anionic polymerization initiator for primarily diene monomers. The initiator was formed in nonpolar solvent such as cyclohexane and toluene by the addition of two equivalents of sec-butyllithium to one of the nonconjugated diene 1,3-bis(α-phenylethenyl)benzene.

The disappearance of the starting diene was easily followed by UV/Visible spectroscopy. Rate expressions were evaluated based on the assumptions of a consecutive reaction mechanism and association behavior of the alkyl lithium. Arrhenius behavior was observed and an activation energy of 19 Kcal/mole was determined.

Unlike the spectroscopic techniques, gas chromatography was able to separate the unreacted diene, mono-, and diaddition products but dramatic increases in sensitivity were realized by using a capillary column techniques, thus allowing the direct analysis of initiator solutions that were routinely used for high molecular weight

polymerizations. Quantitative determination of all reaction components
confirmed the existence of a consecutive reaction mechanism for this
addition and the data strongly suggested that the second rate constant
was an order of magnitude faster than the first in cyclohexane.

Using the chromatographic technique to monitor initiator formation,
the dianionic diaddition product was maximized by the simple addition of
more sec-butyllithium. Polydiene homopolymers were then routinely
prepared with predictable molecular weights and narrow polydispersities.
Successive addition of isoprene and styrene resulted in triblock
copolymers that incorporated both monomers over a wide compositional
range. Novel triblock systems that contained t-butyl methacrylate end
blocks and an isoprene center block were prepared by addition of THF
which facilitated the efficient crossover.

A new trialkyl sodium magnesiate initiator was evaluated as an
alternative to alkyllithiums for the polymerization of vinyl and cyclic
monomers. Homopolymerizations of isoprene and styrene showed slow
initiation rates and uncontrollable molecular weights relative to sec-
butyllithium. This initiator also polymerized methyl methacrylate in
high yields without modification of its basicity and steric bulk.

DEDICATION

This writing and the hard work that went into it is dedicated to

because it was always nice to come home.

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PART I

Difunctional Organolithium Initiator Studies

I. INTRODUCTION

The anionic polymerizations of nonpolar vinyl monomers such as the dienes and styrenes require strongly basic initiators. It is also important that initiation is fast relative to propagation. Alkyllithiums meet these requirements and are also soluble in hydrocarbon solvents, the medium of choice for diene polymerizations. These initiators are highly associated in nonpolar media, with the aggregation number being a function of the alkyl group. A variety of techniques have been used to determine the degree of association as well as the mechanism of the initiation process. The living chain ends of the polymer are also associated and the degree to which they are continues to be a debated question. It is well established that polystyryllithium is associated into dimers in hydrocarbon solvents while association numbers for polybutadienyl- and polyisoprenyl lithium of between 2 and 4 have been observed by viscosity and light scattering techniques.

Interestingly enough, the association can be broken up by the addition of polar additives to the point that "monomeric" organolithiums have been observed. In addition, significant increases in initiation and polymerization rates were also observed. This has been attributed to the formation of solvent separated ion pairs (and to a lesser degree free ions) which have increased reactivity relative to tight ion pairs.

Because diene polymers contain a double bond for every repeat unit, generally three different geometrical and also three stereochemical structures are possible. The former are the cis and trans 1,4-structures which have the double bond in the backbone, and the 1,2-

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adduct (or 3,4- in the case of isoprene) which has the double band pendent to the polymer backbone. The relative amount of these structures has a rather dramatic effect on the thermal characteristics of the polymer. Increasing the 1,2- (or vinyl) content results in an increase in the glass transition temperature which is generally an undesirable characteristic if one wishes to obtain a low Tg. Several reaction variables will change the amount of vinyl content in the polymer. These include polymerization temperature, initiator concentration, solvent, and counter ion size. Of these, changing the solvent polarity and the counterion have the most dramatic effect. Interestingly enough, in some cases, it was possible to prepare nearly 100% pure 1,2 polydienes, if dipiperidinoethane (Dipip) modified cyclohexane was used as the solvent.

Though mechanistically very complex, these monofunctional initiators have been very effective in preparing a variety of di- and triblock structures. Unfortunately, this type of synthetic technique limits the number of possible triblock copolymers to those containing primarily styrene and dienes and their substituted derivatives.

One method of circumventing this limitation was by the use of a difunctional initiator. If the polymer can be prepared by synthesizing the center block first and the two-end blocks concurrently, one monomer addition step will be avoided. In addition, the polymeric anions generated after the first monomer addition are strongly basic (such as a polydienyl anion) and a rapid and efficient initiation of a monomer whose corresponding anion is a weaker base (such as a methacrylate) can

be achieved. These types of triblock systems can not be prepared by a monofunctional initiator.

Typically, difunctional initiators have been prepared in solution by two different synthetic approaches: coupling of two radical anions, and addition of a monofunctional organolithium to a compound with two reactive double bonds. Of the two, the latter is the more effective route, since it does not necessarily require the use of polar solvents.

Spectroscopic techniques have been used to follow the addition reaction of sec-butyllithium to nonconjugated dienes, because of the highly colored nature of the reaction products. Chromatographic techniques have, as well, proven to be the most effective method of elucidating mechanistic and kinetic parameters, because all important starting materials and reaction products can be followed over the course of the reaction.

Use of a difunctional initiator in actual polymerizations have often times given undesirable results. Broad molecular weight distributions and uncontrolled molecular weights have been observed. This was most likely due to the presence of mono- and/or polyfunctional initiators that were impurities in the system.

II. LITERATURE REVIEW

A. Diene and Styrene Polymerizations

1. Introduction

In recent years, polymerizations of vinyl monomers via initiation with strongly basic organoalkali metal compounds have received considerable interest. Using the appropriate conditions of extremely high purity solvents and monomers under inert atmospheres which are free of air and water, undesirable side reactions can be prevented and quantitative conversion of monomer to polymer can be achieved.

After all the monomer has been consumed, each active polymer chain end contains an anion and its counterion (metal cation). The sp^3 hybridized anion is relatively unreactive towards side reactions such as disproportionation and combination reactions, which are often observed with cationic and free radical polymerizations. This increased stability has resulted in these polymerizations being termed "living" due to the absence of any terminating reaction. Indeed, they remain active for very long periods of time (years, in fact!), which makes this type of polymerization ideally suited for the sequential synthesis of block copolymers. This synthetic approach requires the addition of a second monomer after polymerization of the first monomer is complete. The technique of sequential monomer addition thus allows the preparation of a wide variety of di-, tri-, and multiblock copolymers which display unique physical properties.

The polymerization of isoprene by sodium and potassium was first reported by Mathews and Strange (1) in 1910 and later by Harries (2) and

Schlenk (3). The first report of the use of lithium and organolithiums

to polymerize butadiene was made by Ziegler (4) which was later

clarified and expanded to include polymerization of other important

conjugated dienes such as isoprene and 2,3-dimethylbutadiene (5,6,7).

Ziegler (7) was able to show that when sodium reacts with

butadiene, a disodium adduct was formed. This was demonstrated by

addition of methylaniline and by measuring the amount of sodium

methylanilide that was produced. For every mole of butadiene that was

reacted, two moles of sodium methylanilide were produced. This

suggested that some mechanistic process other than a free radical

process was occurring, but an anionic mechanism was not suggested. In

fact an anionic polymerization mechanism was not recognized for this

reaction until much later (11).

One of the first kinetic studies of an anionic polymerization was

conducted by Higginson and Wooding (8). They studied the polymerization

of styrene by potassium amide in liquid ammonia (which formed a

homogenous solution) and proposed the following mechanism. They

$$KNH_2 \rightleftharpoons K^+ + NH_2^-$$ (1)

$$NH_2^- + CH_2{=}CH \longrightarrow NH_2CH_2{-}CH^- K^+ \xrightarrow{\text{styrene}} {\sim}{\sim}{\sim}CH_2{-}CH^- K^+$$ (2)

$${\sim}{\sim}{\sim}CH_2{-}CH^- K^+ + NH_3 \longrightarrow {\sim}{\sim}{\sim}CH_2{-}CH_2 + KNH_2$$ (3)
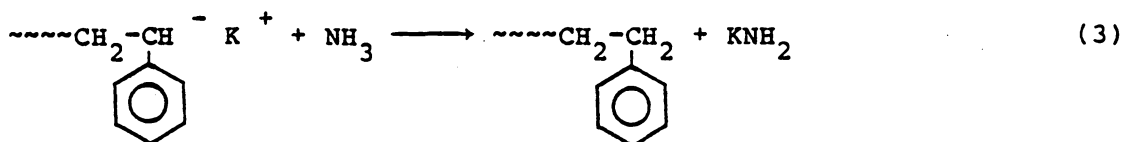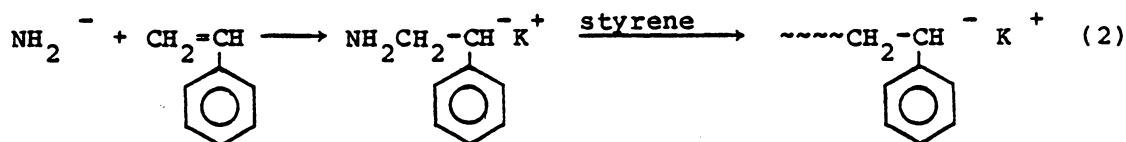
envisioned that the solvent acted as a chain transfer agent that limited molecular weight and broadened the molecular weight distribution.

Interest in the actual study of anionic polymerization followed the discovery that lithium initiators, such as dispersions of metallic lithium (9) and alkyllithiums (10), could produce materials that were very similar to natural rubber. It was known that fused ring hydrocarbons such as naphthalene produced a highly colored complex in the presence of an alkali metal in certain etheral solvents, if air and water are excluded (11). However, the exact structure of these colored species was not known. These complexes were shown to polymerize butadiene and styrene at a very rapid rate. It was also shown that these polymeric species were difunctional and carbanionic in nature. Polymer chains containing two carboxylic acid groups per chain were observed after reaction with carbon dioxide (11).

Later work by Weissman and coworkers (12,13) and Hoijtink (14) proved these alkyl metal/fused ring complexes to be monomeric radical anions which have an extra electron in the lowest unoccupied π orbital. The solvent (in this case THF) aids in the electron transfer process from the sodium to the naphthalene and stabilizes the resulting complex, e.g.,

$$\text{(naphthalene)} + \text{Na} \xrightarrow{\text{THF}} [\text{(naphthalene)}^{\bullet -}]\text{Na}^+ \tag{4}$$
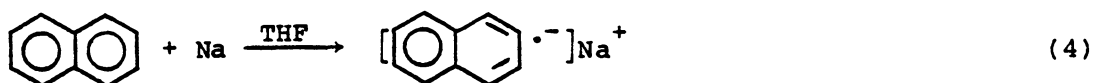
Weissman and coworkers (13) also showed that the ease of formation and stability of the complex depends on the electron affinity of the fused ring system. They were able to establish the electron affinity scale, bisphenyl < naphthalene < phenanthrene < anthracene.

Szwarc and co-workers [15,16] showed this reaction indeed took place via an electron transfer process in which the radical anion of naphthalene transfers an electron to styrene monomer. The resulting radical anion of styrene was very reactive and quickly dimerizes to form the more stable dianion. This process was illustrated below.

$$[naphthalene \cdot^-]Na^+ + CH_2{=}CH(C_6H_5) \longrightarrow naphthalene + [CH_2{-}CH(C_6H_5) \cdot^-]Na^+ \qquad (5)$$

$$2[CH_2{-}CH(C_6H_5) \cdot^-]Na^+ \longrightarrow Na^+ {}^-CH(C_6H_5){-}CH_2{-}CH_2{-}CH(C_6H_5)^- Na^+ \qquad (6)$$
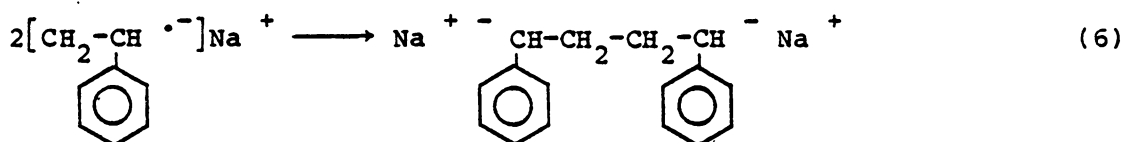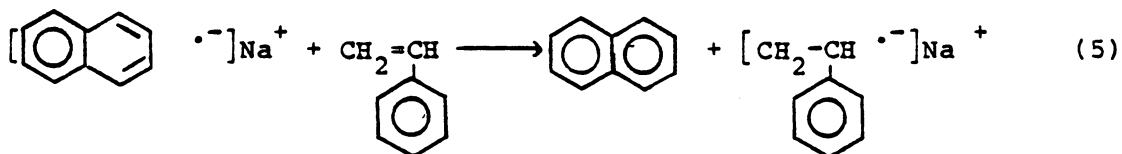
This dianion was capable of adding more monomer by anionic attack on additional styrene molecules to form high molecular weight polystyrene.

Some of the unique features of this polymerization were, firstly, the very fast initiation step, and secondly, the fact that in the absence of any termination or chain transfer processes, the chains grew until all of the monomer was consumed. Lastly, a narrow molecular weight distribution was obtained for the resulting polymer due to the slow rate of propagation relative to initiation.

A second type of anionic initiator which was alluded to earlier was the use of lithium metal catalyst for the stereospecific polymerization, to yield high cis 1,4-polyisoprene. The proposed anionic mechanism of polymerization also involved initiation by electron transfer from the metal to the monomer. As an example, the lithium metal initiation of butadiene is shown below.

$$\text{Li} + CH_2=CH-CH=CH_2 \longrightarrow \overset{\bullet}{C}H_2-CH=CHCH_2^-\text{Li} \qquad (7)$$

$$2\overset{\bullet}{C}H_2-CH=CH-CH_2^-\text{Li}^+ \longrightarrow \text{Li}^+CH_2^--CH=CHCH_2-CH_2-CH=CHCH_2^-\text{Li}^+ \qquad (8)$$

and/or

$$\overset{\bullet}{C}H_2-CH=CH-CH_2^-\text{Li} + \text{Li} \longrightarrow \text{Li}^{+-}CH_2-CH=CH-\overset{-}{C}H_2\text{Li}^+ \qquad (9)$$
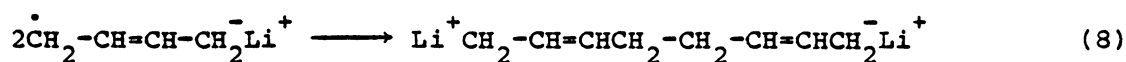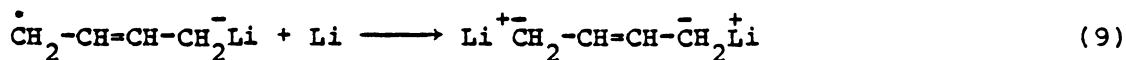
The radical anion that was generated in equation (7) can either couple with another radical anion in equation (8) or undergo an additional electron transfer with the metal as in equation (9). In either case, both processes lead to dianionic species. The important features which determine the preferred reaction were concentration, solvent, and reactivity of the metal.

The occurrence of the second electron transfer step in equation (9) was strongly suggested by the work of Ziegler (7) and later by Robertson and Marion (17) who showed the presence of disodium species that contained only one molecule of dimethyl 1,3-butadiene. O'Driscoll and Tobolsky (18) also suggested that the radical anion formed in equation (8) may polymerize monomers at the radical site prior to combination for the copolymerization of styrene and methyl methacrylate using lithium metal as the catalyst. However, other studies of this copolymerization (19) suggest that these early results are mainly due to the heterogeneity of the system rather than to a specific radical mechanism.

A third type of anionic initiator involves the use of organometallics such as alkyllithiums and Grignard reagents. These initiators have advantages over the electron transfer complexes and alkali metals in that both ethereal and hydrocarbon solvents may be used and that a homogeneous solution results, regardless of the solvent

employed. This extends the choice of possible solvent/monomer

combinations available for anionic polymerization.

Because electron transfer and subsequent coupling reactions were

avoided, a monofunctional propagating species was generated by simple

anionic attack at the vinyl site of the monomer. This leads to chain

growth from only one end, with the initiator fragment remaining at the

other end. The stoichiometric number average molecular weight was then

given as:

$$\bar{M}_s = \frac{\text{grams monomer}}{\text{moles initiator}} \tag{10}$$

This was in marked contrast to the electron transfer mechanisms

which generated difunctional anionic species, such that chain growth

occurs at both chain ends with the initiator fragment in the center of

the chain. In this case, the stoichiometric number average molecular

weight was given as:

$$\bar{M}_s = 2 \times \frac{\text{grams monomer}}{\text{moles initiator}} \tag{11}$$

Many organolithium compounds react slowly with vinyl monomers such

as styrene, relative to the rate of propagation in hydrocarbon solvents.

As an example, Worsfold and Bywater [20] have reported that styrene

initiated by n-butyllithium in benzene follows the following

relationship at 30°C, which was reportedly the minimum ratio of monomer

to initiator needed for the initiator to completely disappear.

$$[\text{Styrene}][n\text{-}C_4H_9]^{-4/3} > 504 \tag{12}$$

Similar behavior was also seen for the initiation of dienes. Here,

decreasing the reaction temperature allows one to use a smaller ratio of

monomer to initiator. Even though lowering the temperature reduces both the initiation and propagation rates, it has a larger effect on the rate of propagation, due to its higher energy of activation relative to that for the initiation step.

2. Homogeneous Initiation by Organolithium Reagents

The slow initiation rate of these diene polymerizations in hydrocarbon solvents was due primarily to the fact that organolithium compounds are associated in nonsolvating media. It has been suggested that before the actual initiation takes place, the associated species must first dissociate into smaller aggregates and "monomeric" species, which can be quite slow in nonpolar media. Subsequently the monomeric organolithium was the actual initiating species (32). This mechanism will be discussed in more detail later. Table 1 summarizes the association number for a variety of organolithium initiators in several common hydrocarbon solvents used for anionic polymerization. It appears from this listing that the linear organolithiums have a higher degree of association (except for the case of methyllithium) than the corresponding branched isomers. This higher degree of association was thought to be due to the decreased steric crowding present in the associated complex.

For styrene and butadiene polymerizations involving organolithiums, the homogeneity of the solution and the absence of any termination or transfer reactions makes it possible to measure directly both the kinetics of the initiation and propagation steps of the living polymerization. In simple terms, the initiation reaction should be a bimolecular reaction between the monomer and initiator and the

TABLE 1

Association States of Organolithiums in Hydrocarbon Solvents (155)

Compound	Solvent	Concentration range (M)	Association Number	Reference
C_2H_5Li	Benzene	not given	6	21
		0.03 - 0.4	6	22
		0.03 - 0.4	4.5 - 6.0	23
		0.02 - 0.23	6.07 ± 0.35	24
	Cyclohexane	0.02 - 0.10	5.95 ± 0.3	24
		0.006 - 0.08	6.0 ± 0.12	26
	Benzene	0.006 - 0.19	6.1 ± 0.18	26
$n-C_4H_9Li$	Cyclohexane	0.4 - 3.3	6.17 ± 0.12	27
		0.002 - 0.6	6.0	26
	Benzene	0.5 - 3.4	6.25 ± 0.06	27
		not given	~7	28
$s-C_4H_9Li$	Cyclohexane	0.11 - 0.4	4.12 ± 0.09	29
	Benzene	0.17 - 0.5	4.13 ± 0.05	29
$t-C_4H_9Li$	Cyclohexane	0.005 - 0.3	4.0 ± 0.05	26
	Benzene	0.05 - 0.18	3.8 ± 0.2	30
		0.26 - 0.66	4.0 ± 0.04	26
Methyl Lithium	Cyclohexane	0.2	2.0	31
	Benzene	0.1, 0.3	2.1, 1.9	31

propagation step should show the same order for the monomer and the growing chain concentrations.

Generally, this was not the case. What was often found was that the reaction order was first order in monomer concentration regardless of temperature, solvent polarity, or other reaction variables. However, this step shows a definite fractional order dependence on the initiator concentration depending on solvent and possibly even the monomer concentration.

Originally, the order of the initiation reaction was thought to be directly related to the degree of association for the organolithium in the particular solvent (32). However, a comparison of Table 1 and Table 2 shows any relationship between the association number of the initiator and the reaction order may be only coincidental. From Table 2, reaction orders can vary from 1/6 to 1 depending on conditions such as changes in solvent polarity.

It has also been noted that the presence of impurities such as lithium alkoxides or other Lewis bases can alter the rate constant and reaction orders for both the initiation and propagation steps. Roovers and Bywater (38) report that the presence of lithium n-butoxide lowers both the initiation and propagation rates of the n-butyllithium initiation of styrene in benzene. It has also been shown that lithium n-butoxide eliminates the induction period for the n-butyllithium initiation of isoprene in cyclohexane (36). The addition of secondary or tertiary organolithiums to ethylene only takes place in the presence of ethers or amines (68). The addition of a small amount of tetrahydrofuran has been shown to greatly increase the initiation

TABLE 2

Initiation Kinetics of Organolithium Species
In Hydrocarbon Solvents (155)

Initiator	Monomer	Solvent	$T^{\circ}(C)$	Reaction Order (RLi)	Ref.
n-C_4H_9Li	Styrene	Benzene	30	0.167	30
		Cyclohexane	50	1.0	33
	Butadiene	Cyclohexane	40	0.5 - 1.0	34
	Isoprene	Cyclohexane	30	0.5 - 1.0	35
s-C_4H_9Li	Styrene	Cyclohexane	50	1.0	33
	Butadiene	Cyclohexane	50	1.0	33
	Isoprene	Benzene	30	0.25	29
		Cyclohexane	50	1.0	33
			30	0.75	29
			25	0.66	36
		n-Hexane	30	0.7	37

reaction if n-butyllithium was used (69). This effect clearly demonstrates that initiation impurities and the nature of the solvent can alter the reaction kinetics.

Two mechanistic approaches have been suggested to explain these fractional orders in initiator concentrations. The first mechanism (31) suggests that the initial step is the dissociation of the associated complex:

$$(RLi)_n \xrightleftharpoons{K_e} n(RLi) \tag{13}$$

This is followed by reaction of the monomeric species with the vinyl monomer

$$RLi + M \xrightarrow{k_1} R-M \ Li \tag{14}$$

where

    n refers to the association number,

    X denotes the number of unassociated species, and

    M refers to the monomer.

This mechanism was based on the concept that only the unassociated species can initiate polymerization. Thus, if the equilibrium constant in equation (13) were small, the reaction rate would be proportional to $[(RLi)_n]^{1/n}$.

This mechanism suffers from several experimental as well as theoretical deficiencies. First, the experimental techniques used to determine the degree of association require very high concentrations of organolithiums as opposed to the lower amounts needed when used in actual polymerizations to prepare high molecular weight polymers.

Therefore, a direct comparison to actual polymerizations may not be possible.

The effect of the concentration of initiator and monomer on the reaction order was amplified by the following example. When Worsfold and Bywater (32) first proposed this mechanism, they based their ideas on results of the polymerization of styrene by n-butyllithium at $30^{\circ}C$ using a low ratio of styrene to initiator, i.e., about 10. Under these conditions, initiation rates were slow relative to propagation. Recently, it has been demonstrated (39) that polymer initiation rate constants were greatly increased when the monomer to initiator ratios are high, i.e. 100 to 1. This was implied indirectly by narrow molecular weight distribution of the resulting polymer.

Secondly, the early mechanism fails to take into account the presence of cross-associated complexes between the organolithium and the growing chain end. It has been shown by viscosity measurements that polyisoprenyllithium can form these cross-associated complexes with n-butyllithium (40) and sec-butyllithium (37). These complexes will certainly complicate the reaction kinetics. When 2,3-dimethyl-1,3-butadiene was initiated with n-butyllithium in hexane, the conversion versus time curves had a sigmoidal shape indicating an induction period. Also, the rate of propagation shows a negative order in organolithium concentration (70).

Morton, Pett and Fetters (41) report the association of polyisoprenyllithium with ethyllithium in n-hexane and propose the following equilibrium:

$$(R-M_nLi)_2 + (C_2H_5Li)_6 \rightleftharpoons 2[R-M_nLi \cdot (C_2H_5Li)_3] \qquad (15)$$
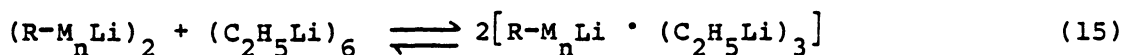
where the polyisoprenyllithium chain is given by RM_nLi. Equilibrium constants of 6.5 were determined for the formation of the cross-associated complex.

Lastly, Brown (42,43) has argued that the enthalpy change for the dissociation of, for example, n-butyllithium is too large to permit a sizeable concentration of unassociated species. He suggests instead that the monomer reacts directly with the associated complex. Several others (44,50) have since supported this claim and have demonstrated several ways in which this could result in fractional reaction orders.

It was quite clear that the initiation reaction of styrene and diene monomers via reaction with organolithiums is a complicated reaction and was highly dependent on reaction conditions. Despite these complexities, there were some general trends by which one can compare reactivities of initiators with styrene and diene monomers in hydrocarbon solvents. The decreasing order of reactivity of organolithiums for these monomers is as follows:

styrene: methyl > s-butyl > i-propyl > n-butyl and ethyl > t-butyl

dienes: methyl > s-butyl > i-propyl > t-butyl > n-butyl and ethyl

and the effect of solvent on reaction rate is given as:

toluene > benzene > n-hexane > cyclohexane.

However, even though toluene produces faster reaction rates, it may be a poor solvent choice (particularly at high temperatures) because of its ability to act as a chain transfer agent with organolithium species (49,50).

3. Propagation Kinetics of Dienes and Styrenes

The propagation kinetics of styrene and the 1,3-dienes initiated by organoalkali metals have been extensively studied using a variety of counter ions and solvents. In principle, the propagation reaction should again be a simple bimolecular reaction between the monomer and the growing chain. In most cases, this assumption was again found to be untrue. The reactions were first order in monomer concentration but generally a fractional order in the growing chain concentration. This again indicates association of the active chain ends.

In hydrocarbon solvents, the polystyryllithium chain ends do show association but the degree to which these anions are associated is still a debated question. It has been reported that if lithium (22,32,40,52,53) or sodium (51) was used as the counter ion, the chain ends were associated as dimers. For potassium counter ions (51), the degree of association reportedly can change from one at low concentrations to dimers at high dilutions. Cesium, the largest cation, apparently shows no association (51).

It appears that this association was largely electrostatic in nature such that as the cation becomes larger, these forces become weaker. Using a similar argument here as was used for the initiation step, Roovers and Bywater (38) postulated that only the monomeric active chain end can add additional monomer, which suggests some type of equilibrium between dimeric and the reactive monomeric species.

In the case of styrene polymerized in benzene, a one-half order dependence on the active chain concentration was found (32,40). Using viscosity measurements of the active chain ends, a degree of association

of two was determined. Then, assuming that only monomeric ion pairs can react with additional monomer, one-half order kinetics result (40,54,55).

The mechanism and the resulting kinetics for this polymerization were given by:

$$\frac{R_p}{[M]} \cong k_p K_e^{1/2} \, ([RM_nLi]_o/2)^{1/2} \qquad\qquad (16)$$

where

R_p was the rate of propagation,

[M] was the monomer concentration,

k_p was the propagation rate constant,

K_e was the dissociation constant for dimeric polystyryllithium chains, and

$[RM_nLi]_0$ was the concentration of polystyryllithium.
Morton (56) estimated the propagation rate constant by an indirect method which used viscosity measurements to determine the equilibrium constant for dissociation of the associated complex.

In stark contrast to the straightforward kinetics of the styrene system, the propagation kinetics of the diene monomers in hydrocarbon solvents were much more complicated. Initial kinetic studies of polyisoprenyllithium formation in hexane (57) and cyclohexane (35,57) indicate a fractional order of one-fourth. Some assumed this to indicate association complexes of four for the polyisoprenyllithium, if this was analogous to the polystyryllithium case. However, viscosity (41,54,55) and light scattering (54) experiments indicated that the polyisoprenyllithium was associated in pairs. This suggests that, as

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before, the fractional order kinetics cannot be directly related to the degree of association of the chain end.

Polymerizations of butadiene using organolithium initiators exhibit even more complicated propagation kinetics than isoprene. When propagation rates were measured in hexane (57) and cyclohexane (34), fractional orders of about one-sixth were obtained. Other studies (58) in benzene and hexane again show fractional orders, but vary from one-sixth to one-fourth, respectively.

If one uses the polystyryllithium analogy, the polybutadienyl-lithium should be associated as hexamers or tetramers. However, viscosity measurements (54) support an association number of two. Here again, no direct comparison of reaction order and association of the active chain ends can be made. Table 3 briefly summarizes reaction orders for monomer and chain ends in hydrocarbon solvents.

These kinetic studies clearly show that the initiation and propagation reactions have many unsolved mechanistic questions. These reactions are further complicated by the effect of counterions, concentrations of initiator and monomer and polymerization solvents, which further complicate attempts to elucidate these processes.

It appears that the relative strength or interaction between the carbanionic carbon and the corresponding positively charged metal has a large effect on reaction rates and stereochemistry of diene polymer. These initiators are effected by the type of counterion and polarity solvent.

TABLE 3

Propagation Rate Studies in Hydrocarbons (155)

Solvent	Initiator	[Initiator]	Order [M]	Order [I]	Ref.
		Styrene			
Benzene	$n\text{-}C_4H_9Li$	$10\text{-}3 - 10^{-1}$	2	0	59
		$<2 \times 10^{-2}$	1	1	60
		$>2 \times 10^{-2}$	variable	0	60
Cyclohexane	$n\text{-}C_4H_9Li$	$(5\text{-}100) \times 10^{-5}$	1	0.5	34
	$s\text{-}C_4H_9Li$	$(7\text{-}70) \times 10^{-4}$	1	0.5	33
		Isoprene			
n-Hexane	$n\text{-}C_4H_9Li$	$(5\text{-}100) \times 10^{-4}$	1	0.25	61
		$\text{-}16) \times 10^{-3}$	1-2	0	62
		$\text{-}140) \times 10^{-5}$	1	0.5	63
Cyclohexane	$n\text{-}C_4H_9Li$	$.6\text{-}6.5) \times 10^{-3}$	1	0.17	64
	$s\text{-}C_4H_9Li$	$(1.5\text{-}6.0) \times 10^{-2}$	1	0.5	33
		$.6\text{-}6.5) \times 10^{-3}$	1	0.17	64
		$(0.06\text{-}16) \times 10^{-3}$	1	0.25	35
Benzene	$n\text{-}C_4H_9Li$	$(1\text{-}10) \times 10^{-3}$	1-2	0	65
		$(3\text{-}35) \times 10^{-3}$	1	0.2-0.4	66
	$s\text{-}C_4H_9Li$	$(0.7\text{-}10) \times 10^{-3}$	1	0.5	67
		Butadiene			
n-Hexane	$n\text{-}C_4H_9Li$	$(0.9\text{-}12) \times 10^{-3}$	1	0.5	40
Cyclohexane	$s\text{-}C_4H_9Li$	$(0.7\text{-}15) \times 10^{-3}$	1	0.33	33
		$(1.5\text{-}60) \times 10^{-2}$	1	0.5	33

4. Cross-Associated Complexes

The possibility of cross-association between the growing chains and the initiator before all the initiator was consumed was often not addressed when discussing propagation kinetics. The cross-associated complexes could indeed alter the propagation as well as initiation kinetics.

Several qualitative observations have been made on the effect of mixtures of n-butyllithium and polyisoprenyllithium as measured by viscosity techniques (151). Similar effects were also observed for sec-(152) and t-butyl lithium (153). Morton (154) was able to quantify this cross-association phenomenon using ethyllithium and living polyisoprene. They found that the cross-association reaction was described by:

$$(PI-Li)_2 + (Et-Li)_6 \underset{\longleftarrow}{\overset{K_e}{\longrightarrow}} 2(PI-Li \cdot 3Et-Li) \qquad (17)$$
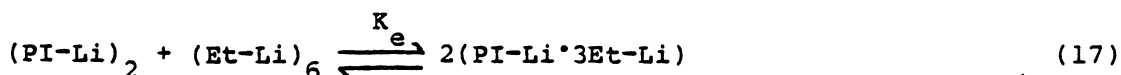
with an equilibrium constant of about 6, which was indicative of a strong tendency for cross association.

These results indicate that as initiation begins, the cross-associated complex, represented by (PI-Li·3Et-Li), can tie up significant quantities of initiator. This complex surely has a different initiation rate than the hexameric ethyllithium. This suggests that measurement of true initiation rate constants would be extremely difficult except at the very beginning of the reaction and that reported initiation rates should be only apparent rate constants.

5. Ion Pairs and Reactivity

Ion pairs can be considered to be of at least three different types and can be characterized by the relative distances between the anion

and the corresponding metal cation. The "separation" between the two is a function of the nature of the solvent, counter ion, and the reaction temperature. In polar media, the ions can have solvent molecules between them (solvent separated ion pairs) or can even be present as free ions as opposed to tight ion pairs that exist in nonpolar solvents. The concentrations of each type of ion pairs can be described by the following series of equilibrium:

$$A^- B^+ \rightleftharpoons A^- \,||\, B^+ \rightleftharpoons A^- + B^+ \qquad (18)$$
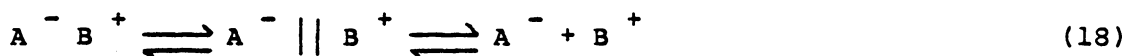
Actual evidence for the existence of the tight and solvent separated ion pairs was shown by Hogen-Esch and Smid (71). Investigations into the effect of temperature, counter ion, and solvent effects on the extent of solution of fluorenyl sodium suggested that the two ion pairs existed in equilibrium with each other as:

$$F^- Na^+ + nSol \rightleftharpoons F^- \,||\, Na^+ \qquad (19)$$

where n indicates the number of solvent molecules involved in the equilibrium.

Not only are solvent separated ion pairs formed in polar solvents, but to a lesser extent free ions are also present (generally concentrations of free ions are less than 1% (77) of the total active center concentration). These two species have shown very different reactivities (72,73,74,75); the order of reactivity was given as free ions > solvent separated ion pairs >>> tight ion pairs. Table 4 illustrates how increasing the solvating power of the solvent increases the rate of polymerization of styrene by sodium naphthalene at 25°C. This was thought to be due to the increased concentration of free ions and solvent separated ion pairs as the solvent polarity was measured and

TABLE 4

Solvent Effects on the Anionic Polymerization of Styrene (156)

Solvent	Dielectric Constant	Polymerization Rate k_p (liter/mole-sec)
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	5.5	550
1,2 Dimethoxyethane	7.6	3800

to a lesser extent on the degree to which the ions can dissociate.

Propagation rates were also highly dependent on the nature of the counter ion. Table 5 clearly indicates that the reactivity of the living chain end increased with increasing size of the cation for polystyrene in dioxane at 25°C using the same initiator system. The major factor that influenced the reactivity of the ion pair with changing counterion in the same solvent was its ability to dissociate.

The electronic environment at the anionic site can also influence the tight ion pair/solvent separated ion pair equilibrium. For example, the fluorenyl salts discussed earlier have extensive delocalization of the electron pair which facilitates the formation of solvent separated ion pairs.

There were also studies which suggest that temperature can shift the tight ion pair/solvent separated ion pair equilibrium. One example of this was studies of sodium naphthalene in THF which was well known to have different solvating power at different temperatures. At 25°C, only one absorption peak was observed in the UV/Visible spectrum, indicating the presence of tight ion pairs. At -40°C, two distinct peaks were observed while at -70°C one peak was again observed but at longer wavelengths. This indicates a change to solvent separated ion pairs as the temperature was lowered (71). Conductance studies of radical anion salts in ether solutions confirm the existence of both types of ion pairs in these systems (81).

With all the different ion paired species present, each with different reactivities, it quickly becomes apparent that the observed rate constant was actually a function of each species' concentration and

TABLE 5

Effect of Counterion on Polymerization Rate Constant

of Polystyrene at 25°C (156)

Counterion	a(77)	k_p ($M^{-1}sec^{-1}$) b(78)	b(79)
Li^+	0.9		
Na^+	3.4	3-5	6.5
K^+	20		28
Rb^+	21.5		345
Cs^+	24.5		15

a) Capillary flow technique.
b) Solution dilatometry technique.

the actual bimolecular rate constants for each species. The apparent

bimolecular rate constant, k_{app}, was given as:

$$k_{app} = (1-\gamma)k_{\pm} + \gamma k_{-} \tag{20}$$

where γ was the mole fraction of free ions, and $k_{\pm}$ and k_{-} are the actual

bimolecular rate constants for ion pairs and free ions, respectively.

From the equilibrium:

$$A^{-} // B^{+} \underset{\xrightarrow{\hspace{1cm}}}{\overset{K_{diss}}{\rightleftharpoons}} A^{-} + B^{+} \tag{21}$$

the mole fraction, γ, was given as:

$$\gamma^{2}[M^{-}]/(1-\gamma) = K_{diss} \tag{22}$$

where $[M^{-}]$ was the concentration of active chain ends. In these

studies, equation (20) $\gamma^{2}[M^{-}] = K_{diss}$ was valid and equation (20)

reduces to the linear expression

$$k_{app} = k_{\pm} + \frac{(k_{-} - k_{\pm})K_{diss}^{1/2}}{[M^{-}]^{1/2}} \tag{23}$$

If the apparent rate constant was plotted versus $[M^{-}]^{-1/2}$, a

straight line results with the intercept being equal to $k_{\pm}$ and the slope

being equal to the term $(k_{-} - k_{\pm})K_{diss}^{1/2}$. The value of K_{diss} can be

determined by either conductivity measurements or other techniques.

From conductivity measurements, the dissociation constants for lithium,

sodium, potassium, rubidium, and cesium are 2.2×10^{-7}, 1.5×10^{-7},

0.8×10^{-7}, 0.1×10^{-7}, and 0.02×10^{-7}, respectively (82,83,84). The

propagation rate constant for free ions alone can now be calculated.

From this simple graphical method, it was possible to separate the

individual rate contributions for the different types of ion pairs from

the total apparent rate constant. Table 6 summarizes the individual

TABLE 6

Individual Rate Constants for Styrene Polymerization at 25°C (156)

| Gegenion | Polymerizations in THF | | | In Dioxane |
	k_p (ℓ/mole sec)	$K \times 10^7$ (m/ℓ)	k_p (free)	k_p
Li^+	160	2.2		0.94
Na^+	80	1.5		3.4
K^+	60-80	1.8	6.5×10^4	19.8
Rb^+	50-80	0.1		21.5
Cs^+	22	0.02		24.5

rate constants for the polymerization of styrene in THF and dioxane with a variety of counterions (75,79) where k_p refers to the propagation rate constant for the ion pair and k_p(free) refers to the rate constant for free ions alone.

It appears from this table that regardless of the nature of the etheral solvent that was used, the reactivities of the free ions were relatively unchanged. However, this was not the case for the rate constant for the ion pairs. These rate constants vary by as much as three orders of magnitude depending on the counter ion.

The solvent has a much larger effect on the propagation rate constant for the ion pairs than the counterion. It now appears that in addition to the dielectric constant of the solvent, the ability of the solvent to complex with the chain end presumably by coordinating with the cation played an important role. Table 7 illustrates the dramatic solvent effect on the propagation rate of the ion pair.

To summarize the data in Tables 6 and 7, it was shown that the solvent and counter ion both can effect the propagation kinetics of the ion pairs with the solvent showing the more pronounced effect due to the increased dissociation of the ion pair structure. In addition, in solvents of low solvating ability, propagation rates increase as the counter ion becomes more electropositive because of a similar argument. However, the reverse order was observed in solvating media. More reactive solvent-separated ion-pairs were formed more readily with the more electropositive cations because of the stronger interaction of the ether with the cation resulted in rate increases.

TABLE 7

Ion Pair Propagation Rate Constants (ℓ/mol$\cdot$sec)

for Polystyrene Salts at -25°C (155)

Solvent	Li^+	Na^+	K^+	Rb^+	Cs^+	References
Dioxane	0.94	3.4	20	21.5	24.6	79
THF	<10	14	73	83	53	80,157
THP (pyran)	160	80	~66	~55	22	74,75
Dimethoxyethane	—	3600	--	--	—	87

6. Mixed Solvent Polymerizations

Surprisingly little study has been given to the propagation kinetics in nonpolar solvents that contain small amounts of ethers and amines. An early attempt at studying these mixed systems by Bywater and Worsfold (88) focused on the influence of added THF on the polymerization of styrene in benzene. When the ratio of THF to active chain ends was small, rate enhancements were observed. When this ratio was increased above 10 to 1, the reaction rate declined markedly. Two reactive complexes were proposed as being involved in this process. Both a relatively reactive monoetherate and a less reactive dietherate were thought to be present at the higher concentrations of THF. However, no confirmation of this suggestion has been published.

The influence of THF, diphenyl ether, and anisole on the polystyryllithium chain ends in benzene has been studied using viscosity measurements (54,89). These additives have been shown to dissociate the complexes. The degree of association decreases from two in hydrocarbon solvents to one in the presence of excess THF. Assuming an equilibrium condition was established between the dimeric active chain end and the polar additive with the monoetherate, the equilibrium constant would be a measure of the extent of deaggregation. A reactivity scale can be established (89) as THF >> anisole > diphenyl ether, if all of the THF was converted to the monoetheral adduct. It now appears that the extent to which ether can complex with the active chain end greatly effects the ion pairs' reactivity toward propagation (55,88). In addition, if

larger amounts were added, less reactive complexes were formed, leading
to slower propagation rates.

Tertiary amines have also been shown to effect the rate and
reaction order of vinyl polymerizations. Langer (90) discovered that
alkyllithiums will polymerize ethylene to high molecular weight in the
presence of the bidentate ligand N,N,N',N'-tetramethylethylenediamine
(TMEDA) and proposed that the lithium chain end has the chelated
structure:
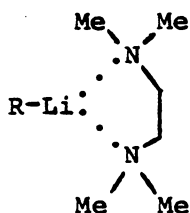
Helary and Fontanille (91) studied the polymerization of styrene by
alkyllithiums in the presence of TMEDA. In the absence of the polar
modifier, the propagation reaction showed a reaction order of one half
for active chain concentration but when TMEDA was added in a one to one
ratio to lithium, first order kinetics resulted.

The addition of TMEDA has also shown rate enhancement in some cases
(92) and slower rates in others (91,93) for isoprene polymerizations.
As in the styrene case, the change in the rate depends on the
concentration of the chain end relative to the amount of added TMEDA.

From studies conducted by Davidjan, et al. (94), a series of
equilibrium expressions were postulated for the complexation of TMEDA
with the chain end. This scheme suggests that several active species
can be polymerization sites. They concluded that some species were more

reactive than others, the uncomplexed, nonaggragated organolithium being more reactive than the organolithium/TMEDA complex.

UV/Visible spectroscopy has been used to distinguish between the different types of ion pairs and changes in aggragation. The absorption maximum for polyisoprenyllithium in hexane (95) shows a shift to higher wavelengths from 270 to 272 nm as the concentration was raised, but at lower concentrations, a shoulder was also observed at about 315 to 320 nm. This was attributed to the dissociation of tetrameric aggragates into dimeric species at low concentrations.

Similar shifts in the peak absorption maxima were also observed when polar modifiers were added in hydrocarbon solvents. Helary and Fontanille (96) have studied the effect of an added tertiary amine, tetramethyltraazocyclotetradecane (TMTA), on the propagation of polystyryllithium at 20°C in cyclohexane. When the ratio of added TMTA to lithium was unity, the absorbance maximum shifts from 326 nm for polystyryllithium alone to 345 nm. This indicates an increase in solvation, which increases the interionic separation.

A systematic investigation into the energetics of interaction between the polar additive and active chain ends were undertaken (97-100). The enthalpies of interaction were determined for a variety of additives as a function of the ratio of the base to active chain end concentrations (R). Using dilute solution calorimetry, the entropic solvation effect gives information on the nature of the coordination process between the base and the chain end.

The enthalpies of interaction between these Lewis bases and the active chain end were measured for a variety of alkyllithiums in

hydrocarbon solvents at 25°C and for ratios of the Lewis base to lithium concentrations of less than 0.08. This allows one to define an order of basicity based on these enthalpic interactions for each alkyllithium. Surprisingly, every alkyllithium showed the same basicity order. These results are unexpected because both hexameric and tetrameric aggregates of alkyllithiums were examined.

The basicity order was found to the THF > 2-methyl tetrahydrofuran > diethyl ether > triethylamine (99). These authors suggest that the lack of dependence of association number on the order of basicity suggests that this was in fact a fundamental property of these interactions. However, the effect of different degrees of association of the final complex or of possible metallating side reactions was not addressed. Table 8 summarizes these results (97-99).

As mentioned earlier, bidentate ligands such as TMEDA can effectively coordinate to alkyllithiums and can result in increased rates of polymerization. Calorimetry results quantitatively confirmed this assumption as the enthalpic interaction of TMEDA with n-butyllithium was 9.1 kcal/mole while THF was only 7.5 kcal/mole.

The enthalpic interaction of Lewis bases with polymeric organolithiums have also been determined using the calorimetry. Basicity order for a variety of polar additives to, for example, polystyryllithium, was very similar to that obtained for the alkyllithiums, namely TMEDA > THF > Et_2O ~ $N(Et)_3$ (101,102).

One interesting observation was that the entropies of interaction between bases and polystyryllithium was less than those with alkylithiums. This may be due in part to the fact polystyryllithium was

TABLE 8

Enthalpic Interactions of Bases with Alkyllithiums

at 25°C in Hexane (97-99)

Base	ΔH (Kcal/mole)[a]
THF	7.5 (0.07)[b]
Diglyme	6.5 (0.06)
Diethyl ether	1.8 (0.06)
Triethylamine	1.7 (0.06)
TMEDA	10.3 (0.04)

[a] 0.08 M n-C_4H_9Li in hexane

[b] [Base]/[Li] ratio

less associated (dimers) than alkyllithiums (tetramers or hexamers) and hence was less hindered. These results are presented in Table 9.

7. Microstructural Changes in Diene Polymerizations

The anionic polymerization of 1,3 dienes has received detailed study primarily due to the dramatic influence of reaction variables on the stereochemistry of the polymer that was formed. The gegenion, reaction temperature, solvent, and even the concentration of organometallic initiators can influence the microstructure of the polymer backbone. Because of the large amount of data generat d on this subject it was difficult to compare results from many sources. However, it was clear that changing any one of these reaction variables can change the amounts of 1,4- and 1,2- (or 3,4-) addition products.

As mentioned earlier, the 1,4- content of diene homopolymers should be kept as high as possible, because this results in the lowest glass transition temperature. Increasing the vinyl content raises the T_g which was often undesirable. Figure 1 shows the effect of 1,2- content on the T_g polybutadiene (164).

Butadiene, the lowest homolog of the conjugated dienes, has been polymerized by every alkali metal and its corresponding organic alkylated derivatives. In hydrocarbon media it was apparent that the alkali metal used has an effect on the resulting polybutadiene microstructure. In addition, as the polarity of the solvent was increased, dramatic effects were also observed.

In general, results indicate (103) that the use of lithium metal gives the highest overall 1,4- content polybutadiene while the use of any of the remaining alkali metals result in increasing 1,2- content as

TABLE 9

Enthalpic Interactions of Bases with Polystyryllithium[a]

at 25°C in Benzene (101-102)

Base	ΔH[b]
TMEDA	13.3
THF	9.8
Diethyl ether	0.3
Triethylamine	0.3

[a] $M_n \sim 4 \times 10^3$

[b] [Base]/[Li] ratio 0.02
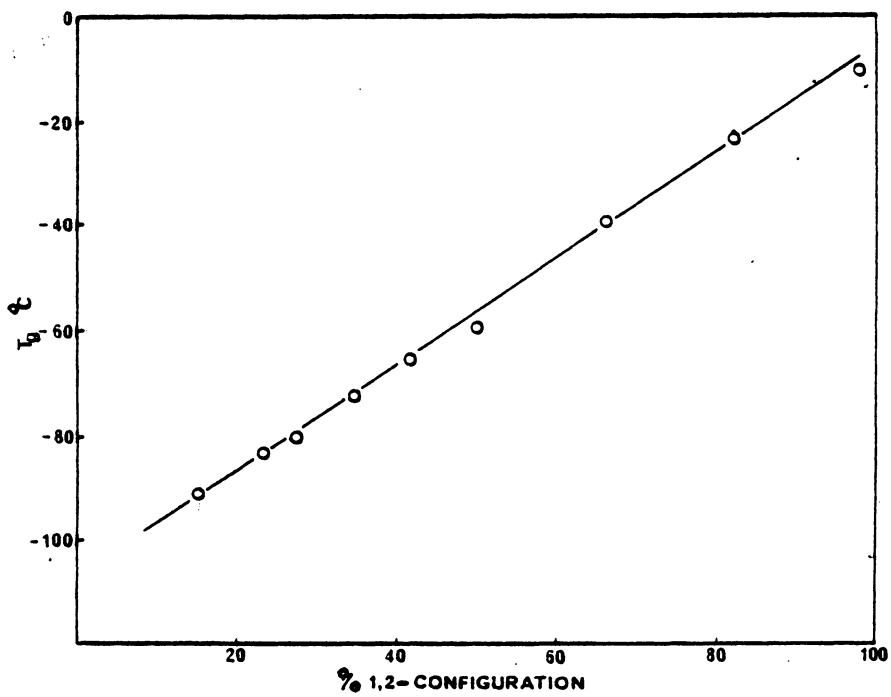
Figure 1. Relationship of Glass Transition Temperature to Percent 1,2-
Configuration in Polybutadiene (164).

the size of the metal and covalent nature of the carbon-metal bond was

increased. Similar trends were observed in solvating media such as

ethers where higher 1,2-polybutadiene content results with increasing

cation size (104). Table 10 illustrates this trend for results of

polybutadiene microstructure polymerized at $0°C$ when the counterion was

changed and in solvents with different dielectric constants.The more

pronounced effect on microstructure was observed when the solvent

polarity was changed. In general, the highest amount of 1,4- addition

was obtained when using very nonpolar solvents, or no solvent at all.

Increasing the polarity of the solvent and lowering $\bar{M}_n$ leads to

increased vinyl content. Table 11 shows this stereochemical effect on

the microstructure for polybutadiene.

Similar results were observed for isoprene polymerizations (105)

when the solvent polarity was changed; namely, 1,4- content was

maximized in non-polar media and vinyl content was high in polar

solvents. One difference with the polymerization of isoprene was that

vinyl content results from addition across the 3,4- double bond. In

most cases, little or no 1,2- addition was observed because of the

increased electron density and increased steric bulk at this site.

The spectra of living polymerization solutions have been examined

as a means of elucidating the mechanism of the polymerization. These

methods include UV/Visible spectroscopy and NMR and have given

information about the nature of the anion and the corresponding cation

of living polydienes.

Absorption spectra of polydienyllithiums were highly dependent on

the solvent and on the concentration of the anions. At relatively high

TABLE 10

Effect of Counterion and Solvent on Polybutadiene Microstructure (156)

Solvent	Alkali Metal Initiator	cis-1,4	trans-1,4	1,2-
Pentane (0°C)	Li	35	52	13
	Na	10	25	65
	K	15	40	45
	Rb	7	31	62
	Cs	6	35	59
THF (-78°C)	Li-naphthalene	0	4	96
	Na-naphthalene	0	9	91
	K-naphthalene	0	18	82
	Rb-naphthalene	0	25	75
	Cs-naphthalene	0	25	75

TABLE 11

Microstructure of Polybutadiene Initiated with Organolithiums (135,158)

Solvent	trans-1,4-	cis-1,4-	1,2-
Hexane	39	52	9
Cyclohexane	⊣	⊦ 90*	10
Benzene	52	36	12
THF		13	87
TEA	⊣	⊦ 52*	48

* total 1,4- content (cis and trans)

concentrations (10^{-3} M), the peak absorbance of polyisoprenyllithium appears at 272 nm but increases to 275 nm at low concentrations (10^{-6} M). In addition, a shoulder appears at 315 to 320 nm (95). These spectral changes were interpreted as resulting from the dissociation of tetramers to dimers at the lower concentrations. Butadiene polymerizations in THF with lithium and sodium (151) showed two absorption peaks, one at 285 nm and another at 325 nm and the absorption of each changed with temperature. It was reported that the absorption at lower wavelengths was due to the cis form of the active chain end and the other was due to the trans form. Similar results were observed in isoprene polymerizations (154).

8. Mechanism of Diene Polymerizations

One mechanism used to describe these results has been suggested from ^{1}H NMR studies on model compounds. Worsfold and Bywater (106) have proposed a propagation mechanism involving unassociated chain ends which was kinetically controlled. The kinetic study showed that >90% of the chain ends were in the cis configuration. Isomerization to the trans configuration may take place and was thought to result in the trans-1,4-alkene structures present in the polymer backbone.

There is more "competition" for monomer units at high concentrations of active organolithium species. Thus, the average time between each successive addition of monomer was longer which allows for a greater degree of relaxation and hence a greater likelihood of the trans configuration. Conversely, at low chain end concentrations (high [M]/[I]), isomerization was less likely and results in increased cis configuration was observed.

Further studies on active polydiene chain ends in hydrocarbon solvents have shown "4,1 covalent polybutadienyllithiums". Morton and coworkers (107-110) have proposed the mechanism shown in Figure 2. This mechanistic scheme shows the polybutadienyllithium chain end as an example and was used to account for the effect of solvent on chain microstructure.

The 1,4- microstructure was visualized as being formed by a four-center interaction between the incoming monomer unit and the δ bonded carbon-lithium bond. The 1,2- addition results from the incoming monomer unit reacting with the γ-carbon which was π-bonded to the lithium ion. When the majority of solvent was hydrocarbon and a polar modifier was added, increased 1,2 content was observed. Weaker complexing agents such as ethers and triethylamine have to be added in substantial concentrations relative to active chain ends before increased 1,2- content was observed. On the other hand, addition of powerful chelating agents such as TMEDA results in predominately 1,2- addition, even at low concentrations relative to the active chain end concentration.

According to the above mechanism, this would suggest that as the polarity of the solvent was increased, the more delocalized structure was favored and 1,2- addition increases. The solvation by the polar modifier also increased the ionic character of the anionic chain end, making it more reactive and substantial increases in polymerization rates were observed. Halasa, et al. (111) reported the preparation of structurally pure 1,2- polybutadiene with n-butyllithium which has been modified with 1,2- dipiperidinoethane (dipip) as the initiator.
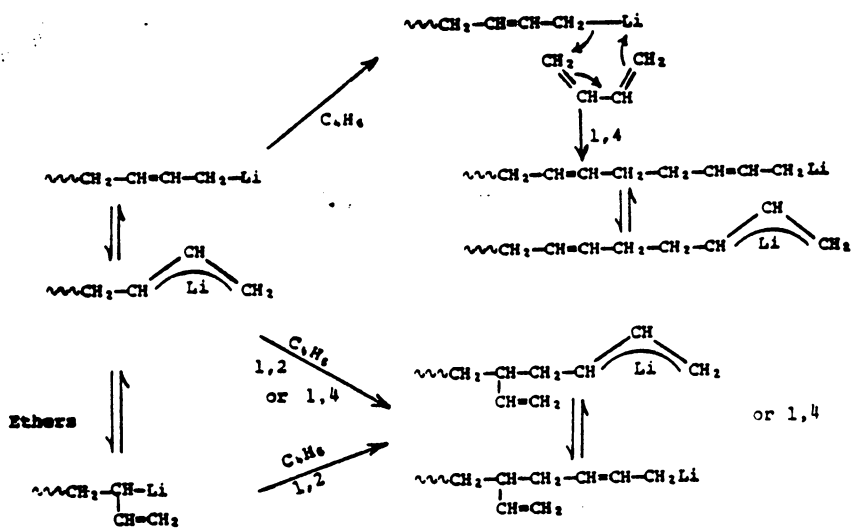
Figure 2: Mechanism of Addition of Butadiene to Polybutadienyllithium (106)

Substantial rate increases were also observed (112) with increasing

dipip concentrations. Also, the faster the polymerization rate, the

higher the 1,2- content produced in the polymer backbone.

One other curious result was that increasing the temperature

reduces the amount of 1,2- addition. This effect was most evident when

the base to initiator ratio was low. This was explained by the

increased dissociation of the base-lithium complex with increasing

temperature.

A mechanism involving complexation with the lithium and the anionic

chain end has been proposed (111). The first step in this mechanism was

the complexation of the dipip with the chain end. This assumption has

been supported by NMR studies on model compounds (112). The next step

was the complexation of one of the double bonds of, for example,

butadiene to the lithium. The third step was the insertion of the two

carbons of the complexed double bond between the carbon-lithium bond.

This process was then repeated for each addition of monomer. The

complete process is shown in Figure 3.

This profound effect of increasing temperature in decreasing 1,2-

content was explained by the fact that as the temperature was increased,

the lithium-dipip complex dissociates, thus allowing a somewhat

increased 1,4- addition, as would be expected in hydrocarbon structure.

This temperature effect was also seen for some of the weaker complexing

polar additives. This suggests that even for the weaker polar

additives, some type of complexation may be taking place, rather than

separation of the ion pairs alone. Table 12 summarizes these results,

in addition to those results obtained using other polar modifiers.
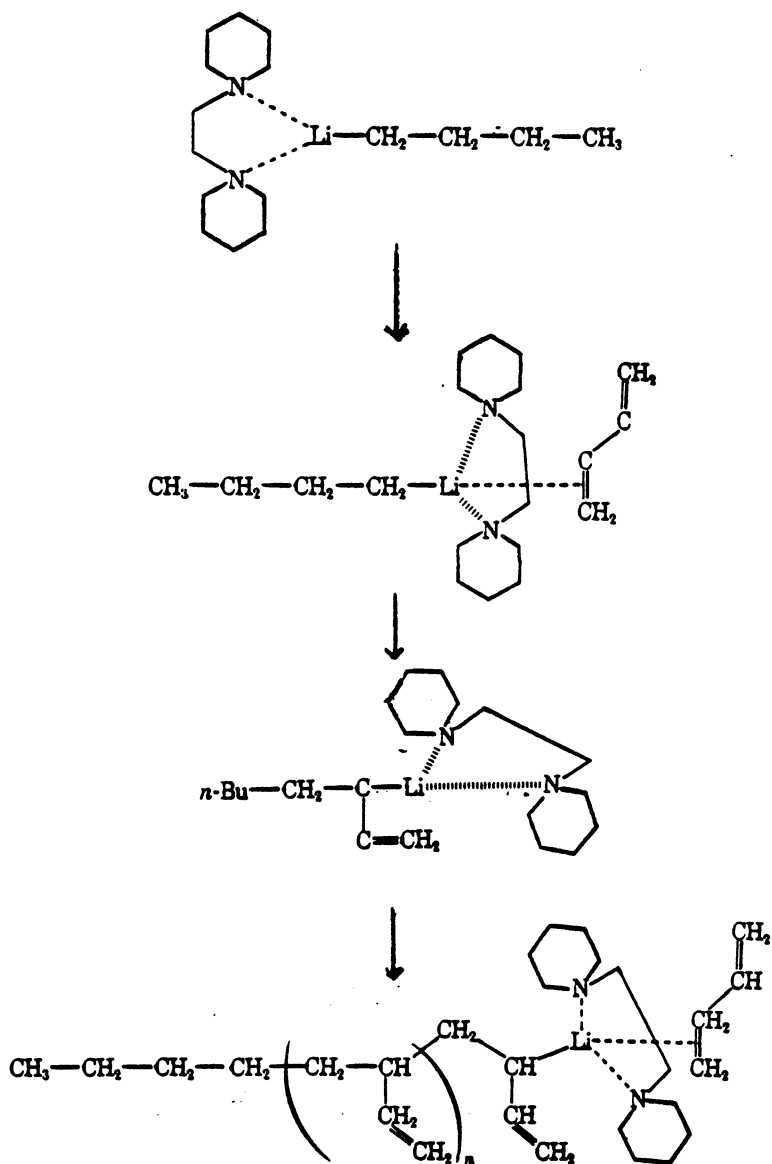
Figure 3:   Propagation Mechanism of Butadiene with
            Dipiperidinoethane (111)

TABLE 12

Effect of Polar Additives on Polybutadiene

Microstructure in Hexane Solvent (158)

Base	Base/Initiator (R)	% 1,2- content		
		30°C	50°C	70°C
Triethylamine	270	37	33	25
Ether	96	36	26	23
	12	22	14	14
THF	5	44	25	20
	85	36	26	23
TMEDA	1.14	76	61	46
*Dipip	1	99	68	31
	10	99	85	84

*1,2- dipiperidinoethane

B. Block Copolymer Preparation

1. Introduction

Because of the living nature of polymeric lithium, it is now possible to design and control polymer architecture such that component segments or blocks can be sequentially formed. These blocky systems can be prepared using anionic initiators. This allows one to prepare each block with a well-defined molecular weight and narrow molecular weight distribution in the absence of any termination. The front block of, for example, polybutadiene, can be formed initially. Then, a second monomer such as styrene can be added and polymerized to form the second block of polystyrene.

Three basic linear architectures can be produced using this technique and are shown schematically in Figure 4 (113). The simplest version described earlier consists of a diblock structure composed of a number of polymerized units of monomer A chemically bonded to a number of polymerized units of monomer B. A logical extension of this was a triblock structure consisting of a long segment of B monomer units placed between two segments of A monomer units. A third type block copolymer consists of multiple blocks which contain many alternating blocks of A and B monomer units.

The ABA type block copolymers have shown the most interesting properties of these three basic types. Moreover, new elastomeric materials with thermoplastic characteristics, termed thermoplastic elastomers were prepared. These materials exhibited properties similar to those of crosslinked materials at room temperature, yet were moldable at elevated temperatures (114).

A. Diblock Copolymer

AAAAAAAA-BBBBBBB

B. Triblock Copolymer

AAAAAAA-BBBBBBBBBB-AAAAAAA

C. Multiblock Copolymer

(-AAAA-BBBB-AAA-BB-AAAAAA-BBBB-AA-)n

Figure 4: Three Basic Linear Architectures for Block Copolymers (113)

The synthesis of well-defined block copolymers of this type was made possible through the use of homogeneous, termination free anionic polymerization initiated by organolithiums. The preparation of these well-defined A-B-A type block copolymers can be achieved by three different methods: 1) a three stage process using a monofunctional initiator, 2) a two stage process using a monofunctional initiator to form a diblock, followed by coupling of two diblocks together using a difunctional coupling agent, and 3) a two stage process using a difunctional initiator which polymerizes the center block first followed by the two end blocks at the same time.

2. Monofunctional Initiators

The method of successive formation of the three blocks requires high purity conditions and results in some difficulty in terms of obtaining a monodisperse third block (113). The most widely used commercial process for the synthesis of styrene-butadiene-styrene (Kraton) and styrene-isoprene-styrene (Cariflex) triblocks apparently uses a coupling agent (115). One of the problems with the linking procedure was that linking of the diblocks was not quantitative; this results in loss of mechanical properties (116) due to small amount of diblock contamination. Neither of these methods can be used if the first block (such as polylactone or polyacrylate) does not initiate the second monomer (for example, dienes) or if the first block has a low ceiling temperature.

3. Difunctional Initiators

The use of a difunctional initiator has some decided advantages over the other two methods. Firstly, triblock copolymers can be

prepared in only two steps by growing the polymer chains from the "inside out". The first addition of monomer forms the center block. Then, following the addition of a second monomer, the two end blocks can be prepared at the same time.

Secondly, low molecular weight prepolymers having functional groups only at the chain ends may be prepared. For example, if hydroxyl groups are located only at the chain ends, these materials can be used as soft segments for the preparation of linear polyurethanes. Lastly, new classes of thermoplastic elastomers can be prepared if, after the first polymerization step, the living anion is a strong enough base to initiate a polar monomer such as methyl methacrylate.

Several criteria are required of a difunctional initiator that have further hampered development in this area. First, the initiator should be soluble in hydrocarbon solvents. This was often difficult to achieve when there are two ionic groups on one small molecule. Secondly, functionality must remain exactly 2.0. Otherwise, monofunctional or polyfunctional species may be present which are often undesirable. Unfortunately, many previous systems have failed to meet these criteria.

As an example, dithioalkanes such as dithiobutane have been used as initiators. Shortcomings of these compounds are insolubility in hydrocarbon solvents (117) and the loss of difunctionality. This leads to monofunctional impurities that generate diblock impurities and loss of desirable physical properties.

Several difunctional alkyllithium initiators have been prepared in homogeneous solutions using polar solvents such as THF and diethyl ether (118,119). From an earlier discussion, this results in reduced 1,4-

content polybutadiene and undesirably increasing the glass transition temperatures for the diene block.

One method of preparing difunctional initiators was by coupling of two radical anions. An early example of this coupling procedure was shown by Fetters and Morton (120) who prepared dimers of 1,1-diphenylethylene in hydrocarbon solvents modified with 5% to 50% anisole and using lithium metal as the catalyst (121). A similar process studied by Setzhorn (122) was used to prepare oligomers of α-methylstyrene using toluene as a solvent at high temperatures. Unfortunately, difunctionality was not demonstrated and problems may have resulted from chain transfer processes with the solvent.

A series of commercialized difunctional initiators were prepared by dimerization of radical anions of diene monomers to increase solubility. The initial compounds were prepared in dimethyl ether but were also available in mixtures of benzene and dimethyl ether (123). Later versions containing aromatic moieties have been synthesized. Unfortunately, a distribution of mono-, di-, and trifunctional species were generated. Degradation also resulted and erratic polymerization results have been obtained (124).

Difunctional isoprenyllithium has also been prepared via a coupling reaction in nonpolar solvents without addition of polar additives (125). Again, precise control of molecular weights was not possible (126).

A second method of synthesizing difunctional organolithium reagents was by the addition of a monofunctional organolithium such as sec-butyl lithium to a compound which contains two reactive double bonds. The divinyl compound should have the reactive double bond not in conjugation

with the other, so that they react independently, and are of equal
reactivity. In addition, these systems should have a high ceiling
temperature to avoid oligomerization and loss of difunctionality.

The use of 1,3- divinylbenzene as a possible precursor was first
patented by Morrison and Kamienski (127) and further studied by Lutz
(128) and Popov (129). Unfortunately, this compound will easily
polymerize, which led to functionalities of greater than two.

Sigwalt and coworkers (130,131) describe the use of the dilithium
initiators formed from the reaction of butyllithium with bis(p-
isopropenylphenyl) alkanes or 2,(n-1)-diphenyl-alkadienes shown below.

$$C_4H_9CH_2\text{-}\overset{\overset{\displaystyle Li^+}{\cdot\cdot}}{\underset{\bigcirc}{C}}\text{-}(CH_2)_8\text{-}\overset{\overset{\displaystyle Li^+}{\cdot\cdot}}{\underset{\bigcirc}{C}}\text{-}CH_2C_4H_9$$
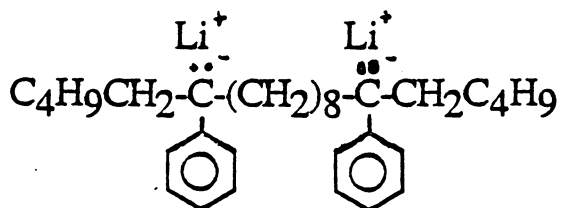
These initiators were formed in nonpolar solvents without polar
additives. Two drawbacks of the above system were: first, this
compound precipitates from hexane after three days at room temperature
and secondly, the synthesis of starting materials was difficult.

Another precursor, m-di-isopropenyl benzene (DIB), has been reacted
with alkyllithiums to form a soluble difunctional initiator. Foss and
coworkers (132) report that the product of the reaction of DIB with sec-
butyllithium in the presence of a small amount of triethylamine followed
by reaction with isoprene improved solubility in hydrocarbon solvents
and also increased the reaction rate. However, the polydispersity of
the resulting polyisoprene was relatively broad (Mw/Mn = 1.3). The

presence of higher concentrations of the amine tended to form

trifunctional species and reduced 1,4- addition of the diene.

Cameron, et al. (133), have also reported the reaction of DIB with

butyllithium in benzene or cyclohexane. At moderate or elevated

temperatures, purely difunctional species did not result, but rather a

mixture of di- and polyfunctional products was observed. Even in the

presence of tertiary amines, the products were similar. They concluded

that the use of this system as a difunctional initiator was suspect.

Surprisingly, Lutz, et al. (134), reached a completely different

conclusion for this system. They state that in benzene solution, a

difunctional initiator was formed without added polar modifiers. Also,

polymerization of styrene and isoprene was achieved. However, a mixture

of mono-, di-, and trifunctional species were observed from GPC results

and an excess of sec-butyllithium was added to increase yields of

difunctional species. This did present problems due to unreacted sec-

butyllithium that was also present and precipitation occurred.

In a series of papers, Sigwalt et al. (134,139), describe the

synthesis of divinyl compounds

$$CH_2=C-(CH_2)_n-C=CH_2$$

and

$$CH_2=C-\langle O \rangle-(CH_2)-\langle O \rangle-C=CH_2$$

with CH_3 groups
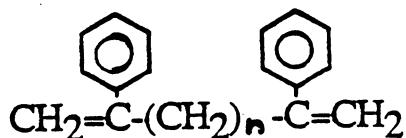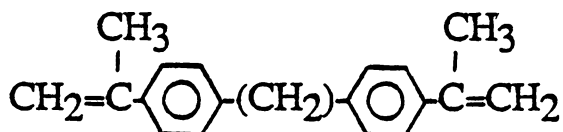
which will react with sec-, or t-butyllithium to form a dilithium

initiator. This initiator was then used to prepare triblock copolymers of styrene-isoprene-styrene and styrene-butadiene-styrene. Mechanical properties of these copolymers seem to be comparable to those for Kraton standards. Problems with this system were again, insolubility in hydrocarbon solvents even at low concentrations. In addition, an excess of butyllithium was used to increase the addition, the rate of which unfortunately resulted in diblock contamination. When a stoichiometric amount was used, the reaction was not complete even after one week at room temperature.

Tung and coworkers (136-138) reported the use of difunctional initiators based on "double 1,1-diphenylethylenes" of the following structure where R can be a variety of moieties such as p-phenyl, biphenyl, p,p-biphenyl ether, and m-phenyl. These divinyl compounds when reacted with sec-butyllithium produce a hexane insoluble but cyclohexane soluble dilithium initiator which can be used for block copolymer synthesis.

Hocker and Lattermann (139,140) studied the use of 1,3- and 1,4-bis(α-phenylethenyl)benzene (R = p-phenyl and m-phenyl in the following structure) in polycombination electron transfer reactions to form

$$
\begin{array}{cc}
CH_2 & CH_2 \\
\| & \| \\
\langle\bigcirc\rangle\text{-C-(R)-C-}\langle\bigcirc\rangle
\end{array}
$$
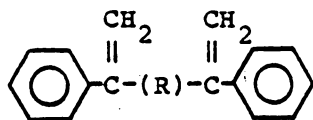
multifunctional lithium species. These compounds do not homopolymerize under normal anionic conditions. They also found (141) that the meta isomer will quantitatively react with sec-butyllithium to form a

hydrocarbon soluble dilithium initiator which was suitable for polymerizations of diene monomers.

One very comprehensive study (159) evaluated a variety of difunctional initiators in terms of several criteria. These included the ease of formation based on the reaction of sec-butyllithium with the diolefins, solubility in hydrocarbon solvents, initiation rate, and cost. They concluded that 1,4-bis(4-(1-phenylvinyl)phenyl)butane was the most suited for diene polymerizations.

Living difunctional polybutadiene was prepared using 1,3-bis(α-phenylethenyl)benzene (160), then functionally terminated with episulfide to form mercaptan end groups. This was then copolymerized with a second monomer under free radical conditions to form novel triblock copolymers.

One interesting application of these highly conjugated dienes was not as an initiator, but as linking agents for monofunctional living polymers. Nuffer (161) used 4,4'bis(1-phenylvinyl)-1,1'-biphenyl as a linking agent for polystyrylbarium in THF. They also found that the second double bond reacted quite slowly relative to the first. Quirk (162) was able to use the 1,3-substituted bis(α-phenylethenyl)benzene to couple polystyryllithium and poly(styrene-b-isoprenyl)lithium to produce star branched copolymers.

III. INTRODUCTION TO RESEARCH

A. Fundamental Studies

The fundamental aspects of this study have focused on studying the kinetics of formation of a difunctional initiator. The actual initiator was formed by the addition of two equivalents of sec-butyllithium to one equivalent of 1,3-bis(α-phenylethenyl)benzene, using cyclohexane as the solvent.

The dilithium species has a high extinction coefficient in the visible region. This feature made it possible to work at concentrations that were typically used to make high molecular weight polymers (i.e., 10^{-3} moles per 500 ml of solvent). Fortunately, the starting diene was transparent in the visible region, but strongly absorbs in the ultraviolet region. Thus, this reaction was easily followed by UV/Visible spectroscopy.

The experimental techniques used to prepare the samples for analysis required the rigorous purification of all reagents as well as the use of high vacuum techniques (10^{-6} torr) and all-glass reactors. The glass reactor was equipped with a quartz cell at the top. While maintaining a constant temperature, the two reagents were thoroughly mixed in the solvent to start the reaction and a series of spectra were recorded as a function of reaction time by simply turning the reactor upside down and placing it in the spectrophotometer.

Unfortunately, the spectroscopic method of following this reaction was limited, since not all the components concentrations of interest could be determined independently. For example, the monoaddition product (where sec-butyllithium was added to only one double bond)

adsorbs at the same wavelength as the diadduct (both double bonds reacted). One method of analyzing for all three components (including the unreacted diene) in the initiator solution was by gas chromatography. All components were easily separated from one another using a standard packed column and a thermal conductivity detector. For this analysis, a high pressure nitrogen reactor was used and samples were taken from the reactor with time. This analysis method also had two major drawbacks. First, concentrated initiator solutions were needed because of poor detector response. Secondly, extensive sample handling was required before a sample was analyzed, which increased the likelihood of termination.

With the acquisition of a capillary gas chromatograph, these problems were solved. This type of system and a flame ionization detector allowed enhanced sensitivities to be realized. Low concentrations of initiator (10^{-3} M) could be analyzed directly without additional sample handling.

B. Polymerization Studies

This difunctional initiator was directly formed in the reactor and used to polymerize diene monomers, with the goal being to prepare polymers of predictable molecular weights and narrow molecular weight distributions. Initial polymerization studies using butadiene were routinely unsuccessful, even if reaction variables, such as solvent/polymer ratio, polymerization temperature, and initiator concentration were changed. Molecular weight values were much higher than predicted and molecular weight distributions were very broad.

Possible explanations for these erratic polymerization results were 1) incomplete initiator formation, 2) branching side reaction taking place at high conversions, and 3) inefficient initiation from both anionic sites at the same time. Of the three, the first possibility was the easiest to quantify.

Before monomer was added to the initiator solution, the solution was checked by the chromatographic method for any unreacted 1,3-bis(α-phenylethenyl)benzene. If any unreacted material was detected, additional sec-butyllithium was charged into the reactor until less than 1% of unreacted material was present. When initiator formation was maximized, polymerizations of butadiene proceeded as expected with predictable molecular weights and narrow molecular weight distributions.

Polymerizations of isoprene with this difunctional initiator were also attempted. Though more difficult to polymerize because of a faster polymerization rate, isoprene was cleanly polymerized if initiator formation was maximized.

Now that homopolymerizations were proceeding well, some block copolymers were synthesized. Purified styrene was added to living polyisoprene to produce a series of styrene-isoprene-styrene block copolymers. In all cases, narrow molecular weight distributions were obtained with near 100% styrene incorporation.

This work was extended to the preparation of some novel triblock systems containing hydrophobic and hydrophilic groups, with a polyisoprene center block and a poly(t-butyl methacrylate) incorporated as the two end blocks. Successful synthesis of these systems required

the modification of the solvent polarity. To achieve the effective

crossover of living polyanion from isoprene to t-butyl methacrylate,

tetrahydrofuran was added in equal volume with cyclohexane prior to the

methacrylate addition. Thermal characterization of these copolymers

showed the presence of a phase separation with a rubbery plateau between

the glass transition temperatures of each phase.

IV. EXPERIMENTAL

A. High Vacuum System

Initiation and propagation reactions via an anionic mechanism required the rigorous purification of all materials such that any results were highly dependent on experimental techniques and the techniques used prepared glassware and reaction components. Any reactive impurities, primarily water and air, must be removed from monomers, solvent, initiators, and glassware by the appropriate purification procedures.

In general, organolithium initiators used here have concentrations of between 10^{-5} to 10^{-4} M, so the level of any terminating impurities which could react with the organolithium initiator or living chain end must be kept below 10^{-6} M. In order to maintain these rigorous reaction conditions, an all-glass high vacuum system (10^{-5} torr) employing a series of stopcocks similar to the system described by Morton and Fetters (146) was used. Using these conditions, premature termination of the active species was prevented.

A schematic of the high vacuum apparatus that was used in this study was shown in Figure 5. This vacuum system was composed of both a primary and secondary manifold. The primary manifold was constructed of 40 mm diameter heavy walled Pyrex glass tubing and the secondary manifold was made of 12 mm diameter heavy-walled Pyrex tubing. To maximize the attainable vacuum, these manifolds were kept as short as possible. Connected to the secondary manifold were several male ground glass joints (F) where round bottom flasks can be attached which can contain, for example, high boiling monomers which were efficiently
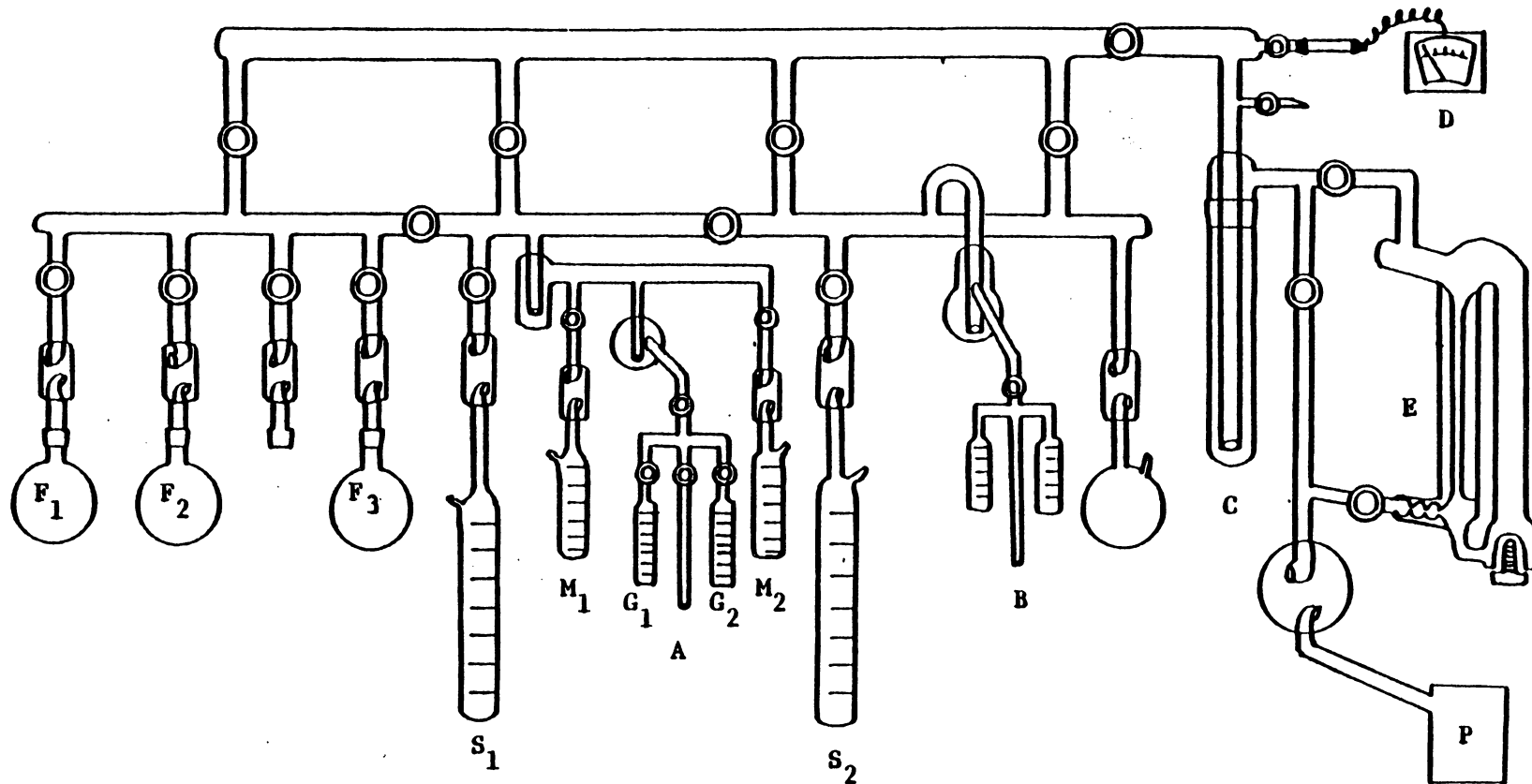
Figure 5. High Vacuum Line

distilled at low temperatures under high vacuum conditions. Round

bottom graduated cylinders were also attached to the secondary manifold.

These contained solvents (S) or diene monomers (M) which were stirred

over organometallic reagents. The diene monomers were kept cold by

packing the graduated cylinders in dry ice/isopropanol. Two grease

traps were also attached to the secondary manifold which contain

sections that were used to heat-seal additional glass equipment onto the

vacuum line.

The heart of the system consists of a cold trap (C) which was

cooled to liquid nitrogen temperatures and a Hastings-Teledyne high

vacuum gauge (D) for measuring the pressure in the system. Finally, a

mercury diffusion pump (E) in conjunction with a Sargent-Welch

mechanical vacuum pump (P) was used to establish and maintain vacuum in

the system. High vacuum Teflon[R] Rotaflow[R] stop cocks were used to

isolate various sections of the vacuum line which minimized

contamination by siloxane or fluorocarbon greases that were used to

lubricate the Pyrex glass stop cocks.

B. Purification

1. Introduction

When using high vacuum techniques, special all-glass reactors were

used. Prior to use, glassware were cleaned first with hydrofluoric acid

followed by distilled water and ammonium hydroxide washes and then dried

in a drying oven. All glassware that was heat-sealed to the vacuum line

was tested for leaks under vacuum with a Tesla coil. Transfer of

solvents or initiator solutions was performed by a series of glass

breakseals which were broken by a magnetic stirrer which was moved by a magnet from outside the glass.

The transfer of volatile materials such as monomers, solvents, or even organolithiums was achieved by distillation at reduced pressures. This requires less time and lower temperatures and prevents possible decomposition. All materials to be distilled must first be degassed. This was done by freezing the liquid in a Dewar flask of dry ice/isopropanol or liquid nitrogen and drawing a vacuum for about fifteen minutes, before thawing. This freeze/thaw cycle was repeated two or three times until a high vacuum (10^{-5} torr) was obtained over the frozen liquid.

The solution was now easily distilled by simply cooling the receiver in liquid nitrogen or dry ice/isopropanol and warming the source with warm water or, in extreme cases, a silicone oil bath with constant stirring, for materials that boil above $100°C$. Distillation was begun by first completely opening the stop cock to the receiver flask then slowly opening the stopcock leading to the source until the solution begins to distill. The distillation should proceed slowly enough so that the distillate does not recondense in the secondary manifold. If condensation does occur, the solution may not be thoroughly degassed.

One method for the further purification of solvents and vinyl monomers was to store them over organometallics. The resulting solution was often designed to be highly colored which was a clear indication that the system was free of reactive impurities.

Hydrocarbon solvents were stored over polystyryllithium which was a deep red-orange color and was used as a colorometric indicator of solvent purity. This colored species was the result of the reaction between n-, or sec-butyllithium and a small amount of styrene or 1,1-diphenylethylene. The preferred lithium was n-butyl, as if there was any unreacted lithium present, it would not distill from one flask to another.

Compounds containing vinyl groups were stored over dibutylmagnesium (Lithium Corp. 0.72 M in hybar solvent that is a mixture of branched alkanes) which in the case of styrene produces a pale yellow color. This again indicates that reactive impurities have been removed with little, if any, polymerization taking place.

The above solutions were stored in graduated cylinders with rounded bottoms or round bottom flasks. The organometallic solutions were added to these flasks by syringe through a 12 mm thick-walled glass side arm which was capped at the end by a rubber serum cap. Addition was accomplished by first flushing the syringe with either nitrogen or argon and then adding to the flask under a flow of argon through the flask and out the side arm. The gas flow was stopped and the flask was evacuated to remove any solvent present. Any further additions can be made at this time through the side arm under an inert atmosphere and evacuated as before with the lower portion of the flask being cooled in a dry ice/isopropanol bath. The side arm was then sealed off by heating under vacuum with the hand torch and checked for leaks with a Tesla coil. Solvent was then distilled into the flask as described above and stored at room temperature.

The purification of reactants and solvent was of utmost importance for the preparation of the difunctional initiator. This was important not only because the anionic species that were generated are highly reactive but also because impurities can influence the reaction kinetics. In particular, polar compounds substantially increase the reaction rate and should be removed before use. A discussion of how the various reagents were purified before use is provided in the next section.

2. Cyclohexane

Cyclohexane was known to contain traces of olefinic impurities which must be removed. Cyclohexane (Phillips 66, 99%) was first stirred over concentrated sulfuric acid (about a 10% solution) for at least a week at room temperature. This removes the olefinic impurities by converting them to sulfonates, which then become soluble in the acid layer.

The cyclohexane layer was decanted into a round bottom flask containing crushed calcium hydride. The cyclohexane was distilled into a round bottom flask containing a sodium dispersion in paraffin wax and stirred overnight before being placed on the vacuum line. Following the degassing procedure, the cyclohexane was distilled into a flask containing the low molecular weight polystyryllithium which produces the characteristic red colored solution. Cyclohexane can now be distilled from this flask as needed.

3. Toluene

Toluene was purified by a similar procedure as cyclohexane. However, storage over polystyryllithium for long periods of time is not

advised. The polystyryl anion can undergo chain transfer reactions with toluene by abstracting a proton from the methyl group of toluene resulting in the anion changing color.

4. Tetrahydrofuran

A variety of polar compounds were used as additives to completed reactions containing the difunctional initiator. In general, the molar ratio of organolithium to polar additive was 0.2 (e.g. 1 to 5 or less polar additive to organolithium).

Purification of tetrahydrofuran (THF) from Fisher Scientific was needed before use to remove any inhibitor, oxidation products, and water that may be present and was affected by a double distillation procedure. The ether was first distilled from the purple colored complex formed from the addition of benzophenone to sodium dispersion after stirring overnight. The THF was distilled under a nitrogen atmosphere through a 20 cm Vigreux distillation column into a flask containing more of the benzophenone/sodium metal complex. This time the solution was again purple in color. This colored solution was then distilled a second time over a short path, under vacuum, into a clean round bottom flask. The purified THF can be removed by syringe or distilled directly into any reaction flask or if a more accurate measurement was needed, distilled first into one of the graduated cylinders of (G in Figure 5) and then into the reactor of choice. The latter may be the method of choice due to the volatility of the THF and the ease with which water was absorbed when exposed to air.

5. Triethylamine and Tetramethylethylenediamine

The following purification procedure was used because of the reduced volatility and increased reactivity of some of the other polar additives. Triethylamine and TMEDA (Aldrich) were purified mainly to remove air and water prior to use. The amines were first stirred over crushed calcium hydride overnight in a round bottom flask equipped with a drying tube. The flask was then connected to the purification apparatus shown in Figure 6.

The entire apparatus was heat sealed to the vacuum line at (A) and flask (B) which contains the tertiary amine and calcium hydride was connected to the ground glass fitting and was degassed under vacuum by the now familiar procedure of freezing and thawing. The distillation was performed at, or slightly above, room temperature using a heated water bath. The receiver flask (C) was cooled with liquid nitrogen. A constant vacuum was drawn for the duration of the distillation, to increase the rate of distillation. The receiver was then sealed off at the constriction.

The receiver flask (C) was now attached to the split-down apparatus which was shown in Figure 7. The entire assembly was heat sealed to the vacuum line and pumped down until a high vacuum was attained (10^{-5} torr). With gentle heating, the glass was collapsed at the constriction to the vacuum. The break seal at (B) was broken and the amine was split down into the ampules (C). Any excess was stored in flask (A). With time, these amines will develop a yellow color. If this occurs, redrying and redistilling should be done before use.

VAC.
(A)

(C)

(B)
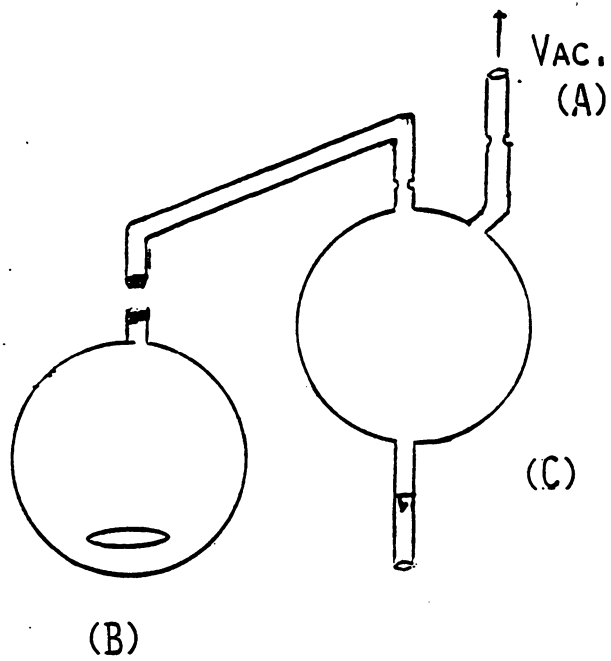
Figure 6. Distillation Apparatus

The final step was to freeze with liquid nitrogen both the ampules and flask (A) concurrently so that distillation from one to the other was avoided. Now, using the hand torch with a gentle flame, the glass was collapsed at the narrow portion of each ampule and also at the constriction near flask (A). Flask (A) may be attached to another split-down apparatus and a similar procedure followed if more amine was needed.

6. Dipiperidinomethane and Dipiperidinoethane

Dipiperidinomethane and 1,2-dipiperidinoethane (Aldrich, 98%) were purified using an analogous procedure. However, because of the higher boiling points, the distillation must be done at elevated temperatures. This was accomplished by heating the source (B in Figure 6) with a water bath at 50°-55°C. The distillate was then split down into small ampules using the apparatus shown in Figure 7.

Caution should be taken when thawing any glassware that contains these amines after freezing in liquid nitrogen. The coefficient of thermal expansion for these compounds was apparently large enough so that the fragile glass break seals will break if thawing takes place too rapidly.

7. Ethylene Oxide

Ethylene oxide (Eastman Kodak) must be purified before use to remove air and water as well as the primary decomposition product, ethylene glycol, which will act as a terminating agent for anionic species but will not impart the desired hydroxyl functionality. Distillation of ethylene oxide under an inert atmospheres (N_2) afforded the highest purity.
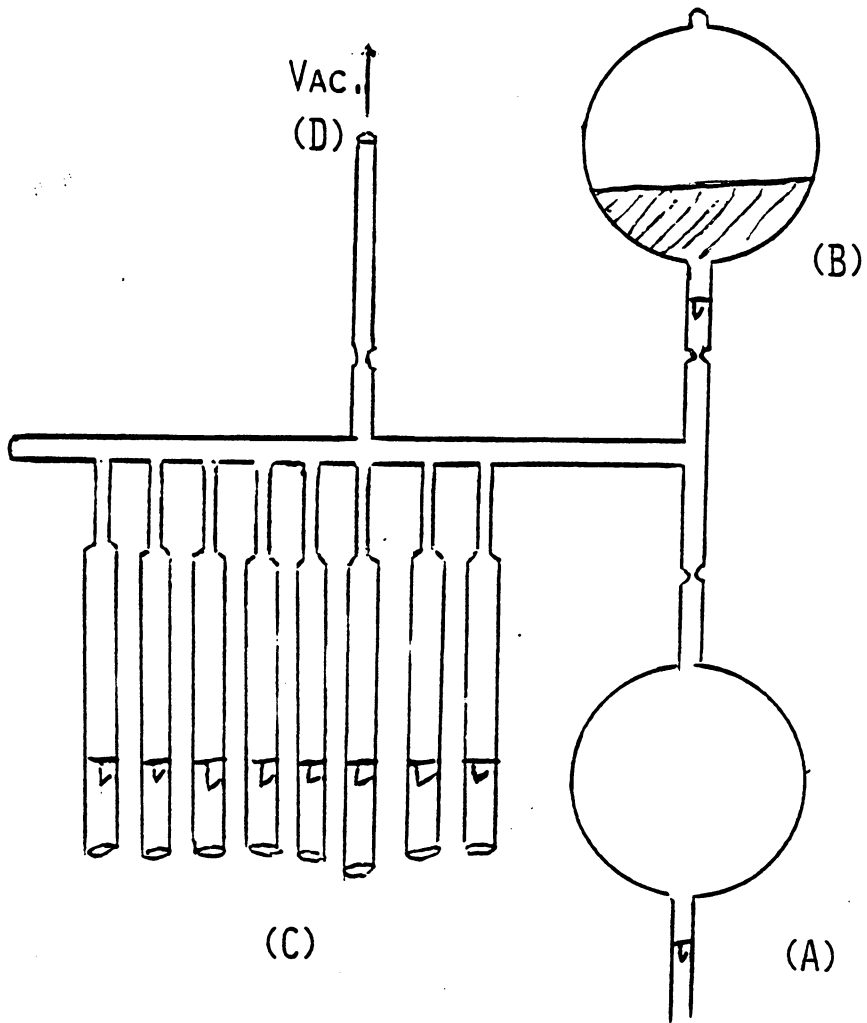
Figure 7. Split-Down Apparatus

Ethylene oxide was stored in a bottle sealed with a rubber septum over calcium hydride and under an inert atmosphere in a freezer at about -40°C prior to use. This compound was then distilled through a clean, dry, double ended needle and bubbled directly into the reactor that contained the living polymer solution.

8. Sec-butyllithium

The purification of organolithium compounds was necessitated by the fact that commercially available material contains impurities such as ROLi and LiOH which were incapable of initiating carbanionic polymerizations. However, these impurities can alter the kinetics of initiation and propagation. Purification of certain organolithiums was easily done by high vacuum distillation (147). Figure 8 shows a schematic diagram of the distillation apparatus which was used for the purification of sec-butyllithium.

This apparatus was first heat sealed onto the vacuum line, evaluated and checked for leaks. The heavy walled tubing was temporarily capped with a serum cap and the glassware was flamed to remove water and other volatiles from the inside of the glass.

A solution of sec-butyllithium (Lithium Corp. 1.4 N in cyclohexane) was then added through the side arm of flask (A) under a blanket of argon by syringe. The solution was frozen with liquid nitrogen and the side arm removed by heat-sealing under vacuum.

The flask was then warmed with a water bath and the solvent was removed under vacuum with constant stirring. The receiver flask (B) was then cooled with liquid nitrogen while the source (A) was warmed with a water bath to 60-65°C while a constant vacuum was applied to the

HEAVY
WALLED
TUBING

↑ Vac.

(A)

(B)
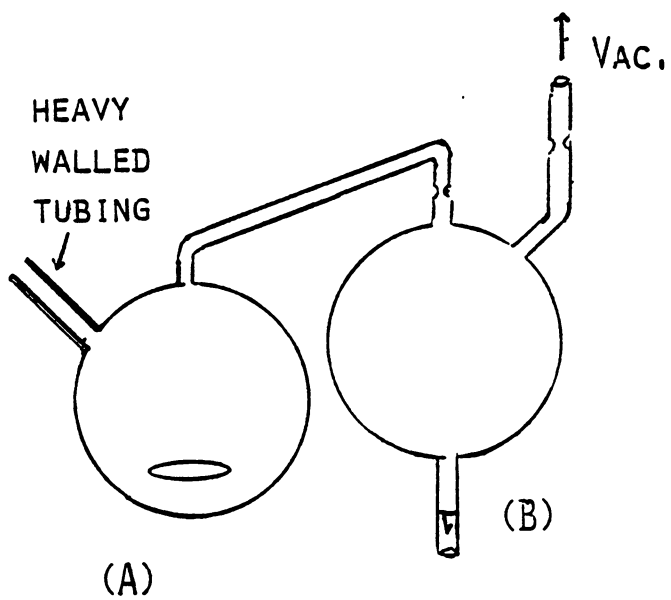
Figure 8. Sec-butyllithium Distillation Apparatus

distillation apparatus. The short path between both flasks can be heated with heating tape to speed the distillation.

After distillation was complete, the receiver flask was heat-sealed from the apparatus at the constriction but remained connected to the vacuum. The desired amount of cyclohexane can be distilled into receiver flask (B). The final step was to heat-seal this flask from the vacuum at the constriction.

If the distillation was done properly, a clear solution should result. If the distillation was done above about 75°C decomposition of the sec-butyllithium can take place. In some case, a pink color was observed after heat sealing. This appears to be a common occurrence yet does not seem to affect results, if kept to a minimum.

The last step was to split this solution down into small ampules. This can be accomplished by using the split-down apparatus previously shown in Figure 7 and following the previously stated procedure. The exact volume in the ampules should be marked before cooling and heat sealing as cyclohexane can distill over into the ampules and change the volume in each one.

One ampule of the sec-butyllithium was used for analysis by a titrametric method using standardized 0.1 N HCl in alcohol to a phenolphthalein end-point to determine its concentration. This was accomplished by the following procedure.

The volume in the ampule was first determined by comparison with an empty ampule which has been calibrated with known volumes. The contents of the ampule was broken into an Erylenmeyer flask containing water and the phenolphthalein indicator. The solution was titrated with the

standardized HCl to a pink endpoint. From the volume of titrant used, the concentration of sec-butyllithium was determined. This method gives the concentration of total base present including any alkoxides or hydroxides which may be present in an impure sample. However, since the distillate was highly pure, these impurities should not be present and an accurate value can be obtained.

A second method using a double titration was also be employed to determine the concentration of alkyllithium solutions (148). The first step was to hydrolyze the sec-butyllithium, followed by titration for total base with standardized HCl. The second step involves treatment with an organic dihalide such as 1,2-dibromomethane followed by hydrolysis and titration with standardized HCl. This titration gives the concentration of any residual base which may be due to alkoxides or hydroxides that were present. The difference between the two titration values was taken as the concentration of sec-butyllithium present.

A third titration method used biphenylmethanol as an indicator. One milliliter of sec-butyllithium was added to about 20 ml of dried xylene which contained about 0.01 g of biphenylmethanol. This results in a dark yellow to orange solution. The entire procedure was done under a nitrogen atmosphere. The solution was titrated to a clear endpoint with standardized sec-butyl alcohol in a cyclohexane (0.25 M). This step was done to condition and remove any impurities from the system. The second step was then to add 0.5 ml of sec-butyllithium to this solution and titrate with the standardized sec-butanol. This procedure was repeated several times so that an average concentration for the sec-butyllithium solution was obtained.

9. 1,3-bis(α-phenylethenyl)benzene

The 1,3-bis(α-phenylethenyl)benzene (DDPE) was obtained from Dow Chemical Co. as a yellow liquid which upon standing will slowly crystallize. The resulting yellow crystals must be purified before use.

Initial attempts at purification involved a simple recrystallization from methanol, which was purged with nitrogen. The crystals were filtered under nitrogen and dried in a vacuum oven. The needle-like crystals that were obtained were still slightly yellow in color.

A more effective purification method appears to be first distilling from dibutyl magnesium under high vacuum conditions. This distillation procedure avoided the possibility of contamination by protonic sources that could result because of trapped methanol from the above recrystallization procedure. The apparatus that was used for this distillation was shown in Figure 9.

This apparatus was connected to the vacuum line, evacuated and checked for leaks with a serum cap sealing the heavy walled tubing. After flaming the evacuated vessel, 5 to 10 ml of dibutylmagnesium solution was added to flask (A) by syringe under a blanket of argon. The apparatus was again evacuated to remove the hydrocarbon solvent from the dibutylmagnesium. Now the DDPE can be added to flask (A) under a blanket of argon by syringe through the side arm. This was best done by first melting the DDPE using warm water then filling a warm syringe and emptying it into flask (A). The solution was stirred overnight at room temperature.

The side arm was sealed off while drawing a vacuum on the apparatus. Distillation was now achieved by heating the source with an
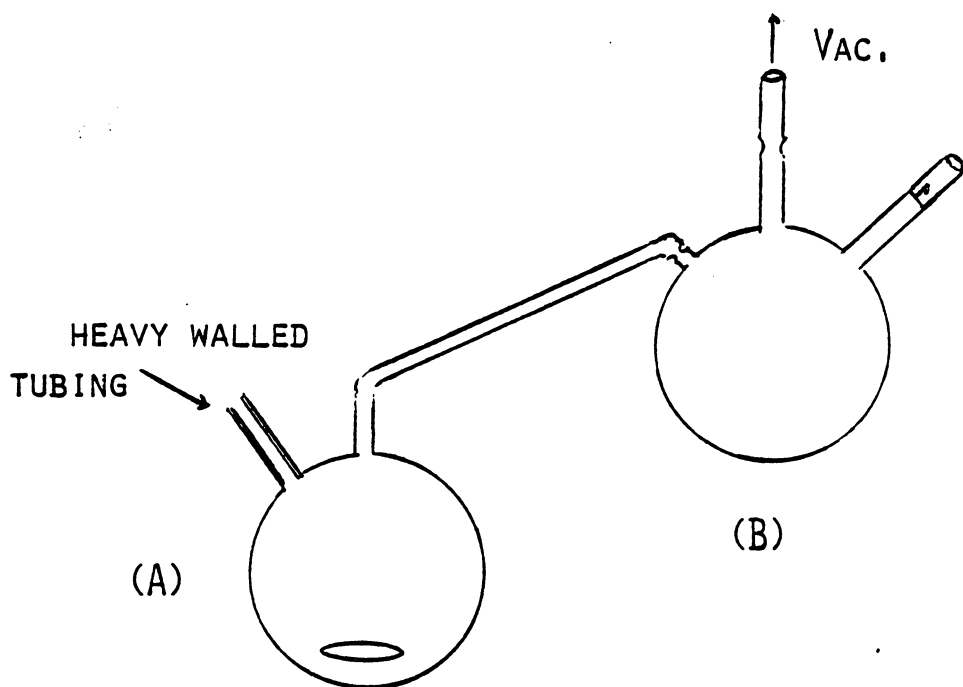
Figure 9.   1,3-Bis(α-phenylethenyl)benzene Distillation Apparatus

oil bath to about 130-135°C, while drawing a constant dynamic vacuum and cooling flask (B) with liquid nitrogen. The short path was kept warm with heating tape and after distillation was complete, the receiver flask was heat-sealed both from the path and from the vacuum. The product was a clear colorless liquid.

This was then dissolved in chloroform and extracted three times with water to remove any residual magnesium salts from the distillate. The solvent was removed and the clear liquid was recrystallized from methanol. All steps should be performed under an inert atmosphere to prevent oxidation. A white solid was obtained which had a melting point of 38°C. A simple calorimetric (149) test was used to determine if any magnesium salts were present in the distilled DDPE. After extraction with water, the collective aqueous layers were added to about 25 ml of pH 10 buffer. To this was added several drops of a Calmagite indicator solution. The indicator has the following structure.
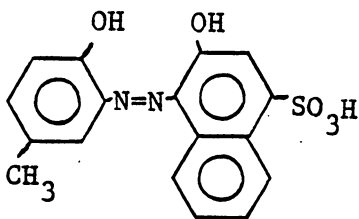
A positive test for magnesium was observed, indicating that some alkyl magnesium was distilled over at these elevated temperatures.

A second and the most effective distillation approach was to distill DDPE from n-butyl lithium. For this procedure, the crude DDPE was charged into the distillation as before then heated with a water bath to about 45-50°C. Under argon, n-butyl lithium (Lithium Corporation, 1.4 M in cyclohexane) was added slowly while stirring.

Several color changes were observed. First, a purple solution was observed which turned to brown with more added n-butyl lithium. Finally, a bright red color was observed. At this point, a slight excess of n-butyl lithium was added to ensure all impurities were reacted.

The solution was allowed to stir for several hours at this temperature. The solvent was then removed slowly under vacuum to prevent bumping. This solution was kept under the applied dynamic vacuum over night to remove all traces of solvent and distilled as before.

Differential Scanning Calorimetry (DSC) was used to determine the melting points of both the crude starting material and the purified material using a Perkin-Elmer Model 2 DSC. Samples were run at 10°C/min. in a nitrogen atmosphere. Samples were only run once because the samples would easily super cool and showed no melting point for the second run.

One way of removing the desired amount of DDPE from the distillation flask was by the following method. DDPE was transferred under an inert atmosphere through a double ended needle into a preweighed, rubber septumed 25 ml volumetric flask, that had been flame dried. After the desired amount of DDPE had been transferred to the flask, the weight was recorded and then diluted with cyclohexane. The desired amount of solution was removed by syringe and placed into the glass apparatus shown in Figure 10. This flask had previously been under vacuum, then filled with argon. A vacuum was then applied to remove the solvent. The desired amount of purified cyclohexane was
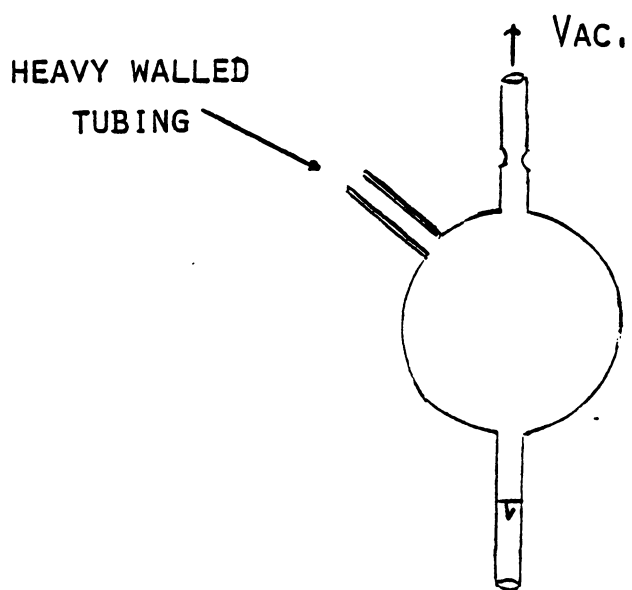
Figure 10. Flask for Dissolving DDPE

distilled into the flask and the flask was heat sealed from the vacuum
line at the constriction and heat sealed at the side arm. The flask was
attached to the split down apparatus shown in Figure 7 and split-down as
before.

C. Initiator Formation (High Vacuum)

The difunctional initiator used in this study was the addition
product of sec-butyllithium with 1,3-bis(α-phenylethenyl)benzene (DDPE).
For this reaction, two moles of sec-butyllithium were used to completely
react with both double bonds of the DDPE. The reaction product was
completely soluble in cyclohexane, even at concentrations of 0.5 M, if
freshly prepared. It was also soluble in solvents possessing a higher
dielectric constant than cyclohexane, such as toluene and benzene, but
has limited solubility in less polar solvents such as hexane. The
reaction sequence is shown below.

(DDPE)   + 2 sec-butyllithium

cyclohexane

1
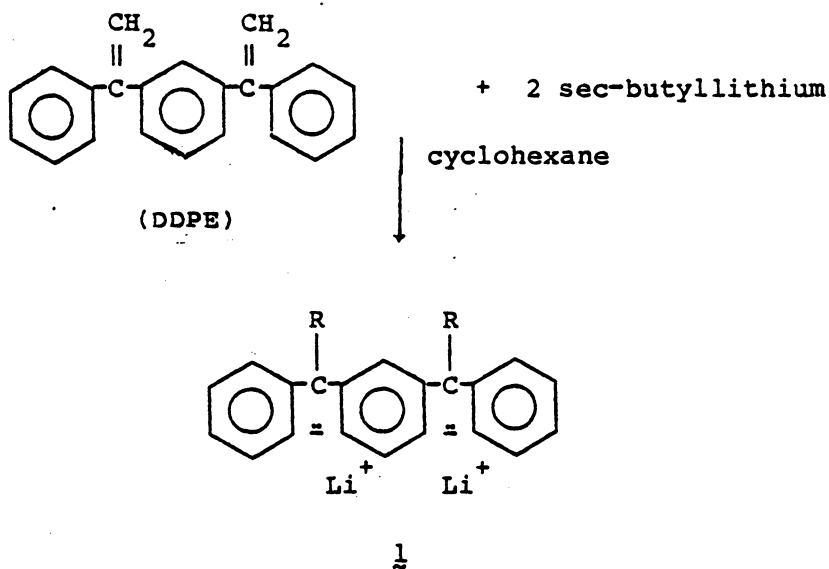
Compound 1 was the difunctional initiator and will be referred to
as the diadduct in later discussions. This highly colored species and

the monoadduct (product with only one double bond reacted) have peak absorbances at the same wavelength.

D. High Vacuum Glass Reactor

An all-glass reactor was used for studying the kinetics of the reaction between sec-butyllithium and DDPE under high vacuum conditions. The reactor has a set of quartz UV/Visible cells attached at the top which allows a spectrum to be obtained. The reactor that was used in this study was illustrated in Figure 11. The reactor itself was divided into two sections; the main reactor section and the purge section. The main reactor consists of a 500 ml round bottom flask (R) to which two side arms have been attached. These side arms provide sections where the ampules containing the reactants were attached. Two break seals were provided which allow for addition of more solvent or attachment of more ampules which may contain the various polar additives. Two quartz UV/Visible cells of 10 mm and 1 mm path lengths were attached at the top of the reactor.

The purge system consists of a 200 ml round bottom flask which contains a side arm having a solution of sec-butyllithium in cyclohexane. This solution was used to condition the main reactor and to remove any impurities from the glassware which could alter the reaction kinetics. The reactor was assembled by heat sealing on the reagent ampules containing the DDPE, sec-butyllithium, the wash sec-butyllithium and if desired, any polar additives. Magnetic stirring bars were used as the break nails.

After heat-sealing the entire reactor onto the vacuum line, it was evacuated and flamed until a high vacuum was obtained of about 10^{-6} torr
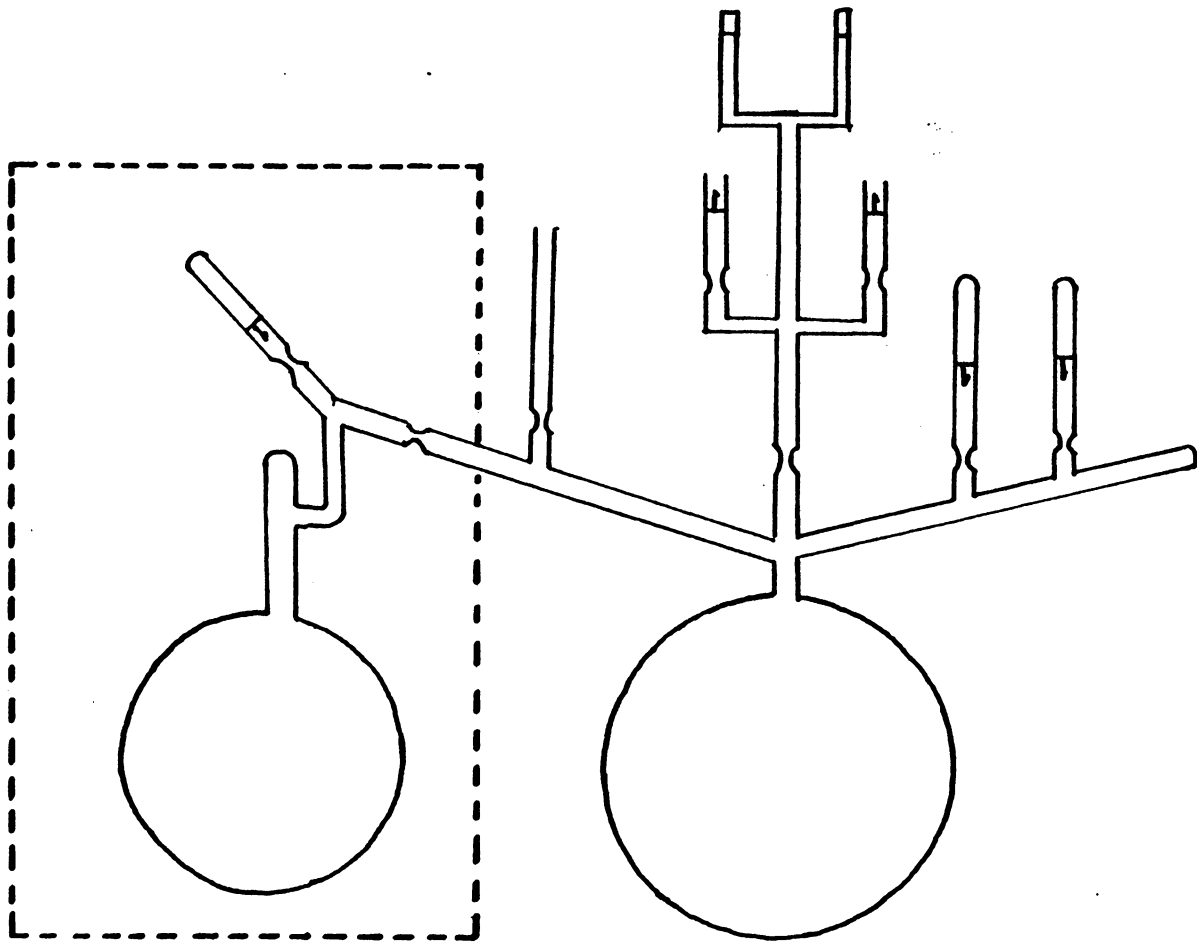
Figure 11. High Vacuum All Glass Reactor

in the apparatus. Approximately 120 ml of purified cyclohexane was distilled into the purge bulb (P) through the vacuum line by cooling the bulb to -78°C and warming the round bottom flask containing the cyclohexane/polystyryllithium solution. The break seal of the wash solution of sec-butyllithium was broken and added to the cyclohexane. The purge bulb was frozen and the entire apparatus was removed from the vacuum line by heat-sealing at the constriction to the vacuum.

The interior surface of the main reactor was thoroughly rinsed with the sec-butyllithium wash solution by tilting the rig and then allowing the wash solution to drain back into the purge bulb (P). This procedure conditions the reactor and removes any reactive impurities from the glassware.

To remove the excess sec-butyllithium from the glassware, it must be rinsed off with cyclohexane. The cyclohexane in the purge bulb was vaporized by warming the bulb with a warm water bath and condensed on the glass of the main reactor by cooling various sections with a liquid nitrogen soaked cotton. Three washes were sufficient to remove traces of sec-butyllithium left from the purging procedure.

The cyclohexane was then distilled from the purge bulb (P) to the main reactor (R) by warming the purge bulb in a warm water bath and cooling the main reactor to -78°C. About 100-110 ml of cyclohexane was distilled into the main reactor. Care must be taken to avoid bumping of the solution during distillation so that the main reactor does not become contaminated with excess sec-butyllithium. After distillation was complete, both the main reactor (R) and the purge bulb were cooled

to -78°C and the purge section was heat-sealed from the main reactor at the constriction.

The main reactor (now minus the purge section) was placed in a circulating water bath which had the temperature controlled to ±0.1°C, until the cyclohexane has reached the desired temperature. When this was achieved, the two ampules containing the two reagents were broken via the break seal and were allowed to mix in the reactor. Thorough mixing of the two reagents was achieved by turning the reactor upside down several times.

A series of UV/Visible spectra were taken at specified times during the reaction by tipping the reactor upside down such that the quartz cells were filled and the entire apparatus was placed in the spectrophotometer. The reactor was then clamped in place using a clamp and ring stand such that no undo stress was placed on the cells which may result in breakage. A dark cloth was placed over the cell compartment in such a way that no stray light could enter the detector from outside sources.

E. Nitrogen Pressure Glass Bowl Reactor

1. Reactor Design

Because of the relative insensitivity of the UV/Visible method, a more sensitive method employing the high pressure polymerization reactor in conjunction with gas liquid chromatographic analysis was used. A schematic diagram of the high pressure nitrogen reactor (150) was shown in Figure 12. To maintain constant stirring, the stirring assembly (2) was driven at a controllable rate by a magnadrive motor (1). This
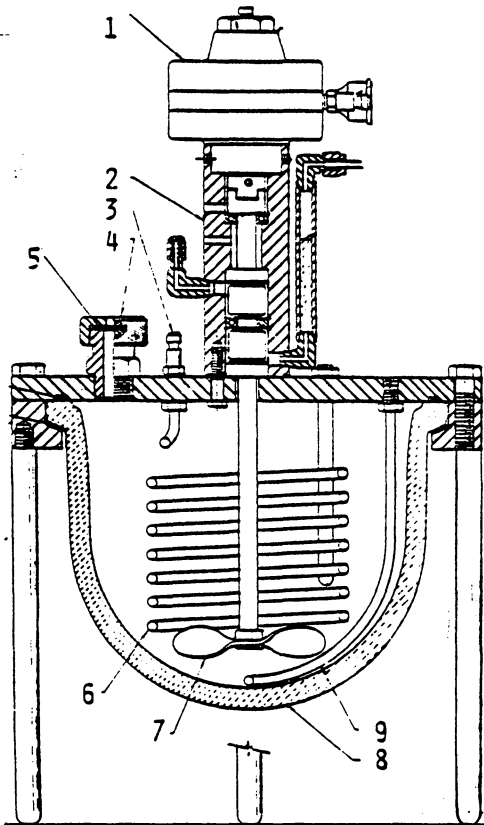
PARTS

1. STIRRING MOTOR
2. STIRRING ASSEMBLY
3. SOLVENT, MONOMER INLET
4. INITIATOR INLET
5. SYRINGE SEAL
6. COOLING/HEATING COIL
7. PROPELLER
8. REACTOR BOWL-GLASS
9. SAMPLE REMOVAL PORT

NOT SHOWN

10. NITROGEN INLET

Figure 12.   High Pressure Nitrogen Reactor

assembly was attached directly to the stirring propeller (7) which agitates the solution.

Solvents were added to the reactor through the inlet port (3). Solvents must first be purified before addition to the reactor. Cyclohexane was used primarily as the solvent. The solvent was pumped from a holding tank under nitrogen pressure through a series of purification columns which contain activated alumina, silica gel, and molecular sieves which serve as an effective means to remove water from the solvent. The solvent was then pumped into a small holding tank which has been graduated in uniform increments. The desired amount of solvent was pumped into the tank and then pumped into the reactor under nitrogen pressure.

2.   Initiator Formation: Nitrogen Pressure Reactor

Initial kinetic studies on the formation of the difunctional initiator were carried out in the high pressure N_2 reactor. Purified cyclohexane was pumped into the reactor and stirred at 60°C. After a short time, the reactor was emptied. This procedure also serves as a method for cleaning the reactor.

After cleaning and refilling with cyclohexane, sec-butyllithium and DDPE were added to the reactor through the initiator inlet (4). The inlet contains a syringe seal (5) which was simply a rubber septum. Purified DDPE dissolved in cyclohexane was added by a syringe with a narrow gauge needle through the septum to the reactor. The purified sec-butyllithium solution was then added to the reactor. First, the system must be purged of reactive impurities. This was done by adding

sec-butyllithium slowly until a pale yellow color resulted. Then, the stoichiometric amount of purified sec-butyllithium was added.

The temperature control of the reaction was effected by controlling the temperature of a steam/tap water mixture that flows through the cooling/heating coil (6). The temperature was controlled to ±2°C of the desired value. Constant heating was achieved through the use of a heating mantle, while running only tap water through the heating coil. Control to ±0.5°C of the desired temperature was obtained using this method.

The glass bowl (8) was of 1/4" thick glass which was rated to withstand at least 100 psi without breakage. The nitrogen pressure was controlled by a series of valves which allow nitrogen to be added through the nitrogen inlet (10). Samples can be removed from the reactor through the sample removal port (9) at specified times during the reaction.

3. Sample Preparation for Chromatographic Analysis

a. Concentrated Samples

Sample preparation required a concentration step and the use of large sample sizes because of poor detector response of the GLC, i.e., small signal output per milligram of sample. Between 1.0 and 1.5 grams of DDPE typically must be added to the reactor. This was achieved by dissolving the desired amounts in cyclohexane and injecting this solution into the reactor via syringe. The container was rinsed several times with cyclohexane and these washings were added to the reactor. The stoichiometric amount of the purified sec-butyllithium solution was then added to the reactor to initiate the reaction.

Approximately 30 ml of this solution was emptied into a graduated cylinder which was purged with nitrogen gas and contained several drops of methanol which served to terminate the active chain ends. After the reaction has been terminated, 25.0 ml was removed and placed in a serum bottle. The sample was evaporated to dryness in a vacuum oven. To the dried samples was added 2.0 ml of cyclohexane to redissolve the sample (sonification in a ultrasonic bath accelerates this process). Generally, the samples contain high concentrations of salts which will clog the GC syringe. These were removed from the solution by addition of about a 0.5 ml of water. Five μl of the cyclohexane layer was injected onto the gas chromatograph.

b. Dilute Samples

The initial procedure was very time consuming and the chance for sample degradation was large due to the excessive sample handling. What was needed was a method to analyze directly initiator solutions from the reactor, which was not a trivial task because of the low concentrations used, i.e. 0.5×10^{-3} moles. Fortunately, capillary gas chromatography proved to be an effective method to analyze these solutions.

Very dilute samples were prepared for these studies. Typically, 0.141 g of DDPE was charged into about 600 ml of cyclohexane in the reactor. The stoichiometric amount of sec-butyllithium was then added after the impurities had been "titrated out". Samples taken directly from the reactor were terminated with isopropanol (termination with methanol produced solubility problems with cyclohexane) and 2.0 μl of this solution were injected onto the gas chromatograph. The initiator solutions may contain significant amounts of unreacted DDPE which cause

broadening of the molecular weight distributions of diene polymers. The following procedure was used to limit the amount of unreacted material in these solutions.

Initiator solutions were first analyzed by gas chromatography and the amount of unreacted DDPE (relative to fully reacted) was determined based on the areas of the two peaks. An additional aliquot of sec-butyllithium solution was then added to react with the remaining DDPE. After 2 hours reaction time, the solution was again checked for unreacted DDPE. If the amount was greater than 1%, the procedure was repeated.

c. Quantitative Characterization of Initiator Solutions

Quantitative determination of actual concentrations of important components of difunctional initiator solutions was achieved using capillary gas chromatography. The most accurate method of determining these components was by using an internal standard method.

Anthracene (Aldrich, 99%) was used as an internal standard because it dissolved in the reaction solvents that were used and did not elute with any components of the initiation solution. Approximately 25 mg of anthracene was dissolved in 25 ml of cyclohexane using an ultrasonic bath. This solution was used as the internal standard stock solution.

Purified DDPE was dissolved in cyclohexane and used as a standard. The concentration of these solutions was generally about 0.4% by weight.

A standard for the diadduct was prepared by adding about a two-fold excess of sec-butyllithium in cyclohexane. The reaction was terminated with a small amount of methanol. The solution was extracted three times with distilled water, dried with $MgSO_4$ and filtered to remove salts and

other insolubles. The sample was dried and the resulting oil was dissolved in cyclohexane in similar concentrations and used as a standard.

0.1 ml of the stock anthracene solution was added into a one milliliter volumetric flask, with the remainder containing the standard component. After thorough mixing, 2 µl of this solution was injected onto the gas chromatograph and response factors were determined for each component.

Several attempts at preparing the pure monoadduct standard in hydrocarbons were unsuccessful. However, this compound can be prepared in about 85% purity in THF, by using a 1:1 ratio of sec-butyllithium to DDPE. However, further purification by recrystallization was not possible. For calibration purposes, an average response factor between the diadduct and DDPE standards was used for the monoadduct.

F. Polymerization Studies

For all polymerizations, the amount of monomer that was charged into the reactor was based on the molecular weight of the polymer and on the weight (in grams) of the polymer to be prepared. A variety of experiments were conducted where the molecular weight was varied. The one variable that was kept constant was the weight of polymer to be prepared. For most cases, 30 grams total weight of polymer was prepared for a weight to weight concentration in solvent of about 5%. Due to the highly associated nature of these high molecular weight living polymers, increasing the percent solids resulted in very viscous solutions which generally produced polymers showing higher polydispersities.

The following equation was used for determining the amount of
initiator to charge to obtain the desired number average molecular
weight for these living polymerizations.

$$\overline{M}_n = \frac{2\,(30g)}{\text{moles of initiator}} \tag{24}$$

As an example, if a polymer with 100,000 molecular weight was desired,
0.6 mmoles of DDPE was charged into a flask and reacted with 1.2 mmoles
of sec-butyllithium.

1. Diene Homopolymerizations

Polymerizations of butadiene using the difunctional initiator were
carried out in this reactor. The first step was the formation of the
difunctional initiator. A similar approach was used as was stated
above, i.e., two moles of sec-butyllithium added to one mole of DDPE in
cyclohexane. In most cases, 0.5 mmoles of DDPE were charged into 650 ml
of purified cyclohexane. The reaction was checked for initiator
formation to ensure complete reaction. The temperature was maintained
at 60°C and the solution was allowed to react for two and one-half hours
after addition of any sec-butyllithium. The temperature was then
lowered to 35°C and purified butadiene or isoprene was added. The
polymerization was assumed to be complete in about 24 hours. Polymers
were isolated by evaporation of the solvent. Scheme 1 shows the
synthesis of diene homopolymers using this difunctional initiator.

2. Functionalization of Isoprene

These polymerizations were done under similar conditions as stated
above, i.e., the initiator was formed at 60°C and checked chromato-
graphically for complete formation. The desired amount of isoprene was

Scheme 1. Diene Homopolymer Synthesis

$$R \quad\quad R$$
$$C \quad\quad C$$

"IN"

Li$^{\oplus}$ Li$^{\oplus}$

40° C,   CH$_2$=C

$$\overset{R}{\underset{CH=CH_2}{}}$$

Li $^{\oplus}$ $\ominus$~~~~~~~IN~~~~~~~$\ominus$ Li $^{\oplus}$

CH$_3$OH
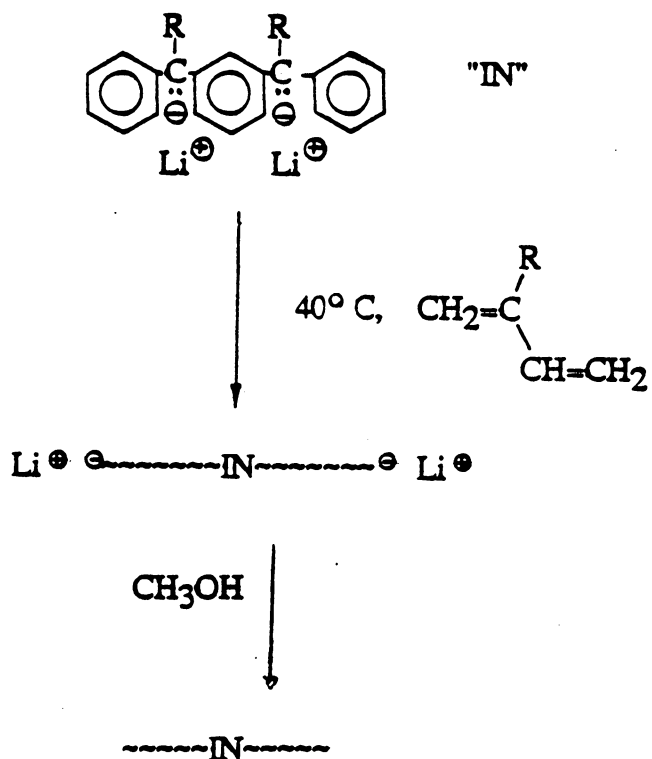
~~~~~IN~~~~~

added and polymerized for 24 hours at 35°C. However, in this case, the theoretical isoprene molecular weight was 2,500 daltons at a concentration of about 2% solids (weight to weight with cyclohexane). Approximately 9.6 mmoles of DDPE was charged in 600 ml of cyclohexane followed by the addition of about 12 g or isoprene.

After the polymerization was complete, purified ethylene oxide was bubbled directly into the reactor until the solution became colorless. The living polymer solution was terminated with a small amount of acidic (HCl) methanol and isolated by evaporation of the solvent to give the hydroxyl terminated polyisoprene. Scheme 2 illustrated the synthetic route used to prepare this polymer.

3. Styrene-Diene Copolymers

Styrene-isoprene-styrene triblock copolymers were also synthesized in the polymerization reactors. Purified styrene was added to the living polyisoprenyllithium by syringe. The crossover reaction seems quite slow at the lower temperature, but after 8 hours the reactions was complete and the polymerization was terminated with about 0.5 ml of methanol. Polymer isolation was achieved by precipitation into a 50/50 mixture of isopropanol/methanol. The synthesis of styrene-diene-styrene triblock copolymers is shown in Scheme 3.

4. Diene-Methacrylate Copolymers

Preliminary research in this area focused on the synthesis of triblock copolymers containing t-butyl methacrylate end blocks and an isoprene center block. Extremely pure solvents and monomers were used due to the complicated series of transfer steps required to achieve this synthesis. In addition, all metal and glassware that was used was

Scheme 2. Functionalized Polyisoprene Synthesis

$$CH_2 \quad CH_2$$

$+$ 2 sec-butyl Li

Toluene, 40°C, 2 hr

isoprene

$$Li^{\oplus} \, {}^{\ominus} \sim \sim (-CH_2-\overset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_2-)_x \sim \sim I \sim \sim (-CH_2-\overset{\underset{\displaystyle CH_3-\overset{}{C}}{|}}{CH}-)_y \sim \sim {}^{\ominus} \, {}^{\oplus}Li$$

$$CH_3-\overset{\underset{\displaystyle CH_2}{||}}{C}$$

, H$^+$/ MeOH

HO$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim$OH

Scheme 3. Styrene-Diene-Styrene Triblock Synthesis

"IN"

40° C, $CH_2=C$ with R, $CH=CH_2$

Li$^{\oplus}$ $^{\ominus}$———————IN~~~~~~~$^{\ominus}$ Li$^{\oplus}$

$CH_2=CH$, CH_3OH

————~~~~~IN~~~~~————

scrupulously cleaned and dried before use to prevent premature termination of the anions.

The difunctional initiator was first formed in cyclohexane in the reactor as described earlier. After using the chromatographic method to check for complete initiator formation, the desired amount of isoprene was pumped into the reactor and was polymerized under the previously described conditions.

At this point, it was thought that the steric nature of the anion should be modified to facilitate an efficient crossover to the methacrylate. For this reason, about 5% of styrene (by weight) was then added to the reactor to cap the polyisoprene chains. After the polymerization was complete, a small portion (200 ml) of the mixture was transferred to a 500 ml round bottom flask that was sealed with a rubber septum. The flask had been thoroughly dried under a nitrogen atmosphere. The transfer of these living anions to the round bottom flask was achieved by pressuring the solution through a syringe needle that was connected from the dip-tube on the reactor directly into the round bottom flask that contained a magnetic stirring bar.

An equal volume of doubly distilled THF was added to the flask after transfer was complete. The THF was added at low temperatures (-78°C) to prevent possible terminating side reactions between the anion and THF. Care should be taken when adding the cold THF to the cyclohexane as the solution may begin to freeze. However, after all the THF has been added, the solution was able to be cooled to -78°C without freezing.

The solution was cooled to -78°C with a dry ice/isopropanol bath after addition was complete. The desired amount of purified t-butyl methacrylate was then syringed into the flask. The monomer was added very slowly to prevent possible side reactions. If monomer was added quickly, the propagation rate was very rapid and the solution temperature increased which led to addition across the carbon-oxygen double bond. After about two hours, the polymer was terminated with a small amount of methanol and isolated by precipitation.

The precipitation of these polymers was quite difficult initially. The non-solvent system that gave the best results used methanol with about 5% isopropanol (to solubilize the cyclohexane). The polymer was isolated by addition of the solution into this mixture with stirring. At this point, distilled water was added until the polymer particles became large enough to filter. Methacrylate-diene block copolymers were synthesized by the following procedure which is shown in Scheme 4.

G. Monomer Purification

1. Butadiene and Isoprene

Butadiene was purified by pumping the monomer under nitrogen pressure through purification columns containing alumina, silica gel, and molecular sieves. For polymerizations done in the reactor, the desired amount of purified butadiene was then pumped into a holding tank which had volume calibrations. After the desired volume was in the holding tanks, it was pumped directly into the reactor.

For the high vacuum work, the purified butadiene from the holding tank was emptied into a round bottom flask containing calcium hydride that was kept cold in a dry ice/isoproponal bath. The flask was placed

Scheme 4. Methacrylate-Diene Copolymer Synthesis

"IN"

Li⊕   Li⊕

40°C, CYCLOHEXANE

$$CH_2 = \overset{\underset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$

Li⊕ ⊖ ~~~~~PI~~~~IN~~~~PI~~~~⊖ Li⊕

1. THF (1:1), -78°C

2.

$$CH_2 = \overset{\underset{\displaystyle \overset{\displaystyle C=O}{|}}{C}}{\overset{\displaystyle CH_3}{|}}$$

$$\overset{\displaystyle O}{|}$$

$$C(CH_3)_3$$

3. CH$_3$OH

$$(-\overset{\underset{\displaystyle \overset{\displaystyle C=O}{|}}{C}}{\overset{\displaystyle CH_3}{|}} - CH_2 -)_n ~~~~~PI~~~~~ (-CH_2 - \overset{\underset{\displaystyle \overset{\displaystyle O=C}{|}}{C}}{\overset{\displaystyle CH_3}{|}} -)_n$$

C(CH$_3$)$_3$ C(CH$_3$)$_3$

on the vacuum line and stirred for several hours with constant cooling

to limit possible pressure buildup due to the vaporization of butadiene.

The monomer was then distilled into a large graduated cylinder that

contained dibutyl magnesium and kept cold.

Isoprene was purified in a similar fashion for use both in the

reactor and for the high vacuum work. Fortunately, isoprene is not as

volatile as butadiene and it was easier to handle. However, the same

precautions were used during distillation and storage.

2. Styrene

Styrene monomer obtained from Fisher Scientific was first passed

through a basic alumina column under nitrogen and collected in a two-

neck, round bottom flask. This step removes the inhibitor and most of

the water.

The second step requires distillation from dibutyl magnesium under

modest vacuums, using an all glass apparatus. The description of the

components and glassware has been extensively discussed elsewhere (163).

The distillation of styrene was begun by first degassing the

monomer using the freeze/thaw cycle discussed earlier under modest

vacuum (500 millitorr) two or three times. It was also advisable to

flame the glassware during this procedure to remove traces of water from

the glass. After the monomer completely degassed, an inert atmosphere

(N_2) was placed over the solution and dibutyl magnesium was added until

a yellow color resulted. A slight excess was added and reacted for

several hours. This generally required 3-4 ml of dibutyl magnesium.

The solution was again degassed which serves the dual purpose of both

removing the nitrogen as well as the solvent that was present in

solutions of dibutyl magnesium. Distillation was achieved by heating the source with a hot water bath and cooling the receiver flask with dry ice/isopropanol. The distilled styrene was syringed directly from the receiver flask to the reactor or was pressured into another clean, dry, water and air free·flask with a double-ended needle for short term storage in a refrigerator.

3. t-Butyl Methacrylate

The effective purification of t-butyl methacrylate was crucial because the major impurity, t-butanol, will act as a terminating agent for the living polymer chains. The following purification procedure was used to remove this impurity as well as other protonic sources (166,167).

t-Butyl methacrylate (Rohm Tech) was first distilled from finely crushed calcium hydride. At this point, the monomer was placed in a septum capped brown bottle and stored in the freezer. Monomer stored in this fashion remained free of excessive polymer formation for long periods of time.

The second step was to distill the monomer from a trialkyl aluminum. Unlike linear alcoholic impurities, the branched alcohols react quite slowly with triethylaluminum. To circumvent this problem, triethylaluminum with about 20% of the more reactive diethylaluminum hydride was used as the purification agent.

The apparatus and the purification procedure that has been discussed elsewhere (163) was employed in this case as well except that the mixed purification agent was used. After distillation was complete,

the monomer was frozen and kept in the dark until needed. The monomer

was then thawed and removed by a syringe with a long needle when needed.

H. Instrumental Analysis Techniques

1. UV/Visible Spectroscopy

The spectrophotometer was auto-zeroed at a wavelength where the

solution does not absorb. A wavelength of 650 nm was chosen for zeroing

purposes. The spectrum was then taken by scanning at 120 nm/min from

650 to 190 nm at a chart speed of 5 nm/cm. The absorbance value was

taken directly from the digital readout panel of the spectrometer. The

maximum absorbance range of the instrument was 3.0 absorbance units.

The concentrations of reactants and products were kept low enough so

that the maximum absorbance did not exceed 2.0 absorbance units and a

linear detector response was maintained over the concentration range.

A Perkin-Elmer Model 552 microprocessor controlled UV/Visible

spectrophotometer equipped with a Model C 550-0555 thermoelectric

temperature controlled cell was used for this analysis. The temperature

controlled cell was set at the same temperature as the thermostated

water bath. Since the analysis time was short relative to the time

between each spectral run, the reaction mixture was not quenched.

2. Gas Chromatography

The gas chromatograph that was used initially was a Gow-Mac Series

550 instrument equipped with a thermal conductivity detector. For the

analysis, the detector and injector temperatures were set at 250°C and

the column temperature was maintained at 220°C. Helium was used as the

carrier gas with a flow rate of 80 ml/min. through the column. The

column was a four foot by one quarter inch aluminum column packed with

3% OV-101 on 100/120 mesh Anachrom/ABS. A Gow-Mac recorder Model 70-750, that was set at an output reading of 1 mV, was utilized.

The capillary chromatographic system consists of a Varian 6000 gas chromatograph equipped with a split/splitless injector and a flame ionization detector. The carrier gas was helium and breathing air mixed with hydrogen were used for flame gases. A summary of the chromatographic conditions are listed below.

Column Temperature:

    185°C for 0.5 min

    185°C to 235°C at 5°/min

Column Type: Hewlett-Packard Capillary column, crosslinked methyl silicone

Film thickness: 0.33 microns

ID: 0.2 mm length: 12 meter

Flow Rate: 2 ml/min He

Split Ratio: 50/1

Injector Temperature: 260°C

Detector Temperature: 275°C

Attenuation: 8

Range: 10^{-12} (Auto Zero On)

Air Flow Rate: 300 ml/min

H_2 Flow Rate: 25 ml/min

3. Fourier Transform Infrared Spectroscopy

a. Instrumentation

A Nicolet MX-1 FT-IR spectrophotometer was used and essentially all samples were films cast on sodium chloride windows. In most cases,

residual solvent did not overlap with any peaks of interest. However, if aromatic hydrocarbons were used as solvents, they were removed by placing the window in a vacuum oven overnight.

Typical operating conditions required the accumulation of 27 scans with a sensitivity of 4 cm^{-1}. Data was obtained from 4000-600 cm^{-1} as all peaks of interest appeared in this region. For qualitative interpretation, the output was obtained in percent transmittance but for improved accuracy, absorbance outputs were obtained for quantitative determinations.

b. Diene Microstructure

Quantitative determination of the relative amounts of stereochemical isomers along the diene backbone was easily obtained from this technique. Extinction coefficients have been established for each of the out of plane wagging modes for the vinyl C-H bonds of the cis, trans, and 1,2- configurations (165). Based on these extinction coefficients, the relative amounts of each component can be determined.

4. Proton NMR Spectroscopy

a. Instrumentation

All proton NMR studies were done on the Bruker WP-270 multinuclear NMR with a super conducting magnet. All polymer samples were dissolved in $CDCl_3$ at about 5% concentrations. It was thought that because the solvent peak was close to the aromatic protons (~7.3 ppm), that errors in integrating these protons would occur. However, one experiment using deuterated hexane showed no difference in peak integration compared with the deuterated chloroform.

b. Diene Homopolymers

Proton NMR on homopolymers of polybutadiene and polyisoprene were done in conjunction with FT-IR studies to confirm the high 1,4- content of these polymers. A broad singlet peak appearing at about 5.1 ppm, relative to TMS, due to the cis and trans 1,4-linkages and a doublet at about 4.8 ppm due to the 1,2-vinyl protons were ratioed to calculate the relative amounts of each.

c. Diene-Styrene Triblock Copolymers

For these systems, the NMR spectrum was used to determine the relative incorporation of the two monomers into the copolymer. A broad peak appearing at about 7.2 ppm due to the aromatic protons was ratioed to the vinyl protons of the diene phase to determine the amount of each monomer incorporated.

d. Diene-Methacrylate Triblock Copolymers

NMR spectroscopy was again used here as a method of determining relative amounts of monomer incorporation. As before, the diene phase was characterized by the vinyl protons of the 1,4- and 1,2-addition products. With the incorporation of t-butyl methacrylate, a singlet peak at about 1.4 ppm due to the t-butyl protons was observed. The ratio of the vinyl protons to the t-butyl protons was used to determine the percent incorporation of the two monomers.

The series of 3 weak peaks appearing at about 0.9 ppm were due to the α-methyl protons of the methacrylate and were due to the three possible tactic triads. Unfortunately, signal overlap with the more substituted esters occurs and quantitation was not possible. The

stereochemistry can be determined if desired by using the ^{13}C NMR integration of the carbonyl carbon (166,167).

5. Gel Permeation Chromatography (GPC)

Molecular weights and molecular weight distributions were determined by GPC. A Waters instrument equipped with a set of 500Å, 10^3Å, 10^4Å, and 10^5Å ultrastyragel columns at 30°C was used for the analysis.

Two detectors connected in series were used for sample detection. One was the universal refractive index detector and the other was a variable wavelength UV detector (Waters 490 Detector). The wavelength selected was determined by the class of polymer being analyzed. For dienes and methacrylates, 218 nm was used as the vinyl and carbonyl group absorbed strongly at this wavelength. Styrene containing polymers were analyzed at 254 nm.

All polymer samples were prepared by dissolving 0.5 mg in 5 ml of uninhibited THF, then filtered through a 0.45 μ filter and 100 μl was injected into the column via a Wisp 710B auto injector. Dried and uninhibited THF (stored under N_2) was used as the solvent.

6. Thermal Analysis

Thermal analysis was performed on the copolymers by a Perkin Elmer System 2 instrument. Differential scanning calorimetry (DSC) results were obtained on 5-10 mg of sample in sealed aluminum pans heated at 10°C/min. Thermal mechanical analysis (TMA) results were obtained by placing a pointed probe with a 1 g weight onto a thin polymer film and heating at 10°C/min.

V. RESULTS AND DISCUSSION

A. Purification of 1,3-Bis(α-phenylethenyl)benzene

The reaction of two moles of sec-butyllithium with one mole of DDPE in cyclohexane was investigated, with the objective of forming the dilithio compound shown previously. Elucidation of the kinetics and the mechanisms of the addition was the initial purpose of this project. The determination of the purity of the DDPE was crucial, because of the strict purity requirements needed for anionic polymerization. The DSC scans of the crude and purified material are shown in Figure 13. The crude material has a very broad melting range with maximum at about 45°C. After purification, the melting point was 38°C and the melting range was sharp. This substantial decrease in the melting point after purification was unusual, but it appears that some of the impurities are high melting and were removed by the purification method. The compounds that may be removed could include polar ketone or isomeric impurities. These impurities may include the diketone starting material, the monoketone monovinyl compound and also the para isomer.

Another qualitative indication of purity was achieved by reacting DDPE with the stoichiometric amount of sec-butyllithium, and subsequently using the dianion to polymerize butadiene. The UV/Visible spectrum of the resulting "living" polybutadienyllithium using the unpurified DDPE shows an absorbance at 430 nm, even after two subsequent 10 gram additions of butadiene. On the other hand, using the purified DDPE purified by distillation from n-butyllithium, no detectable absorbance at 430 nm was observed after addition of one 10 gram aliquot of butadiene as illustrated in Figure 14.

Figure 13. DSC Thermogram of Crude and Purified DDPE

ABSORPTION FOR DIANION ALONE

ABSORPTION AFTER FIRST
ADDITION OF BUTADIENE

ABSORPTION AFTER SECOND
ADDITION OF BUTADIENE

PURIFIED STARTING MATERIAL
AFTER ADDITION OF BUTADIENE

280   320   360   400   440   480   520   560   600

WAVELENGTH (NM)

Figure 14.   UV/Visible Spectra of Butadiene-capped DDPE

It appeared from this study that there were still some highly colored species present which were ionic in nature, but which were weakly basic and therefore incapable of initiating polymerization of more than one unit of butadiene. This also suggests that some of the para isomers may still be present and that this impurity results in a slow rate of initiation at the second anionic site. Moreover, an alkoxide formed by reaction of sec-butyllithium with any one of the ketone impurities will generate a colored species which again would not initiate butadiene.

One complicating factor in the handling of DDPE was that it was highly susceptible to oxidation reactions at the double bond when exposed to an oxygen containing atmosphere. The Fourier transform infrared (FTIR) spectrum of a sample of DDPE which had been exposed to air showed this point clearly. The appearance of a broad peak at about 3300 cm^{-1} indicates the presence of an alcohol functionality. Also the appearance of a peak at 1250 cm^{-1} was an indication of ether (or possibly epoxide) formation after only 1 hour exposure to the atmosphere. Thus, impurities as well would form colored species when reacted with sec-butyllithium. For this reason, DDPE should always be handled under vacuum or an inert atmosphere to prevent these side reactions.

B. High Vacuum Technique

1. Kinetic Analysis

The rate of the addition of sec-butyllithium to DDPE was easily followed by UV/Visible spectroscopy under high vacuum conditions. The reaction components in the solution that were of importance were

unreacted DDPE, the monoaddition product and the diaddition product.
The structure of these compounds are listed below:

DDPE   Monoadduct   Diadduct

where R is a sec-butyl group.

While maintaining the stoichiometric ratio of the two reactants,
the absorption peak due to unreacted DDPE (at 227.5 nm) was well
separated from the absorption peak of the resulting anionic species (at
430 nm). As the reaction proceeds, the absorbance peak of DDPE
gradually disappears with a corresponding increase in the peak due to
the anionic species.

Figure 15 shows a series of overlaid UV/Visible spectra which were
taken at various times during the reaction. The reaction temperature
was maintained at 18°C with a molar ratio of 2.1 to 1 (sec-butyllithium
to DDPE) where the starting amount of DDPE was about 4.0×10^{-5} moles at
all temperatures. The reaction was quite slow at this temperature in
cyclohexane and indeed took about 80 hours for quantitative conversion,
as evidenced by the maximum absorbance at 430 nm. Substantial rate
increases were observed at higher temperatures.

This increased reaction rate was clearly shown by the plots of the
DDPE absorbance at 227.5 nm versus reaction time. As the reaction
temperature was raised from 18°C to 60°C, reaction times for complete

Figure 15. Spectrophotometric Study of 1,3-Bis(α-phenylethenyl)-
benzene and Sec-butyllithium in Cyclohexane at 18°C
(BuLi/m-DDPE = 2.1)

conversion were decreased from about 80 hours to about two hours. Figure 16 shows a plot of the disappearance of DDPE with reaction time at the four different temperatures.

Plotting the appearance of the dianion as a function of time showed a corresponding increase in the absorbance over the course of the reaction. The maximum absorbance for the dianion at 60°C was again obtained in about two hours, as opposed to the much longer times needed at lower temperatures. Figure 17 shows the appearance of the ionic species at 430 nm at the four temperatures.

The proposed mechanism of the addition of sec-butyllithium to DDPE suggests a consecutive process (141), where the first mole of sec-butyllithium adds to DDPE to give the monoadduct (or monoaddition product), followed by the addition of the second mole of sec-butyl-lithium to the monoadduct to give the diadduct. Each step of the reaction has its own characteristic rate constant. Therefore, the disappearance of DDPE with time was a function of both the DDPE and sec-butyllithium concentrations. Scheme 4 outlines the proposed mechanism and the various kinetic expressions for each step of the addition.

The kinetic equation that contains the terms for DDPE and sec-butyllithium was used because the DDPE concentration could be monitored with reaction time. Before evaluating this equation, some assumptions had to be made. First, the order in DDPE concentration was assumed to be first order (133) and a fractional order of one fourth was assumed for the sec-butyllithium concentration (155). This was in accord with orders obtained for other "diene" initiation reactions in hydrocarbon solvents. Secondly, the concentration of sec-butyllithium was

Figure 16. Disappearance of DDPE with Reaction Time

Figure 17. Appearance of Ionic Species with Reaction Time

Scheme 5. Proposed Mechanism and Kinetic Expressions

$$\text{DDPE + sec-butyl Li} \xrightarrow{\quad k_1 \quad} \text{Mono}$$

$$\text{Mono + sec-butyl Li} \xrightarrow{\quad k_2 \quad} \text{Di}$$

$$-\frac{d(DDPE)}{dT} = k_1 \, (DDPE)^a \, (Li)^b$$

$$-\frac{d(Mono)}{dT} = k_2 (Mono)^c \, (Li)^d - k_1 \, (DDPE)^a (Li)^b$$

$$\frac{d(Di)}{dt} = k_2 \, (Mono)^c \, (Li)^d$$

equivalent to twice the concentration of DDPE. Making these substitutions, collecting similar terms, and integrating over the appropriate limits yields the final expression where $(DDPE)_t$ was the concentration of DDPE at a given time, t.

$$\frac{4}{(2)^{\frac{1}{4}} (DDPE)_t^{0.25}} = k_1 \, t \qquad\qquad (25)$$

The derivation of this equation is shown in Scheme 5.

Based on the data obtained from the change of DDPE concentration with time, one rate equation was evaluated. Firstly, the first order dependence on DDPE concentrations was determined from the absorbance of DDPE versus time for the four different reaction temperatures (Fig. 18). Linear behavior was observed at all temperatures based on correlation coefficients of 0.99 or greater. This confirmed one of the first assumptions that the first step in the reaction was first order in DDPE concentration as illustrated in Figure 18.

Lastly, if all the assumptions made in regards to reaction orders and concentrations were correct, the plot of $(DDPE)^{-0.25}$ versus reaction time from equation (1) above should yield a straight line. Straight line behavior was, in fact, observed at all temperatures (correlation coefficients of greater than 0.99), the slope of each of these lines providing a direct measure of the first rate constant (k_1) at each temperature and are shown in Figure 19.

In addition to fitting the data based on the one quarter order dependency of the sec-butyllithium concentration, fractional powers of one-half and one-sixth were also attempted. However, in these cases when plotting the resulting integrated expression versus reaction time,

Scheme 6. Kinetic Derivation

$$\frac{-d(DDPE)}{dT} = k_1 \, (DDPE)^a \, (sec\text{-}butyl \ Li)^b$$

Assume: $a = 1$, $b = 0.25$, $(sec\text{-}butyl \ Li) = 2(DDPE)$

$$\frac{-d(DDPE)}{dT} = 2^{1/4} k_1 (DDPE)^{5/4}$$

$$\frac{4}{2^{1/4}(DDPE)_t^{0.25}} + constant = k_1 \, t$$

Figure 18. First Order Plot of DDPE Concentration vs. Time

Figure 19. Plot of (DDPE)$^{-0.25}$ vs. Reaction Time

a poorer fit to a straight line resulted because a correlation

coefficient of less than 0.96 was obtained. Arrhenius behavior was

followed for the addition reaction and a linear relationship between the

natural logarithm of the first rate constant and inverse temperature

should result. In this case, straight line behavior was indeed

observed, as evidenced by a correlation coefficient of greater than

0.99. The slope of this straight line was proportional to the

activation energy for this first step. The calculated activation energy

was found to be about 19 Kcal/mole. Figure 20 illustrates this

Arrhenius plot in addition to the equation used to calculate the

activation energy.

2. Analysis of Post Reaction Products

After the reaction had gone to completion as evidenced by a maximum

absorbance at 430 nm, the reaction products were analyzed by other

spectroscopic techniques for complete reaction. Evidence for complete

reaction was obtained from both FTIR and proton NMR studies.

The FTIR spectrum of a film of DDPE on a salt plate showed a fairly

simple series of peaks at about 3100 cm^{-1} which resulted from aromatic

and vinyl carbon-carbon double bond stretching only. Also, a large peak

appearing at about 900 cm^{-1} which was due to the presence to carbon-

carbon double bonds was observed, as shown in Figure 21.

After reacting the stoichiometric amounts of sec-butyllithium and

DDPE, the dianion was terminated with methanol, which simply added a

proton to each anion. The terminated material was also analyzed by

FTIR. This spectrum shows a much more complicated series of peaks

around 3000 cm^{-1} which are due to the loss of double bond character and

Figure 20. Arrhenius Plot for Reaction of Sec-butyllithium and
1,3-bis(α-phenylethenyl)benzene in Cyclohexane

Figure 21. FTIR Spectrum of DDPB

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addition of aliphatic character from the sec-butyllithium. Also, the peak at about 900 cm^{-1} has all but disappeared due to the loss of vinyl groups. This spectrum is shown in Figure 22.

Convincing evidence for complete reaction was also shown by proton NMR. The NMR spectrum of DDPE in CDCl$_3$ showed the presence of only two peaks, one multiplet at about 7 ppm (relative to TMS) due to aromatic protons and a singlet at about 5 ppm due to the vinyl protons. Integration of the peaks gave the theoretically expected ratio of aromatic to vinyl protons.

After reaction with the stoichiometric amount sec-butyllithium under high vacuum conditions, the reaction product was terminated with methanol. A white solid was isolated after evaporation of the cyclohexane solvent. The proton NMR of this compound in CDCl$_3$ (about a 10% solution) again showed a peak at about 7 ppm due to the aromatic protons. However, no peak due to vinyl protons was observed. A multiplet at about 4 ppm was due to the two tertiary protons added from the methanol was observed. Lastly, the series of absorptions from 1-2 ppm were due to the aliphatic pentyl groups which arise from the addition of the sec-butyl group. The integration of these peaks gave the theoretically expected number of aromatic and aliphatic protons. This spectrum is illustrated in Figure 23.

3. Addition of Polar Modifiers

In spite of the fact that UV/Visible spectroscopy was not sensitive enough to detect all reaction products, it was an effective method for studying the effect of polar modifiers on the ion pair structure and the relative ability to act as a solvating or complexation agent. A series

Figure 22. FTIR of Terminated Reaction Product

Figure 23. Proton NMR Spectrum of Terminated Reaction Product

of mono- and bidentate ligands were added to the preformed difunctional initiator under high vacuum conditions. These resulted in a wavelength shift of the absorption maximum for the ionic species.

It is well established that there exists a series of equilibria between tight ion pairs, solvent separated ion pairs, and free ions. The equilibrium constant could be effected by primarily solvent polarity and to a lesser extent, the ionic concentration and temperature. These equilibria are illustrated below.

$$R-Li \rightleftharpoons R^-||Li^+ \rightleftharpoons R^- + Li^+ \tag{26}$$

In nonpolar solvents which possess a low dielectric constant, tight ion pairs were favored. As the solvent polarity was increased by, for example, the addition of a miscible, nonterminating polar solvent, the equilibria were shifted to the right with an accompanying increase in the concentrations of primarily solvent separated ion pairs.

Spectroscopically, this effect was observed by a shift to longer wavelengths as solvent separated ion pairs were formed. Energetically, solvent separated ion pairs are low energy species because of the delocalization of the ionic charges. Because of the simple equation

$$E = \frac{hc}{\lambda} \tag{27}$$

if the energy required to observe a transition was low, the wavelength at which the transition was observed will be at a high wavelength. Similarly, for tight ion pairs which were high energy species, more energy was required to observe at transition leading to an absorbance at a lower wavelength.

Figure 24 illustrates the above point very clearly. The solid curve was due to the spectrum of the dianion in pure cyclohexane alone. The characteristic wavelength maximum appeared at about 430 nm. After the addition of about 0.2 equivalents of THF, a second peak appeared at a longer wavelength in addition to the standard dianion peak seen previously in pure cyclohexane. This second absorption peak was due to the formation of solvents separated ion pairs. After the subsequent addition of more THF, only one peak with a wavelength maximum at 465 nm was present which was indicative of the complete formation of the solvent separated ion pairs.

A variety of polar modifiers were added to cyclohexane solutions of the dianion from ampules attached to the glass reactor. These included triethylamine, THF, tetramethylethylenediamine (TMEDA), and 1,2-dipiperidinoethane. Table 13 summarizes the wavelength maximum of the dianion after addition of the polar component and the resulting shift from the wavelength maximum for the dianion in cyclohexane alone.

After the addition of the small amount of TMEDA, no wavelength maximum could be obtained due to the loss of color which resulted from termination of the dianion. For both materials, rapid transmetalation reactions were occurring even at room temperature and loss of the visible absorbance resulted.

From this data, there were some additional correlations made between the reported vinyl content in diene polymers when polar modifiers were added to the polymerization solvent and the magnitude of the UV/Visible shift when the same polar material was added to this dianion (see Table 13). In purely hydrocarbon media, high 1,4 content

Figure 24. UV/Visible Spectra of the Dianion with and without THF

Table 13. Wavelength Shifts of Dianion after Addition of Polar Modifiers[1]

COMPONENT	λ_{Max}(nm)	$\Delta\lambda_{Max}$(nm)
Dianion Alone	430	--
Dianion + Triethylamine	462	32
Dianion + Tetrahydrofuran	465	35
Dianion + 1,2-Dipiperidinoethane	468	38
Dianion + Tetramethylethylenediamine[2]	--	--

[1] Molar ratio of modifier to chain end was ≥ 0.2. Solvent was cyclohexane.

[2] Premature termination was observed.

polydienes were obtained and a low wavelength maximum was observed for this dianion in cyclohexane. As the solvating power of the solvent was increased by the addition of a polar component, for example, by addition of triethylamine or THF, the 1,4- content of the polymer decreases and a shift to higher wavelengths was observed. This trend continues until the maximum wavelength shift for the most powerful solvating additive (1,2-dipiperidinoethane) was observed which, as hypothesized, produced the highest 1,2- content polydiene.

C.   High Pressure Reactor

   1.   Kinetic Study

      a.   NMR Study

Proton NMR was used to follow the disappearance of vinyl protons as a function of reaction time at ambient temperature. A gradual disappearance of the peak at about 4 ppm was observed with a corresponding gradual increase in the peaks in the aliphatic region of about 1 ppm. Two representative spectra taken at different times during the reaction are shown in Figure 25. Although the concentrations of the sample were not equivalent in each case, this was not a real problem in quantitating the NMR, because the area of the aromatic proton peak of the initiator was used as a standard peak to ratio the vinyl and aliphatic proton peaks. The area ratio of the aliphatic to aromatic protons was plotted versus reaction time and the resulting curve is shown in Figure 26. This plot was the first evidence that a consecutive reaction mechanism was taking place, because of the behavior of the aliphatic/aromatic ratio. The only missing piece of evidence would be a plot of the

PARTS PER MILLION

Figure 25. Proton Spectra of Reaction Mixture at Different Times

Figure 26. Plot of Integrated Ratios of Aliphatic to Aromatic Protons from Proton NMR

monoadduct concentration which would rapidly increase, then gradually

decrease with time if a consecutive mechanism were taking place.

NMR spectroscopy can not be used to completely elucidate the

reaction kinetics because the actual concentration of the monoadduct can

not be separated from the unreacted DDPE or the diadduct. For this

reason, direct evidence for a consecutive mechanism was not obtained.

b. Chromatographic Study of Concentrated Solutions

Because of the insensitivity of the UV/Visible and NMR methods, a

chromatographic method was developed that separated all components of

interest. Initial work involved reacting one mole of sec-butyllithium

with one mole of DDPE in cyclohexane so that all three components of

interest of interest (unreacted DDPE, mono-, and diaddition products)

would be present in the chromatogram and could be identified. An

aliquot of this solution was terminated with methanol and injected on

the gas chromatograph using the aforementioned conditions. All three

components were well separated from one another, and the total time of

analysis was about 15 minutes. Samples were withdrawn from the reactor

during the course of the reaction and analyzed using this technique.

The gas chromatographic method was sufficient for the analysis of the

samples taken from the reactor and prepared as stated earlier. The

chromatograms of three samples taken at different times during the

reaction are shown in Figure 27. In the chromatogram, the peak due to

the unreacted DDPE gradually decreased with reaction time. The peak due

to the diadduct gradually increased with reaction time. The peak due to

the monoadduct quickly reached a maximum peak height in about a half an

hour, then gradually decreased in height as the reaction continued.

1/2 HOUR

DDPE

8 HOUR

2 HOUR

2 HOUR

DIADDUCT

MONO-
ADDUCT

8 HOUR

1/2 HOUR

Figure 27. Chromatograms of Reaction Mixture of the Dianion
            Formation Reaction as a Function of Reaction Time

To determine the actual concentration of each component in the sample, an external method based on peak heights was used. This was done by preparing a series of standard solutions containing known amounts of the pure material which were injected for calibration purposes.

Standard solutions prepared with purified DDPE exhibited a linear response for Beer-Lambert type plots of concentration of DDPE versus detector response (or peak height) over the concentration range found in each sample. Similar results were obtained for the dianion. Because of the inability to obtain the monoadduct in pure form, the response per milligram of sample was estimated based on the average of the dianion and DDPE responses.

The concentrations of DDPE, mono-, and the diadduct in the samples were then calculated from this calibration curve. This was achieved by measuring the peak heights in the sample and then, from the calibration curve, the peak height corresponds to the amount present.

The concentrations of these three components were plotted versus reaction time to give the curves shown in Figure 28. This work confirms the NMR study which indicates that this reaction was indeed a consecutive reaction process.

One other interesting aspect of this work was that additional information was obtained concerning the rates of sec-butyllithium addition to each of the double bonds of DDPE. By using a computer program (173) to simulate rate data for a consecutive reaction to the actual experimental data, rate constants for each step of the reaction were estimated.

Figure 28.   Plot of Concentration for Reaction
             Components vs. Reaction Time at 50°C

Figure 29 shows a series of computer generated plots of concentration versus time for three components in a consecutive reaction. Immediately evident was the good correlation between this data and the experimental data shown previously. This suggests that the rate constants for each step used to calculate this data were very similar to the actual k_1 and k_2 in the initiator formation reaction.

One striking feature of both the theoretical and experimental data was that the monoadduct concentration never gets very high. In other words, once the monoadduct was formed, the second addition of sec-butyllithium was very fast. In fact, the theoretical curves shown here were calculated using a value of k_2 ten times larger than k_1.

At first glance, this was a rather surprising result as the opposite effect would seem the more likely result. It would appear that the addition of a base to a small molecule already containing a negative charge would be highly unfavorable.

In fact, it was determined that strong bases did add to another base in nonpolar media in ring opening reactions of siloxanolates with butyllithium (169,170). This was attributed to the ability of the siloxanolate to cross associate with unreacted sec-butyllithium (lithium siloxanolate and sec-butyllithium associated together in the same aggregate) which speeds the reaction. A similar argument can be used in this case. Here, the monoadduct can be cross associated with sec-butyllithium. This complex was more reactive towards addition of sec-butyllithium to the remaining vinyl group.

Figure 29. Computer Generated Concentration Plots for a
            Consecutive Reaction Mechanism with Three Components

c. Dilute Solutions

The use of the capillary column and the flame ionization detector permitted enhanced sensitivities over the previous GC system. Initiator solutions were analyzed directly from the reactor after termination with methanol, without the need for a concentration step.

The first experiment was to test the effect of concentration on the kinetics of the reaction. This was accomplished by using a one to one molar ratio of DDPE to sec-butyllithium in cyclohexane and observing relative amounts of the three reaction products of interest (DDPE, mono- and diadducts). Over the concentration range of 2.5×10^{-3} $\underline{M}$ to 1×10^{-1} $\underline{M}$, no observable change was observed in the product distribution indicating that the reaction kinetics were not changing over this concentration range, which were typically used in actual polymerizations.

The purpose of the second experiment was twofold. Firstly, to study if there was any effect on product distribution due to different termination reactions, and secondly, to test the possibility of an equilibrium condition being established between products and starting materials. This was achieved by again reacting a equimolar amounts of sec-butyllithium and DDPE , then adding purified THF, which in one case, serves as a terminating agent at elevated temperatures. The "living anion can abstract a proton from the THF molecule at the carbon adjacent to the oxygen. In the second case, purified THF at $-78°C$ was added prior to termination with methanol.

In neither case, was a change in the product distribution observed. This indicates that firstly, there was no effect on product distribution due to the mode of termination. Secondly, if, in the unlikely event

that an equilibrium condition was established, changing the solvent polarity would shift the equilibrium and hence, the product distribution after termination would have changed. This indeed was not the case which rules out the possibility of a reversible reaction.

The last experiment was to study the effect of added THF on the magnitude of the two rate constants which were determined by product distribution after termination and chromatographic analysis. It was well established that added polar solvents to reactions involving sec-butyllithium showed substantial rate enhancements.

This enhanced rate was very evident in these reactions that contained added THF. The reaction was complete in a matter of minutes which indicated that k_1 and k_2 were both very fast even at $-78°C$. However, the important question remained as to what effect solvent polarity had on k_1 and k_2 relative to each other.

In this set of experiments, toluene was used as the solvent because cyclohexane would freeze at very low temperatures. In addition, all reactions were done at $-78°C$ to limit possible side reactions between sec-butyllithium and THF.

Chromatographic results of the analysis of the product distribution showed the following trends. In pure toluene, the mono- and diadducts as well as unreacted DDPE concentrations were about equal. As the concentration of THF was increased, the amount of the dianion increased with decreasing amounts of DDPE and the monoadduct. It should be kept in mind that k_1 and k_2 were about equal (141) in pure toluene. But in the range of 0-1000 THF to lithium ratio, k_2 was increasing relative to k_1 as THF was added.. However, when the solvent was mostly THF with

small amounts of added toluene, the concentration of the monoadduct increased and the diadduct decreased with little change in the unreacted DDPE with decreasing amounts of toluene. This suggests that k_1 increases in this region compared with k_2 in the range of 4000-5000 THF to lithium ratio.

2. Polymerization Studies

a. Homopolymerizations of Dienes

Polymerization studies of dienes were undertaken using this dianion. Initial studies using butadiene as the monomer indicated that polybutadiene was produced but that its molecular weight was higher than predicted and the molecular weight distribution was broader than generally expected for an anionic polymerization.

Samples were removed from the reactor and terminated with methanol at various times during the polymerization reaction as a means of following conversion with time. Size exclusion chromatograms of these samples show that early in the reaction the molecular weight distribution was narrow as expected. However, as the reaction reached higher conversions, the distribution became much broader and remained broad to 100% conversion.

Figure 30 illustrates this effect. The curve at T = 0.5 hr represents a polymer sample taken at short reaction times. It was characterized by large elution volumes (low molecular weights) and a narrow molecular weight distribution, as expected. The curve at T = 3 hr represents a sample taken at high conversion and was characterized by a low elution volume and a molecular weight distribution that was

Figure 30. Polybutadiene Molecular Weight Determination at
            High and Low Conversions

considerably broader. All distributions were determined using a refractive index detector.

Table 14 summarizes the size exclusion chromatographic results for all the samples taken during the butadiene polymerization. The calculated molecular weight distributions up to about 80-85% conversion remained narrow but as the reaction approaches 90-100% conversion, the molecular weight distribution broadens considerably.

Similar results were observed when samples were analyzed using a UV detector at 218 nm. In most instances, this broadening effect was even more evident, to the point that in some cases a bimodal distribution was observed. This behavior was observed regardless of polymerization temperature, solvent/polymer ratio, or polymer molecular weight.

One explanation for this behavior was that initiation and propagation was not occurring from both ionic sites at the same time. Qualitative evidence confirming this suggestion was the orange color of the polymerization. Typical monofunctional living polymerizations of butadiene are clear. The only source of color would be from an unreacted anion on the initiator. However, the addition of a small amount of a polar modifier to the polymerization reduced the color to a faint yellow without eliminating the low molecular weight tail.

A second explanation was that at high conversions, a branching side reaction was occurring between the living chain end and a double bond along the backbone. This has been observed in some diene polymerizations (171,172) to liberate LiH. However, even at low temperatures and concentrations, this effect was still observed to the same degree, which made this explanation unlikely.

Table 14. GPC Results for Butadiene Polymerization

Reaction Time (MIN)	M_n	Polydispersity
10	26,700	1.16
20	54,200	1.09
30	70,300	1.12
60	86,400	1.28
90	86,700	1.64
180	115,600	1.58

* 10% solids (weight to weight) in cyclohexane

The last possible explanation of this phenomenon was that not all of the double bonds of the DDPE had reacted and that at high conversions, this double bond was being incorporated into the polymer and resulted in some star shaped polymer being formed. This was quite possible due to the fact that solutions of sec-butyllithium degraded with time. This effectively lowers the actual concentration of the solution which makes the amount charged less than needed to react with both double bonds.

One method of testing whether the initiator was completely formed before polymerization was to check it by the chromatographic method. If any double bonds remained unreacted, addition sec-butyllithium was charged into the initiator solution in the reactor and allowed to react. Then, the reaction was checked again for complete initiator formation. Once the initiator was completely formed, the desired amount of initiator was charged into the reactor to begin the polymerization.

Figure 31 illustrates the effect of unreacted initiator on GPC results (from the UV detector at 218 nm). In the upper right is shown a chromatogram of the initiator solution that contains approximately 10% unreacted DDPE. On the left is the GPC of the polybutadiene prepared from this initiator solution. The chromatogram exhibits a bimodal distribution in addition to having a higher molecular weight than was targeted (50,000).

Figure 32 shows the effect of complete formation of the initiator on the resulting GPC of polybutadiene. The initial gas chromatogram of the initiator solution showed about 9% unreacted DDPE. After addition of more sec-butyllithium, the resulting gas chromatogram is shown on the

GPC OF POLYBUTADIENE

GC OF TERMINATED INITIATOR

$M_n = 75000$

$M_w / M_n = 1.63$

DI

DDPE

MONO

0   5   10   15

RETENTION TIME (MIN)

ELUTION VOLUME

Figure 31. Effect of Unreacted DDPE on GPC Results of Polybutadiene

GPC OF POLYBUTADIENE

GC OF TERMINATED INITIATOR

$M_n = 52000$

$M_w / M_n = 1.05$

29

30

31

ELUTION VOLUME

DDPE

MONC

DI

0   5   10   15

RETENTION TIME (MIN)

Figure 32.   Effect of Complete Initiator Formation on
Polybutadiene Molecular Weight Distribution

left side of this figure where the amount of unreacted DDPE was less than 1%.

This initiator solution was then used to polymerize butadiene. The GPC of the polymer is shown on the left side of the figure. In this case where initiator formation was maximized, very narrow and monomodal molecular weight distributions were obtained. In addition, the number average molecular weight was very close to the theoretical molecular weight of 50,000.

This procedure worked very nicely for butadiene polymerization but the next question was how well it worked for the polymerization of isoprene. Isoprene has a higher polymerization rate than butadiene in cyclohexane (168) which could lead to broader molecular weight distribution.

Figure 33 shows a typical GPC of a polyisoprene prepared with the difunctional initiator that was stabilized with Irganox 1010 and isolated by evaporation of the solvent and had less than 1% unreacted DDPE. Even in isoprene polymerizations, a narrow predictable molecular weight distribution was obtained (theoretical molecular weight = 50,000).

b. Hydroxyl Functionalization of Polyisoprene

The isolated hydroxyl terminated polymer prepared by ethylene oxide capping was analyzed in an attempt to characterize the molecular weight of the polymer as well as the number of hydroxyl groups per polymer chain (hydroxyl number). It was critical that the hydroxyl number be 2.0 so that these low molecular weight polymers could be incorporated as soft segments into purely linear polyurethanes.

$$M_n = 50000$$

$$M_w / M_n = 1.04$$

ELUTION VOLUME

Figure 33. GPC of Polyisoprene

Proton NMR proved to be the most effective method of characterizing these polyols. Figure 34 shows a spectrum of about a 10% solution of the polyisoprene polyol in $CDCl_3$. This spectrum is characterized by strong absorbances in the vinyl proton region about 4.5-5.5 ppm that were attributed to unsaturated protons of the isoprene repeat unit as well as aromatic protons from the initiator fragment around 7 ppm and hydroxyl protons at about 3.5 ppm, that were due to the functionalized end groups.

By comparing the vinyl to aromatic protons integrations, a number average molecular weight of 2825 was calculated. Also, a hydroxyl number of two was determined by comparing the hydroxyl to vinyl proton integrations. A hydroxyl number of 2.0 was also determined by comparison of the hydroxyl and aromatic protons. The vinyl proton region also confirmed the expected high 1,4- microstructure of the isoprene backbone.

c. Polymerizations of Isoprene and Styrene

Once high molecular weight diene homopolymers could be reproducibly prepared with predictable molecular weights and narrow molecular weight distributions, the next step was to prepare some triblock copolymers containing styrene and isoprene. It was hoped that these copolymers would have narrow molecular weight distributions, complete incorporation of the styrenic phase, and have physical properties that were comparable to commercial thermoplastic elastomers. Again, the technique of optimizing the initiator formation was used prior to polymerization. The sequential addition of monomers was used for each case, the isoprene

Figure 34. Proton NMR of Hydroxyl Terminated Polyisoprene in CDCl₃

was added first and completely converted to monomer before styrene was added.

Figure 35 shows a typical GPC of a styrene-isoprene-styrene copolymer. Though the calculated molecular weight was not very meaningful since it was based on polystyrene standards, it was significant that high molecular weight and narrow distribution were obtained.

A series of copolymers was synthesized which contained various amounts of hard (styrene) and soft (isoprene) phases. Theoretical incorporations ranged from 80% to 20% of the hard phase. All copolymers were characterized by a narrow molecular weight distribution and high molecular weight.

Proton NMR was used to determine composition. A typical spectrum of a styrene-isoprene triblock copolymer dissolved in $CDCl_3$ is shown in Figure 36. The spectrum was characterized by two important absorption regions, one in the aromatic region and the other in the vinyl region. The ratio of these absorbances was used to calculate relative incorporations of monomers. These calculations agreed well with theoretical values based on monomer charge. In addition, the vinyl proton region clearly indicated high 1,4 content in the diene phase, typical of polymerizations in cyclohexane.

Table 15 summarizes the GPC and NMR data for this series of copolymers. In all cases, molecular weights of the polyisoprene and incorporation of styrene were very close to theoretical values.

A second set of experiments utilized three triblock copolymers which contained 40% styrene and 60% isoprene. However, in this case,

$$M_n = 59000$$

$$M_w / M_n = 1.06$$

ELUTION VOLUME

Figure 35. GPC of Styrene-Isoprene Block Copolymer

Figure 36. Proton NMR Spectrum of Styrene-Isoprene Block Copolymer

Table 15. GPC and Proton NMR Analysis of
Styrene-Isoprene Block Copolymers

Block Mol. Wt. (Theory)	Isoprene Mol. Wt. (GPC)	Composition (^{1}H NMR)
80K I	79K	77%
20K S		23%
60K I	55K	68%
40K S		32%
40K I	35K	44%
60K S		56%
20K I	14K	17%
80K S		83%

All molecular weight distributions (M_W/M_n) were 1.2 or less.
Distributions become slightly broader with increasing styrene content.

the initiator solutions contained 0%, 5%, and 10% excess of unreacted

DDPE before any monomer was added. As expected, the polymers that had

contained excess DDPE had a broad molecular weight distribution, yet

from proton NMR analysis, had the desired incorporation of both

monomers. Additionally, extremely viscous polymerization solutions

resulted with increasing amounts of excess DDPE. Figure 37 illustrates

the effect of 0%, 5%, and 10% unreacted DDPE still in the initiator

solution on the GPC of the copolymers.

c. Diene-Methacrylate Copolymers

In this case, polyisoprene was again used as the center block in

these polymerizations. The isoprene homopolymer was again characterized

by GPC which showed a narrow molecular weight distribution and the

desired molecular weight.

A variety of experiments were attempted to facilitate the efficient

crossover to t-butyl methacrylate. Initial studies were done in

cyclohexane alone with and without the chain end modified with a small

amount of polystyrene. In both cases, proton NMR analysis showed 100%

conversion of the methacrylate. A typical NMR spectrum of the copolymer

is shown in Figure 38.

However, GPC curves of these copolymers prepared in pure

cyclohexane showed bimodal distributions with one of the peaks having

twice the molecular weight of the other. Figure 39 shows a typical

chromatogram of one of these polymers. In addition, cloudy cast films

(from cyclohexane) were obtained. One possibility is that extensive

coupling was taking place to produce large amounts of homopolymer

contamination. Alternatively, the initiator efficiency may be low.

0% Excess DDPE   5% Excess DDPE   10% Excess DDPE

Figure 37. GPC of 60% Isoprene, 40% Styrene Triblock Copolymers with Various Amounts of Unreacted DDPE

270 MHz
CDCl$_3$ (5% wt.)

O(CH$_3$)$_3$

1,4

3,4

α -CH$_3$

TMS

ppm

Figure 38. Proton NMR Spectra of t-Butyl
Methacrylate-Isoprene Block Copolymer

Figure 39. GPC of t-Butyl Methacrylate-Isoprene Block
Copolymer Exhibiting Bimodal Distributions

Further studies were undertaken; the solvent was modified with small amounts of THF (about 10 to 1 THF to lithium chain end). Again, proton NMR analysis showed 100% conversion of the methacrylate, but the GPC curves again showed a bimodal distribution. However, this time the homopolymer contamination was noticeably less than the previous case. It appeared that the addition of a small amount of THF improves the block copolymer yield compared with cyclohexane alone.

The next series of experiments involved modifying the solvent with large amounts of THF. In this case, the cyclohexane was diluted with an equal volume of THF prior to addition of the methacrylate (about 8000 to 1 THF to lithium). Proton NMR showed 100% conversion of the methacrylate, but in this case, Figure 40 shows the GPC curve was monomodal for a methacrylate-diene triblock copolymer. Moreover, a very narrow distribution was noted for samples with and without styrene. One other important aspect of these polymers was that cast films from cyclohexane were clear and transparent. Table 16 summarizes the diene-methacrylate work.

Some preliminary thermal analysis has also been done on these copolymer films. Thermal mechanical analysis of the isoprene-t-butyl methacrylate and isoprene-styrene-t-butyl methacrylate copolymers is shown in Figure 41. For the isoprene-t-butyl methacrylate copolymers, a sharp Tg was observed for each phase with a pronounced rubbery plateau between them which was indicative of a phase separated system. Similarly, for the styrene modified system, two Tg's were observed with the isoprene transition being slightly higher and the methacrylate slightly lower. It appears that some phase mixing of the styrene was

$$\overline{M}w \: / \: \overline{M}n = 1.10$$

23   25   27   29   31

Figure 40.   GPC t-Butyl Methacrylate-Isoprene
             Triblock Copolymer Modified with THF

Table 16. Summary of t-Butyl Methacrylate-Isoprene
Triblock Copolymerizations with and without THF
and Capping of the Diene Phase with Styrene

Sample	Solvent	Molecular Weight (Diene Phase)	%TBMA (^{1}H NMR)	M_w/M_n
Polyisoprene (80K)		79,400		1.10
TBMA-I-TBMA	Cyclohexane	79,400	29	Bimodal*
TBMA-S-I-S-TBMA	Cyclohexane	79,400	29	Bimodal*
TBMA-I-TBMA	THF	79,400	29	1.10**
TBMA-S-I-S-TBMA	THF	79,400	29	1.25**

* Cloudy films from cyclohexane

** Clear films from cyclohexane

Figure 41. Thermal Mechanical Analysis of t-Butyl
Methacrylate-Isoprene Block Copolymers
With and Without Added Styrene in Air

occurring with both phases. In addition, an increase in the modulus was

also observed which was another indication of phase mixing with the

styrene phase.

VI. CONCLUSIONS

The investigations discussed in this thesis form the basis for the following conclusions discussed below.

1. High purity of the DDPE was of paramount importance. When distilled from dibutylmagnesium, this material has fewer impurities than either the as received sample or the recrystallized material. Distillation from n-butyllithium was the best method of purification since the high purity was obtained without contamination by metal ion containing species.

2. Temperatures of 60°C for the reaction between sec-butyllithium and DDPE in cyclohexane permitted conversion to the dianion in approximately two hours under high vacuum conditions as judged by UV/Visible spectroscopy.

3. Quantitative conversion to the dianion was also indicated by ^{1}H NMR and FTIR spectra of the methanol terminated reaction product. No residual absorbances due to carbon-carbon double bonds were observed.

4. From the assumptions that this was a consecutive reaction, orders of one-fourth and one for the sec-butyllithium and DDPE concentrations, respectively, were observed. The apparent energy of activation for the dianion formation was found to be 19 Kcal/mole based on Arrhenius behavior over a range of temperatures under high vacuum conditions.

5. The UV/Visible method was not sensitive enough to detect both the mono- and diadducts which prevented direct confirmation of the proposed consecutive process. However, gas chromatographic analysis of the reaction mixture allowed quantitative determination of the mono- and

diadducts as well as the unreacted DDPE and confirmed the hypothesis of a consecutive reaction.

6. Polymerizations of butadiene and isoprene using this difunctional initiator initially showed a broad molecular weight distribution at high conversions. When the gas chromatographic method was used to maximize initiator formation, diene homopolymers were prepared with narrow polydispersities and predictable molecular weights.

7. Triblock copolymers of styrene and isoprene were prepared in cyclohexane that had narrow polydispersities and the desired incorporation of both monomers.

8. Methacrylate-diene triblock copolymers were prepared with narrow polydispersities and the desired incorporation of both monomers if the solvent was modified with large amounts of THF. Clear films were obtained and thermal analysis exhibited properties expected for thermoplastic elastomers.

VII. SUGGESTED FUTURE STUDIES

Several aspects of this initiation reaction and the subsequent use
of this initiator for polymerization require further elucidation. These
areas include the following:

1. Continuation of the kinetic study using the nitrogen pressure
reactor and the gas chromatographic method to obtain apparent rate
constants and activation energies for rate constants when sec-
butyllithium was added to DDPE in a variety of solvents.

2. Clarify the role of added THF on relative magnitudes of the two
rate constants over a wide range of THF concentrations.

3. Continue to study the effect of solvent polarity on the
physical properties of styrene-diene triblocks to make certain that both
anions on the initiator isoreactive towards initiation and propagation.

4. Prepare t-butyl methacrylate-diene triblock copolymers that are
then hydrolyzed and/or hydrogenated to prepare novel ionomers with
extended use temperatures.

5. Prepare a variety of all acrylic triblock copolymers as a route
to some novel thermoplastic elastomers which can be hydrolyzed to form
purely acrylic ionomers.

VIII. BIBLIOGRAPHY

1. F.E. Mathews and E.H. Strange, British Patent (to London Co.), 24,790 (1910).

2. C. Harries, U.S. Patent (to Farbenfabriken varm. Friedr. Bayer and Co.), 1,058,056 (1913).

3. W. Schlenk, W.J. Appenrodd, A. Michal, and A. Thal, Ber., 47, 473 (1914).

4. K. Ziegler, Ann., 473, 1 (1929).

5. K. Ziegler, F. Dersch, and H. Wollthan, Ann., 511, 13 (1934).

6. K. Ziegler and L. Jakob, Ann., 511, 45 (1934).

7. K. Ziegler, et al., Ann., 511, 64 (1934).

8. W.C.E. Higginson and N.S. Wooding, J. Chem. Soc., 760 (1952).

9. F.W. Stavely, et al., Ind. Eng. Chem., 48, 778 (1956).

10. H. Hsieh and A.V. Tobolsky, J. Polym. Sci., 25, 245 (1957).

11. N.D. Scott, J.F. Walker, and V.L. Hansby, J. Am. Chem. Soc., 58, 2442 (1936).

12. D.E. Paul, D. Lipkin, and S.I. Weissman, J. Am. Chem. Soc., 78, 116 (1956).

13. D. Lipkin, D.E. Paul, J. Townsend, and S.I. Weissman, Science, 117, 534 (1953).

14. G.J. Hoijtink, W.P. Weijland, Rec. Trav. Chim., 74, 277 (1955), and 75, 487 (1956).

15. R. Milkovich, M. Levy, and M. Szwarc, J. Am. Chem. Soc., 78, 2656 (1956).

16. M. Szwarc, Nature, 178, 168 (1956).

17. R.E. Robertson and L. Marion, Can. J. Res., 26B, 657 (1948).

18. K.F. O'Driscoll and A.V. Tobolsky, J. Polym. Sci., 37, 363 (1959).

19. C.G. Overberger and N. Yamamoto, J. Polym. Sci., Part B, 3, 569 (1965).

20. D.J. Worsfold and S. Bywater, Can. J. Chem., 38, 363 (1959).

21. F. Hein and H. Schram, _Z. Physik. Chem._, _A/151_, 234 (1930).

22. T.L. Brown and M.T. Rogers, _J. Am. Chem. Soc._, _79_, 1859 (1957).

23. T.L. Brown, et al., _J. Am. Chem. Soc._, _84_, 1371 (1962).

24. T.L. Brown, et al., _J. Am. Chem. Soc._, _86_, 2134 (1964).

25. T.L. Brown, _J. Organometal. Chem._, _3_, 1 (1965).

26. T.L. Brown, _Acc. Chem. Res._, _1_, 23 (1968); H.L. Lewis, and T.L. Brown, _J. Am. Chem. Soc._, _92_, 4664 (1970).

27. D. Margerison and J.P. Newport, _Trans. Faraday Soc._, _59_, 2058 (1963).

28. G. Wittig, et al., _Ann._, _571_, 167 (1951).

29. S. Bywater and D.J. Worsfold, _J. Organometal. Chem._, _10_, 1 (1967).

30. M. Weiner, et al., _Inorg. Chem._, _1_, 654 (1962).

31. W.H. Glaze and C.H. Freeman, _J. Am. Chem. Soc._, _91_, 7198 (1969).

32. D.J. Worsfold and S. Bywater, _Can. J. Chem._, _38_, 1891 (1960).

33. H. Hsieh, _J. Polym. Sci., Part A_, _3_, 163 (1965).

34. A.F. Johnson and D.J. Worsfold, _J. Polym. Sci., Part A_, _3_, 449 (1965).

35. D.J. Worsfold and S. Bywater, _Can. J. Chem._, _42_, 2884 (1964).

36. A. Guyot and J. Vialle, _J. Macromol. Sci., Chem._ _A4_, 79 (1970); _J. Polym. Sci. Part B_, _6_, 403 (1968).

37. J.E.L. Roovers and S. Bywater, _Macromolecules_, _1_, 328 (1968).

38. J.E.L. Roovers and S. Bywater, _Trans. Faraday Soc._, _62_, 1876 (1966).

39. M. Morton and L.J. Fetters, _Rubber Chem. Technol._, _48_, 359 (1975).

40. M. Morton, E.E. Bostick, and R. Livigni, _Rubber Plast. Age_, _42_, 397 (1961).

41. M. Morton, R.A. Pett and L.J. Fetters, _Macromolecules_, _3_, 333 (1970).

42. T.L. Brown, _J. Organomet. Chem._, _5_, 191 (1966).

43. T.L. Brown, <u>Adv. Organomet. Chem.</u>, <u>3</u>, 365 (1965); <u>Ann. N.Y. Acad. Sci.</u>, <u>136</u>, 95 (1966); <u>Pure Appl. Chem.</u>, <u>23</u>, 447 (1970).

44. W. Glaze, J.E. Hanicak, D.J. Berry, and D.P. Duncan, <u>J. Organomet. Chem.</u>, <u>44</u>, 49 (1972).

45. P.D. Bartlett, C.U. Goebel, and W.P. Weber, <u>J. Am. Chem. Soc.</u>, <u>91</u>, 7425 (1969).

46. W.H. Glaze, T. Lin, and E.G. Felton, <u>J. Am. Chem. Soc.</u>, <u>88</u>, 4101 (1966).

47. J.P. Oliver, J.B. Smart, and M.T. Emerson, <u>J. Am. Chem. Soc.</u>, <u>88</u>, 4101 (1966).

48. H.S. Mukowski and M. Lynn, <u>J. Macromol. Chem.</u>, <u>1</u>, 443 (1966).

49. A.L. Gatzke, <u>J. Polym. Sci.</u>, <u>Al</u>, 7, 2281 (1969).

50. C. Bundy and A.C. Purkis, Liquid Polymers Symposium, University of Surrey, England, Sept. 1972.

51. J.E.L. Roovers and S. Bywater, <u>Trans. Faraday Soc.</u>, <u>62</u>, 701 (1966).

52. M. Morton, E.E. Bostick, R.A. Livigni, and L.J. Fetters, <u>J. Polym. Sci., Part A</u>, <u>1</u>, 1735 (1963).

53. M. Morton, L.J. Fetters and E.E. Bostick, <u>J. Polym. Sci., Part C</u>, <u>1</u>, 311 (1963).

54. M. Morton, L.J. Fetters, R.H. Pett, and J.F. Meier, <u>Macromolecules</u>, <u>3</u>, 326 (1970).

55. M. Morton and L.J. Fetters, <u>J. Polym. Sci., Part A</u>, <u>2</u>, 3311 (1964).

56. M. Morton, <u>Polymer Preprints</u>, <u>5</u>, 1092 (1964); <u>Advan. Chem. Ser.</u>, <u>52</u>, 1 (1966).

57. H. Sinn and E. Patat, <u>Angew. Chem.</u>, <u>75</u>, 805 (1963).

58. M. Szwarc, <u>Science</u>, <u>170</u>, 23 (1970).

59. K.F. O'Driscoll and A.V. Tobolsky, <u>J. Polym. Sci.</u>, <u>35</u>, 259 (1959).

60. F.J. Welch, <u>J. Am. Chem. Soc.</u>, <u>81</u>, 1345 (1959); <u>82</u>, 6000 (1960).

61. M. Morton, R.A. Pett, and J.F. Fellers, Prepr. IUPAC Macromol. Symp., vol. 1, p. 69 (1966).

62. A. Korotkov, N.N. Chesnokova and L.B. Truchmanova, <u>Vysokomol Soedin</u>, <u>1</u>, 46 (1959); <u>Polym. Sci. USSR</u> (Engl. Transl.), <u>1</u>, 10 (1960); <u>Rubber Chem. Techn.</u>, <u>33</u>, 610 (1960).

63. L.J. Fetters, <u>J. Res. Natl. Bur. Stand., Sec. A</u>, <u>69</u>, 159 (1965).

64. A. Guyot and J. Vialle, <u>J. Macromol. Sci., Chem.</u> <u>A4</u>, 107 (1970).

65. J. Minoux, B. Francois, and C. Sadron, <u>Macromol. Chem.</u>, <u>44-46</u>, 519 (961); J. Minoux, <u>Rev. Gen. Caoutch</u>, <u>39</u>, 779 (1962); <u>Makromol. Chem.</u>, <u>61</u>, 22 (1963).

66. D. Margerison, D.M. Bishop, G.C. East, and P. McBride, <u>Trans. Faraday Soc.</u>, <u>64</u>, 1872 (1968).

67. D.N. Cramond, P.S. Lawry, and J.R. Urwin, <u>Eur. Polym. J.</u>, <u>2</u>, 107 (1966).

68a. P.D. Bartlett, S. Friedman, and M. Stiles, <u>J. Am. Chem. Soc.</u>, <u>75</u>, 1771 (1953).

68b. P.D. Bartlett, S.J. Tauber, and W.P. Weber, <u>J. Am. Chem. Soc.</u>, <u>91</u>, 6362 (1969).

69. E.N. Kropacheva, B.A. Dolgoplosk, and E.M. Kuznetsova, <u>Dol. Akad. Nauk. S.S. S.R.</u>, <u>130</u>, 253 (1960).

70. N. Smirnowa, V. Sgonnik, K. Kalninsch, and B. Erussalimsky, <u>Makromol. Chem.</u>, <u>178</u>, 733 (1977).

71. T.E. Hogen-Esch and J. Smid, <u>J. Am. Chem. Soc.</u>, <u>88</u>, 307 (1966); 87, 669 (1965).

72. H. Hostalka, R.V. Figini, and G.V. Schultz, <u>Makromol. Chem.</u>, <u>71</u>, 198 (1964).

73. H. Hostalka and G.V. Schultz, <u>Z. Physik. Chem.</u>, <u>45</u>, 286 (1965).

74. D.N. Bhattacharyya, C.L. Lee, J. Smid, and M. Szwarc, <u>Polymer</u>, <u>5</u>, 54 (1964).

75. D.N. Bhattacharyya, C.L. Lee, J. Smid, and M. Szwarc, <u>J. Phys. Chem.</u>, <u>69</u>, 612 (1965).

76. M. Szwarc and J. Smid, "The Kinetics of Anionic Polymerization and Copolymerization," Chap. 5 in "Progress in Reaction Kinetics", Vol. 2, G. Porter, Ed., Pergamon, Oxford, 1964.

77. D.J. Worsfold, S. Bywater, <u>J. Chem. Soc.</u>, <u>5</u>, 234 (1960).

78. G. Allen, G. Gee, and C. Stretch, *J. Polym. Sci.*, <u>48</u>, 189 (1960);
    C. Stretch and G. Allen, *Polymer*, <u>2</u>, 151 (1961).

79. D.N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, <u>69</u>,
    624 (1965).

80. F.S. Dainton, et al., *Makromol. Chem.*, <u>89</u>, 257 (1965);
    Eur. Polym. J., <u>5</u>, 382 (1969).

81. P. Chang, R.V. Slates, and M. Szwarc, *Phys. Chem.*, <u>70</u>, 3180
    (1966).

82. C. Geacintov, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, <u>84</u>, 2508
    (1962).

83. M. Szwarc, *Acct. Chem. Res.*, <u>2</u>, 87 (1969).

84. T. Shimomura, K.J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem.
    Soc.*, <u>89</u>, 796 (1967).

85. J.E.L. Roovers and S. Bywater, *Can. J. Chem.*, <u>46</u>, 2711 (1968).

86. M. Van Beylen, M. Fisher, J. Smid, and M. Szwarc, *Macromolecules*,
    <u>2</u>, 575 (1969).

87. T. Shimomura, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, <u>89</u>, 5743
    (1967).

88. S. Bywater and D.J. Worsfold, *Can. J. Chem.*, <u>40</u>, 1565 (1962).

89. L.J. Fetters and R.J. Young, in "Anionic Polymerization:
    Kinetics, Mechanisms, and Synthesis," McGrath, J.E., ed., ACS
    Symposium Series 166, Am. Chem. Soc., Washington D.C., 1980, p.
    95.

90. A.W. Langer, *Trans. N.Y. Acad. Sci.*, <u>27</u>, 74 (1965).

91. G. Helary and M. Fontanille, *Eur. Polym. J.*, <u>14</u>, 345 (1978).

92. A. Davidjan, et al., *Macromol. Chem.*, <u>177</u>, 2469 (1976).

93. V. Collet-Marti, S. Dumas, J. Sledz, and F. Schue, *Macromolecules*,
    <u>15</u>, 251 (1982).

94. A. Davidjan, et al., *Macromol. Chem.*, <u>179</u>, 2155 (1978).

95. J.E.L. Roovers and S. Bywater, *Polymer*, <u>14</u>, 594 (1973).

96. G. Helary and M. Fontanille, *Polym. Bull.*, <u>3</u>, 159 (1980).

97. R.P. Quirk, D.E. Kester, and R.D. Delaney, <u>J. Organomet. Chem.</u>, <u>59</u>, 45 (1973).

98. R.P. Quirk and D.E. Kester, <u>J. Organomet. Chem.</u>, <u>C23</u>, 72 (1974).

99. R.P. Quirk and D.E. Kester, <u>J. Organomet. Chem.</u>, <u>127</u>, 111 (1977).

100. R.P. Quirk and D. McFay, <u>Macromol. Chem.</u>, <u>Rapid Commun.</u>, <u>1</u>, 71 (1980).

101. R.P. Quirk, in "Anionic Polymerization: Kinetics Mechanisms and Synthesis," McGrath, J.E., ed., ACS Symposium Series, Am. Chem. Soc., Washington D.C., 1981, p. 117.

102. R.P. Quirk and D. McFay, <u>J. Polym. Sci.</u>, <u>Polym. Chem. Ed.</u>, <u>19</u>, 1445 (1981).

103. A.V. Tobolsky and C.E. Rogers, <u>J. Polym. Sci.</u>, <u>40</u>, 73 (1959).

104. A. Rembaum, F.R. Ells, R.C. Morrow, and A.V. Tobolsky, <u>J. Polym. Sci.</u>, <u>61</u>, 155 (1962).

105. R.S. Sterns and L.E. Forman, <u>J. Polym. Sci.</u>, <u>41</u>, 381 (1959).

106. D.J. Worsfold and S. Bywater, <u>Macromolecules</u>, <u>11</u>, 582 (1978).

107. L.J. Fetters, "Kinetic and Mechanistic Aspects of Polymerizations Involving Organolithium Species," N.Y. Acad. Sci., New York, 1974.

108. M. Morton, R.D. Sanderson and R. Sakata, <u>Polymer Lett.</u>, <u>9</u>, 61 (1971).

109. M. Morton, R.D. Sanderson, and R. Sakata, <u>Macromolecules</u>, <u>6</u>, 181 (1973).

110. M. Morton, L. Falvo, and L.J. Fetters, <u>Macromolecules</u>, <u>6</u>, 190 (1973).

111. A.F. Halasa, D.F. Lohr, and J.E. Hall, <u>J. Polym. Sci.</u>, <u>Polym. Chem. Ed.</u>, <u>19</u>, 1357 (1981).

112. D.J. Worsfold and S. Bywater, <u>Makromol. Chem.</u>, <u>Rapid Commun.</u>, <u>3</u>, 239 (1982).

113. A. Noshay and J.E. McGrath, "Block Copolymers: Overview and Critical Survey," Academic Press, Inc., New York, 1977.

114. A. W. van Breen and M. Vlig, <u>Rubber Plast. Age</u>, <u>47</u>, 1070 (1966).

115. Shell Chemical Co., Belgium Patent, 671460 (1966).

116. M. Morton, <u>Ency. of Polym. Sci. & Techn.</u>, <u>15</u>, 508 (1971).

117. K.C. Eberly, U.S. Patent (to Shell), 2,947,793 (1960).

118. R.P. Zelinski and G.W. Strobel, U.S. Patent (to Phillips), 3,108,994 (1963).

119. R.P. Zelinski and H.L. Hsieh, U.S. Patent (to Phillips), 3,078,254 (1963).

120. L.J. Fetters and M. Morton, <u>Macromolecules</u>, <u>2</u>, (1960).

121. M. Morton, et al., <u>Rubber Chem. Technol.</u>, <u>49</u>, 303 (1976).

122. G. Setzhorn, R. Heldt, and K.F. Gehrke, <u>Wiss Z. TH. Leuna-Messeburg</u>, <u>19</u> (4), 589 (1977).

123. C.W. Kamienski, A.C. Diesing, and R.C. Morrison, U.S. Patent (to Lithium Corp.), 3388178 (1968); 3452112 (1969).

124. R.P. Foss, H.W. Jacobson, and W.H. Sharkey, <u>Macromolecules</u>, <u>10</u>, 287 (1977).

125. B. Francois, M. Vernois, and E. Franta, Fr. Patent (to Agence Nationale de Valorisa de la Recherche), 2300097 (1975).

126. G. Beinert, P. Lutz, E. Franta, and P. Rempp, <u>Macromol. Chem.</u>, <u>179</u>, 551 (1978).

127. R.C. Morrison and C.W. Kamienski, U.S. Patent 3725368 (1973).

128. P. Lutz, E. Franta, and P. Rempp, <u>C.R. Hebd. Sences Head Sci.</u>, <u>Ser. C.</u>, <u>283</u>, 123 (1976).

129. G. Popou and G. Schwachula, <u>Plast. U. Kautch.</u>, <u>26</u>, 263 (1979).

130. P. Guyot, J.C. Favier, H. Uytterhoeven, M. Fontanille, and P. Sigwalt, <u>Polymer</u>, <u>22</u>, 1724 (1981).

131. P. Guyot, J.C. Favier, M. Fontanille, and P. Sigwalt, <u>Polymer</u>, <u>23</u>, 73 (1982).

132. R.P. Foss, H.W. Jacobson, and W.H. Sharkey, <u>Macromolecules</u>, <u>10</u>, 287 (1977).

133. G.G. Cameron and G.M. Buchan, <u>Polymer</u>, <u>20</u>, 1129 (1979).

134. P. Lutz, E. Franta, and P. Rempp, <u>Polymer</u>, <u>23</u>, 1953 (1982).

135. M. Morton and J.R. Rupert, in "Initiation of Polymerization", F.E. Bailey, Ed., ACS Symposium Series, No. 212, 1983.

136. L.H. Tung, G.Y-S. Lo, and D.E. Beyer, *Macromolecules*, 11, 616 (1978).

137. L.H. Tung and G.Y-S. Lo, U.S. Patent (to Dow Chemical), 4,182,818 (1980); 4,196,153 (1980).

138. L.H. Tung, G.Y-S. Lo, J.W. Rakshys, and D.E. Beyer, U.S. Patent (to Dow Chemical), 4,200,718 (1979); 4,201,729 (1980); 4,205,016 (1980).

139. H. Hocker and G. Lattermann, *Makromol. Chem.*, 158, 191 (1972).

140. H. Hocker and G. Lattermann, *J. Polym. Sci.*, *Polym. Sympos.*, 54, 361 (1976).

141. H. Hocker and G. Lattermann, *Angew. Chem. Int. Ed. Eng.*, 19, 219 (1980).

142. Z. Laita and M. Szwarc, *Macromolecules*, 2, 412 (1969).

143. A. Yamagishi, M. Szwarc, L. Tung, and G.Y-S. Lo, *Macromolecules*, 11, 607 (1978).

144. P. Lutz, G. Bernert, E. Franta, and P. Rempp, *Eur. Polym. J.*, 15, 1117 (1979).

145. E. Leitz and H. Hocker, *Macromol. Chem.*, 184, 1893 (1983).

146. M. Morton and L.J. Fetters, *Rubber Rev.*, 48, 359 (1975).

147. W.H. Glaze, J. Lin, and E.G. Felton, *J. Org. Chem.*, 30, 1258 (1965).

148. H. Gilman and K.F. Cartlidge, *J. Organomet. Chem.*, 2, 447 (1964).

149. F. Lindstrom and H. Diehl, *Anal. Chem.*, 32, 1123 (1960).

150. J.M. Hoover and J.E. McGrath, *Polymer Preprints*, 27(2), 150 (1986).

151. M. Morton, E.E. Bostick, and R. A. Livigno, *Rubber Plast. Age*, 42, 497 (1961)

152. A. Garton and S. Bywater, *Macromolecules*, 8, 694 (1975).

153. E. Shue and S. Bywater, *Macromolecules*, 2, 458 (1969).

154. A. Garton, R.P. Chaplin, and S. Bywater, *Eur. Polym. J.*, 12, 697 (1976).

155. M. Morton, "Anionic Polymerization: Principles and Practice", Academic Press, New York, 1981.

156. G. Odian, "Principles of Polymerizations", 2nd Edition, John Wiley & Sons, New York, 1981.

157. L. Bohn, W.K.R. Barnikol, and G.V. Schulz, <u>Macromol. Chem.</u>, <u>110</u>, 222 (1967).

158. R.N. Young, R. Quirk, and L. Fetters, <u>Adv. Polym. Sci.</u>, <u>56</u>, 1 (1984).

159. F. Bandermann, H.D. Speikamp, and L. Weigel, <u>Makromol. Chem.</u>, <u>186</u>, 2017 (1985).

160. L.H. Tung, G.Y-S. Lo, and J.A. Griggs, <u>J. Polym. Sci.</u>, <u>Polym. Chem. Ed.</u>, <u>23</u>, 1551 (1985).

161. R. Nuffer and B. Francous, <u>J. Soln. Chem.</u>, <u>11</u>, 91 (1982).

162. R.P. Quirk, F. Ignatz-Hoover, and W-C. Chen, <u>Polymer Preprints</u>, <u>24(1)</u>, 188 (1986).

163. R.D. Allen, Ph.D. Thesis, Virginia Polytechnic Institute and State University, 1985.

164. E.W. Duck and J.M. Lock, in "Stereo Rubbers", W. M. Saltman, ed., John Wiley & Sons, New York, 1977.

165. J. Haslen and H.A. Willis, "Identification and Analysis of Plastics", Iliffe Book, London, 1965.

166. R.C. Ferguson and D.W. Overnall, <u>Polymer Preprints</u>, <u>26(1)</u>, 182 (1985).

167. T.E. Long, R. Subramanian, T.C. Ward, and J.E. McGrath, <u>Polymer Preprints</u>, <u>27(2)</u>, 258 (1986).

168. I.C. Wang, Ph.D. Thesis, Virginia Polytechnic Institute and State University, August 1981.

169. W. Fessler and P.C. Juliano, <u>Ind. Eng. Chem. Prod. Res. Develp.</u>, <u>11</u>, 407 (1972).

170. C.L. Frye, R.M. Salinger, and F.W. Fearon, <u>J. Org. Chem.</u>, <u>35</u>, 1308 (1970).

171. W.J. Kern, J.N. Anderson, H.E. Adams, T.C. Bouten, and T.W. Bethea, <u>J. Appl. Polym. Sci.</u>, <u>16</u>, 3123 (1972).

172. J.N. Anderson, W.J. Kern, T.W. Bethea, and H.E. Adams, J. Appl. Polym. Sci., 16, 3133 (1972).

173. D. F. DeTar, J. Chem. Ed., 44, 193 (1967).

PART II

Exploratory Polymerization Studies Utilizing
Alkali Metal Magnesiate Initiators

I. Introduction

Alkyllithium initiators have been explored widely academically and used in large quantities commercially to prepare well defined block copolymers that have unique physical properties. These organometallic compounds have the desirable property of forming homogeneous solutions in hydrocarbon solvents which, as described earlier, impart very desirable physical properties to diene polymers. In addition, these compounds are strongly basic which allows very rapid initiation of vinyl monomers relative to propagation and produces very narrow molecular weight distributions.

The main disadvantage of these systems was the high cost of initiator. This was not necessarily an important consideration when high molecular weight polymers are being prepared, as the cost was only a small contribution to the raw materials cost (only small amounts of initiator are needed). However, when low molecular weights were desired, large amounts of initiator were required and the initiator cost can be appreciable.

One method of reducing the potentially high initiator costs was by the use of a telomerization process where the telogen has an acidic proton and acts as a chain transfer agent for the anionic chain end to produce the terminated polymer and a new anion generated from the hydrogen abstraction of the telogen. The new anion then, will initiate polymerization, and in theory, the process could continue indefinitely. Often times, toluene was used in this process, as it served as both the chain transfer agent as well as the solvent.

One problem with this type of system was that the molecular weight distribution of polymer was broad (about 2.0) which was more typical of condensation polymerizations rather than for an anionic polymerization. Also, the molecular weight of the polymer was dependent upon the polymerization temperature. At higher temperatures, lower molecular weights were obtained because of the increased rate of chain transfer.

One novel approach to solving the expense question would to design a molecule that had two or more labile groups which were basic enough to initiate polymerization. One synthetic route to such a compound may be to mix a strongly basic compound such as an organic alkali metal with a relatively weak base such as a diorganomagnesium to form a mixed metal containing "ate" complex.

II. Literature Review

A. Diorganomagnesium Preparation

Dialkylmagnesium compounds containing, in particular, normal and substituted butyl groups, have found use as a component for coordination catalysts used in the polymerization of ethylene. In addition, dibutylmagnesium (DBM) has been used effectively to purify vinyl nonpolar monomers as they react rapidly with compounds that have abstractable protons, but are too weakly basic to catalyze the polymerization of these monomers.

DBM has been prepared by a number of synthetic routes. One important route involves the direct alkylation of an activated magnesium chloride (1,2) in nonpolar solvents, shown below. The "activated"

$$MgCl + 2LiR \xrightarrow{\text{benzene}\atop\text{alkane}} MgR_2 + 2LiCl \qquad (28)$$

species was obtained from the reaction of an alkylmagnesium chloride with benzyl chloride as a means of preparing symmetrically substituted magnesiums.

Another successful route (3) utilized the addition of a Grignard reagent to an alkyllithium to prepare di-sec-butyl derivative.

$$RLi + RMgCl \xrightarrow{\text{ether}} R_2Mg + LiCl \downarrow \qquad (29)$$

The ether was removed by addition of hydrocarbon solvent and subsequent distillation. Mixed alkylmagnesiums were also prepared using this method (4). These compounds remained soluble in hydrocarbon solvents and were essentially halogen free in nonpolar solvents.

The direct reaction of magnesium with an alkyl halide was an additional method for preparing dibutylmagnesium (3,5) in hydrocarbon solvents such as benzene which has been modified with about 5-10% of an ether, as shown below. After complete reaction, the addition of sec-

$$2Mg + 2RCl \longrightarrow MgR_2 + MgCl \qquad (30)$$

butyllithium removed any soluble halides that remained in solution.

Though not feasible from an environmental consideration, DBM's were also prepared by the transfer of ligands from 2-butyl mercury (II) to magnesium metal (6,7). The exchange reaction in hydrocarbon solvent was very slow and the alkylated magnesium product was contaminated with mercury.

$$HgR_2 + Mg \longrightarrow MgR_2 + Hg \qquad (31)$$

Lastly, dibutylmagnesiums have been isolated by the fractional crystallization of the solutions of organomagnesium chloride. From the Schlenk equilibrium, R_2Mg was one of the equilibrium products in addition to MgX_2 which was removed from solution. The first work in this area was by Schlenk (8) who showed that dioxane would react with Grignard reagents to form an insoluble salt (6) and the organomagnesium

$$2Mg(R)X + 2 \underset{O}{\overset{O}{\bigcirc}} \longrightarrow MgX_2 (\underset{O}{\overset{O}{\bigcirc}})_2^\downarrow + MgR_2 \qquad (32)$$

Similarly, Ashby and Becker (9) were able to crystallize $EtMg_2Cl_3 \cdot THF$ from solution by the addition of an equal volume of benzene to THF. Analysis of the solution confirmed the presence of Et_2Mg.

B. Properties

Though less basic than alkyllithiums and less reactive, organomagnesiums are also associated in nonpolar media. The symmetrically substituted n-butyl magnesium was insoluble (10) as were

alkylmagnesiums that contained two methyl and ethyl groups (11). This was attributed to the high degree of association of ethyl and methyl containing compounds which were linear, polymeric aggregates. However, the di-sec-butyl and mixed alkyl groups with n- and sec-butyl formed soluble compounds as a result of lower aggregation numbers (generally thought to be two, three, or oligomeric). Increased solubility was also obtained by the incorporation of bulkier alkyl groups such as n-octyl and 2-ethyl hexyl substituents.

Interestingly enough, there were also some correlations between solubility of DBM's and reactivity to groups bearing a removable hydrogen (10). In these cases, increased solubility had increased reactivity and was most likely due again to the reduced association number of the mixed and branched alkylmagnesiums.

C. Mixed Metal Complexes Containing Magnesium

The first preparation of mixed metal complexes, or "ates", was by Wittig (12). The compound was formed by the reaction of diphenylmagnesium with phenyllithium in diethyl ether to form the 1:1 complex as shown below. The product was then crystallized by the addition of xylene.

$$PhLi + Ph_2Mg \longrightarrow Ph_3MgLi \tag{33}$$

For ratios of lithium to magnesium of less than 2, a 1:1 complex was formed. However at ratios greater than 2, the compound Ph_4MgLi_2 was formed preferentially (14).

Coates and Heslop (15) prepared a trialkyl containing magnesium lithiate by reacting dimethylmagnesium with n-butyllithium in ether. A 1:1 lithium to magnesium complex was isolated as $(nBuLi) \cdot (Me_2Mg) \cdot (Et_2O)$.

Fraenkel (16) also prepared complexes of organolithiums with

dibutylmagnesium. It was suggested that these compounds must be weaker

bases than alkyllithiums due primarily to the increased thermal

stability of the complex.

It was also reported that the direct reaction of a variety of

alkali metals with DBM in hydrocarbons produced similar mixed metal

"ates" (17). Using lithium and $(n-butyl)_2$ Mg compounds with a lithium

to magnesium ratio of between 1:1 and 1:1.5 were prepared while the di-

sec-butylmagnesium gave a 3:1 ratio. Sodium, on the other hand, forms

complexes with 2:1 ratio with magnesium and potassium gave complexes

with a 1:1 ratio with magnesium.

Kamienski (18) reported the addition of diorganomagnesiums (with

phenyl, and normal and branched butyl groups) to butyllithium, sodium,

and potassium; these compounds polymerized butadiene and isoprene. In

some cases, toluene was used as the solvent and reaction temperatures

were controlled so that the telomerization process was occurring. This

resulted in increased yield of polymer per mole of initiator used.

Copolymers of styrene and butadiene were prepared with organo-

metallics of sodium, barium, strontium, and calcium that were mixed with

a variety of other ogranometallics and gave polymers with high 1,4-

content and narrow molecular weight distributions (19). A copolymer of

styrene and acrylonitrile was also prepared in THF using sec-butyl-

lithium modified with cupric diisopropylsalicylate, though low yields

were observed (20).

A most comprehensive polymerization study utilized mixed metal

complexes of phenyl- (21) and butyllithium (22) with DBM to form diene

homopolymers and diene-styrene block copolymers. High conversions and fast propagation rates were obtained with little change in diene microstructure compared with organolithiums alone if the lithium to magnesium ratio was greater than one. However, the polymer molecular weight decreased as the lithium to magnesium content decreased. Surprisingly, one peak was observed in the GPC with a narrow polydispersity which indicated one type of initiation site. Similar results were obtained for styrene homo- and butadiene-styrene copolymerizations.

III. Introduction to Research

The focus of this work was to evaluate the use of a hydrocarbon soluble trialkylsodium magnesiate as an effective anionic initiator for the controlled polymerization of vinyl monomers. Initial studies used this initiator for the polymerization of styrene and isoprene. Further studies showed this initiator to be a weaker base than expected as well as being quite bulky. Thus, it is a more "universal" initiator, an ideal candidate for the polymerization of more polar monomers such as methyl methacrylate.

One other consideration that was of interest from an economic point of view was how many of the three alkyl groups were labile and basic enough to initiate polymerization. If more than one carbanionic site per molecule were able to initiate polymerization, the raw materials cost would be greatly reduced.

IV. Experimental

Initial polymerization studies with styrene and isoprene using the trialkylsodium magnesiate initiator were done in the high pressure nitrogen reactor which has been described earlier. For the methacrylate and siloxane polymerizations, thoroughly cleaned and dried round bottom flasks were used. The flasks were stoppered with a rubber septum and maintained under a nitrogen atmosphere.

A. Purification of Reagents

1. Cyclohexane

Cyclohexane (Fisher Scientific) was purified as follows. After stirring for about one week over H_2SO_4, it was distilled from a sodium dispersion under nitrogen. The solvent was stored in a round bottom flask under nitrogen until needed. Transfer to the reactor or the round bottom flasks was achieved by a double ended needle under a nitrogen atmosphere.

2. Tetrahydrofuran (THF)

THF (Fisher Scientific) was used only to modify the solvent of the siloxane polymerization. Just prior to use, it was distilled from the purple sodium/benzophenone complex under nitrogen into a round bottom flask. After distillization, the THF was transferred by syringe or double ended needle into the round bottom flasks used for the siloxane polymerization.

3. Isoprene

Isoprene was pumped under nitrogen through a series of purification columns that contained alumina, silica gel, and molecular sieves, to remove primarily water and any inhibitor, then pumped directly into a

holding tank. When the desired volume of monomer was in the holding tank, it was pumped directly into the high pressure reactor.

4. Styrene

Styrene (Fisher Scientific) was purified by first passing it through an alumina column to remove the inhibitor. It was then distilled from dibutylmagnesium under reduced pressure over a short path. After distillation, it was transferred to the reactor via syringe.

5. Trialkylsodium Magnesiate

This initiator was obtained as a solution (Lithium Corp., Division of FMC) in a mixture of different hydrocarbon solvents (Concentration of about 1 M in both sodium and magnesium). The solution was orangish-brown in color and completely homogeneous. It was used as received without further purification.

6. Dibutylmagnesium

Dibutylmagnesium (Lithium Corp.) was received as a 0.72 $\underline{M}$ solution in a mixed hydrocarbon solvent. This commercial product actually contained alkyl groups that were 45% n-butyl-, 45% sec-butyl-, and about 10% n-octyl groups. This solution was used directly without further purification.

7. Hexamethylcyclotrisiloxane ("D_3")

D_3 (General Electric) was sublimed under moderate vacuum over a short path into a round bottom flask and then diluted with cyclohexane to make about a 20% solution. The solution was transferred with nitrogen to a narrow mouth bottle and stored under nitrogen. The desired amount was then syringed into round bottom flasks as needed.

8. Trimethylchlorosilane

Trimethylchlorosilane (Petrach) must be stored under an inert atmosphere as it will rapidly react with water to liberate hydrochloric acid. Care must be taken to insure that no acid is present as this will lead to degradation of siloxane containing polymers. Because this compound was used only as a terminating agent for the living siloxanolate chain end, a large excess was always used. Thus, no further purification was required except to completely purge with dry nitrogen.

9. Methyl Methacrylate

Methyl methacrylate (Rohm and Haas) monomer was first distilled from calcium hydride under reduced pressure over a short path, then stored in the freezer. Prior to use, the monomer was purified by distillation from a trialkylaluminum (13) under similar conditions. The desired amount was removed via syringe as needed.

10. 1,1-Diphenylethylene (DPE)

Diphenylethylene (Eastman Kodak) was distilled from n-butyllithium under reduced pressure over a short path. Enough n-butyllithium was added until a bright red color resulted just prior to distillation. After distillation, purified DPE was stored in a brown bottle under nitrogen and kept cold.

V. Polymerization Studies

The high temperature polymerizations of the styrenes and dienes done in the high pressure nitrogen reactor while the lower temperature polymerizations needed for siloxane (room temperature) and methyl methacrylate ($-78°C$) were more easily done in sealed round bottom flasks. The desired amount of the trialkylsodium magnesiate initiator was charged based on the sodium and magnesium concentrations.

The predicted molecular weight of all polymers was based on the charge of monomer and initiator as was given by the following equation.

$$\overline{M}_n = \frac{g\ monomer}{moles\ of\ initiator} \tag{34}$$

For these polymerizations, solutions containing about a 10% polymer to solvent ratio were maintained (weight to weight) as the viscosity was quite low even for high molecular weights. As an example, for typical polymerizations in the reactor, 60 g of monomer was charged to obtain a molecular weight of 100,000. This required an initiator charge of 0. 6 mmoles.

For the diene polymerization, large amounts of solvent and monomer were used so several samples could easily be removed from the reactor without changing the propagation rate significantly. To determine the percent conversion to polymer with reaction time, approximately 20 ml of reaction mixture was placed in a preweighed sample vial (and cap) and terminated with two drops of methanol. The vial was capped immediately and weighed. This total weight was the weight of polymer and solvent.

The solvent and residual monomer were completely removed by drying in a vacuum oven and the vial was again weighed. This was the weight of

the polymer alone. Dividing the weight of polymer by the total weight

gives the fraction of polymer in the sample. This calculation was done

for every sample taken during the polymerization.

If the sample taken at the longest time was assumed to be

completely converted to polymer (100% conversion), the quotient of the

above calculation should be about 0.1. The above quotients for every

previous sample were divided by this number and multiplied by 100 to

give the percent conversion. The following Scheme 7 illustrates this

calculation.

A. D_3 Polymerizations

The ring-opening polymerization of "D_3" was a two step process. By

the choice of solvent polarity, the initiation and propagation steps can

be separated from one another. In nonpolar solvents, the chains were

initiated but propagation was very slow. Increasing the polarity of the

solvent accelerated the propagation rate and polymerization proceeds in

well defined fashion. The procedure for the D_3 polymerization is given

as follows.

First, the initiator was charged into the stirred flask that

contained the cyclic monomer dissolved in cyclohexane. The reaction was

allowed to proceed for several hours at room temperature. The second

step was to start the propagation reaction by modifying the solvent with

about 10% purified THF. This change in polarity increased the

concentration of solvent-separated ion pairs and increased the

propagation rate.

After an overnight reaction, trimethylsilyl chloride was added to

terminate the siloxanolate anion and to give a stable endgroup. After

Scheme 7. Percent Conversion Calculation

	1	2	end
wt. vial + solvent + polymer	30.0000	30.0000	30.0000
wt. vial	<u>10.0000</u>	<u>10.0000</u>	<u>10.0000</u>
wt. of polymer + solvent	20.0000	20.0000	20.0000
wt. vial + polymer	10.1000	11.0000	12.0000
wt. vial	<u>10.0000</u>	<u>10.0000</u>	<u>10.0000</u>
	0.1000	1.0000	2.0000

% Conversion

1. $\dfrac{0.1000}{2.0000}$ x 100 = 5%

2. $\dfrac{1.0000}{2.0000}$ x 100 = 50%

3. $\dfrac{2.0000}{2.0000}$ x 100 = 100%

several minutes, the solution was poured into methanol to solubilize any hydrochloric acid and metal chloride salts that were generated by termination of the chain end. The synthetic scheme of this polymerization is shown in Scheme 8. For the D_3 polymerization, both a sec-butyllithium control and a trialkylsodium magnesiate initiated polymerization were undertaken.

B. Isoprene Polymerizations

All diene polymerizations were performed as described earlier in the high pressure nitrogen reactor. Purified monomer was charged into the reactor followed by the addition of the alkylsodium magnesiate initiator. A slight excess of initiator was added because some of the initiator would be rendered inactive by impurities such as minute quantities of water or other impurities with an abstractable proton that may be present in the system. All polymerization solutions were completely clear and free of insolubles. The reaction sequence is shown in Scheme 9, which also illustrates the two different addition products.

C. Styrene Polymerizations

These polymerizations were also done in the high pressure reactor. Monomer and solvent were charged into the reactor. A small charge of initiator was then added until an orange color was observed. The desired amount of initiator was then charged into the reactor. The synthetic scheme for the styrene polymerization is shown in Scheme 10.

Two important characteristics of these polymerizations were observed. First, the anion was a different color than typical alkyllithium initiated systems because of the difference in counter ion.

Scheme 8. D_3 Polymerizations

R_3MgNa +

$$
\begin{array}{c}
\text{O} \\
\text{Me} \diagdown \underset{|}{\text{Si}} \diagup \diagdown \underset{|}{\text{Si}} - \text{Me} \\
\text{Me} \quad \text{Me} \\
\text{O} \diagdown \diagup \text{O} \\
\underset{\diagup \diagdown}{\text{Si}} \\
\text{Me} \quad \text{Me}
\end{array}
$$

Room Temperature
THF, 24 hrs
$SiCl(CH_3)_3$

$$
R-(-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-)_n-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3
$$

- CONTROL WITH SEC-BUTYL LITHIUM

Scheme 9. Isoprene Polymerizations

$$R_3Mg\,Na \quad + \quad CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$

$$\downarrow \quad \begin{array}{l} CYCLOHEXANE \\ 60^oC \\ MeOH \end{array}$$

$$R\text{-}(\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}=CH\text{-}CH_2)\text{~~~~~}(\text{-}CH_2\text{-}\underset{\underset{\displaystyle CH_2}{\overset{\displaystyle ||}{CH_3\text{-}C}}}{CH}\text{-})\text{~~~~~}H$$

Scheme 10. Styrene Polymerizations

$$R_3Mg\,Na \quad + \quad CH_2=CH$$

1) CYCLOHEXANE, 2-3 hr

2) CH_3OH

$$R\text{-}(\text{-}CH_2\text{-}CH\text{-})_n\text{-}H$$

Secondly, the titration to remove impurities was very slow which indicated that the initiator was a weaker base than sec-butyllithium.

D. Methyl Methacrylate Polymerizations

Methyl methacrylate polymerization were done in sealed round bottom flasks using THF as the solvent at $-78°C$ under a nitrogen atmosphere. Solvent and a four fold excess of purified DPE, when needed, were placed in the reaction vessel. A small amount of initiator solution was charged into the flask to "titrate out" the impurities from the system. The desired charge of initiator solution was then added. This procedure was used to form the more hindered and less basic initiator which was desired for efficient methacrylate polymerizations. After several minutes, purified monomer was added slowly to prevent any exotherm. The polymer was isolated by precipitation in methanol and drying in a vacuum oven.

One reaction was done that used the sec-butyllithium/DPE adduct as the control experiment. Two other experiments were also undertaken, one using the trialkylsodium magnesiate/DPE initiating system, and the other employed the magnesiate initiator alone. The synthetic approach discussed above is illustrated in Scheme 11.

E. Difunctional Butadiene Polymerizations Modified with Dibutylmagnesium.

Because of the success of the mixed metal "ate" complexes as an anionic initiator, it should be possible to modify the difunctional initiator solutions prepared by the addition of sec-butyllithium to 1,3-bis(α-phenylethenyl)benzene (as discussed in Part 1) with dibutylmagnesium to form the mixed lithium magnesiate initiator. This

Scheme 11. Methyl Methacrylate Polymerizations

sec-Butyl Li   + $CH_2=C$ (diphenyl)

↓ THF, -78°C

$CH_3-CH_2-CH-CH_2-C^{\ominus}$ $Li^{\oplus}$
  |
  CH_3 (with two phenyl groups)

↓
1. $CH_2=C$
       |
       CH_3
       |
       $C=O$
       |
       $O-CH_3$

2. CH_3OH

PMMA

initiator will be less basic and more sterically hindered than the dilithium species alone.

The synthetic scheme required first, the formation of the difunctional lithium initiator at 60°C followed by the addition of the desired amount of dibutylmagnesium and was added directly to the initiator solution. The solution was stirred for about 5 to 10 minutes. The temperature was lowered to 50°C and butadiene monomer was added to begin the polymerization. Microstructural information as well as percent conversion and molecular weights were determined as a function of changing the lithium to magnesium ratio. Scheme 12 summarizes the initiator formation and polymerization conditions.

The target molecular weight in all cases was 45,000 daltons at a concentration of about 10% solids (weight to weight) in cyclohexane. About 0.5 mmoles of DDPE was charged into the reactor followed by the addition of 1 mmole of sec-butyllithium. Dibutylmagnesium was then charged into the reactor in sufficient quantities to give the desired ratio of lithium to magnesium.

Scheme 12. Difunctional Butadiene Polymerizations
Modified with Dibutylmagnesium

"IN"

Li⁺   Li⁺

50°C, CYCLOHEXANE

1. R_2Mg

2. $CH_2 = CH-CH = CH_2$

3. CH_3OH

~~~~~PBd~~~~IN~~~~PBd~~~~~

VI. Instrumental Analysis

A. Fourier Transform Infrared (FTIR)

FTIR analysis was primarily for the analysis of the diene homopolymers. As was stated earlier, the stretching vibrations due to the vinyl moieties were measured to determine the relative amounts of the cis and trans-1,4-, and the 1,2- (or 3,4- for isoprene) addition products. The same instrumentation was used for this analysis and has been described earlier.

B. Proton NMR (^{1}H NMR)

This technique was used as a tool for confirming the total amounts of 1,4- and 1,2- content. In addition, the tactic triads of methyl methacrylate were calculated based on the areas for the peaks appearing about 0.8-1.0 ppm (relative to TMS) which were due to the α-methyl group. Similar instrumentation and deuterated solvents were used as discussed earlier.

C. Gel Permeation Chromatography (GPC)

An identical instrument setup and series of columns were used as described earlier. Samples were prepared and filtered before use. The diene and methyl methacrylate homopolymers were analyzed with the UV detector at 218 nm and for styrene at 254 nm.

D. Vapor Pressure Osmometry (VPO)

Number average molecular weights were obtained for siloxane polymers using this technique because GPC analysis using THF as the solvent gives very poor detector response due to the fact that siloxanes have a very similar refractive index to the solvent (THF) and were UV

transparent. Molecular weights were determined with a Wescan Model 223 VPO. Before actual analysis of polymer, the instrument was calibrated with sucrose octaacetate in toluene.

VII. Results and Discussion

A. Siloxane Polymerizations

The living ring-opening polymerization of D_3 was attempted using the sodium magnesiate initiator. The initiation by sec-butyllithium was used as the control since this polymerization has produced well-defined polymers.

The polymerization using sec-butyllithium gave, after 24 hours of reaction time in the mixed solvent of cyclohexane and THF, a high yield and a molecular weight which was close to the theoretical value. On the other hand, using identical reaction conditions, siloxane polymers prepared by the magnesiate initiator gave only about a 50% yield and a low molecular weight for the same reaction conditions.

Although these results initially were not very promising, it appeared that the reaction was not complete after the 24 hour reaction period which was probably a result of the weakly basic nature of the initiator. One limitation of this characterization technique was that any cyclics formed during an equilibrium process will not be detected. This would be an important consideration in evaluating the effectiveness of this initiator for siloxane polymerizations. The polymerization results for both initiators are shown in Table 17.

B. Isoprene Polymerizations

Polymerization studies were done with the magnesiate initiator to determine the efficiency and effectiveness of this initiator for the polymerization of isoprene relative to organolithium initiators. For all the samples taken from the reactor, the percent conversion, molecular weight, and diene microstructure were determined.

TABLE 17

Siloxane Polymerization Results at Room Temperature
in THF Modified Cyclohexane

	CONTROL	R_3Mg Na
Yield	95%	48 %
M_n (theory)	10,000	10,000
M_n (osmometry)	11,950	6,600

A percent conversion versus time plot is shown in Figure 42 for an isoprene polymerization done at 60°C. Very noticeable was an induction period where initially, low conversion was observed for a substantial period of time before the normal polymerization began. After this induction period was over, the expected conversion versus time behavior was observed. The induction period was even more pronounced as the polymerization temperature was lowered.

This behavior was clearly indicative of a slow rate of initiation and was the first indication that this initiator was a weaker base than an organolithium. However, after initiation was complete, the typical behavior observed for "living" anionic polymerizations was also observed in this case as well.

Molecular weight determination by GPC confirmed the slow initiation behavior due to the fact that the molecular weight distribution was broader for typical anionic polymerizations. Typically molecular weight distributions were in the range of 1.2 to 1.4 which was again evidence for slow initiation rates relative to propagation. In addition, much higher molecular weights were obtained relative to predicted values indicating that less than one initiating site per molecule was present or substantial degradation had occurred. The molecular weights and distributions for polyisoprene samples are shown in Table 18.

Microstructural information from FTIR and ^{1}H NMR confirmed the quite high 1,4 content of dienes prepared with this initiator. About 70% 1,4 and 30% vinyl content was observed. This was lower vinyl content than was typically observed for sodium counter ions and was

Figure 42. Percent Conversion of Isoprene with Time
at 60°C in Cyclohexane

TABLE 18

Summary of Isoprene Polymerization at 60°C in Cyclohexane

Sample No.	Time(min)	M_n	MWD
1	60	23,100	1.23
2	90	40,700	1.32
3	120	63,500	1.32
4	210	126,800	1.36
5	300	96,700	1.38
6	420	162,100	1.37

MICROSTRUCTURE OF POLYISOPRENE (^{1}H NMR)

- 70% 1,4 ADDITION
- 30% 3,4 ADDITION

indicative of some type of mixed metal "ate" counter ion being present at the chain end.

C. Styrene Polymerizations

Polymerization of styrene showed similar results. In particular, molecular weights were again much higher than predicted at all reaction temperatures but with fairly narrow distributions. Table 19 shows the molecular weights and distributions for all samples taken for polymerization temperatures of 50°C and 30°C.

General observations were that the "titrating out" of impurities was very slow. Clearly, the initiator was weakly basic though ionic in nature as evidenced by the highly colored anion that was formed. Conversion data confirmed the slower polymerization rate of styrene with this initiator compared with alkyllithiums. This data is shown in Figure 43 for polymerizations at 50°C and 30°C.

D. Methyl Methacrylate Polymerizations

As expected, the control polymerizations using the sec-butyl-lithium/DPE initiator gave predictable molecular weight and a narrow molecular weight distribution with total conversion to polymer. As expected from the proton NMR analysis, predominately syndiotactic triads were detected with very low amounts of isotactic triads.

When the initiator formed by the addition of R_3MgNa to DPE was used as the initiator, high conversion to polymer was again obtained and molecular weight distributions were quite narrow. Unfortunately, molecular weight control was lost as the polymer had very high molecular weight. Proton NMR analysis showed a substantial decrease in

TABLE 19

Results of Styrene Polymerization in Cyclohexane

50°C

Sample No.	Time(min)	M_n	MWD
1	10	83,300	1.18
2	20	200,000	-
3	30	230,000	-
4	40	264,400	1.24
5	50	268,300	1.25
6	60	294,000	1.24
7	70	299,800	1.23

30°C

Sample No.	Time(min)	M_n	MWD
1	20	Bimodal	-
2	40	163,800	1.33
3	60	183,500	1.33
4	90	223,600	1.30
5	150	285,900	1.32
6	210	265,000	1.32

Figure 43.   Percent Conversion of Styrene with Time in Cyclohexane

syndiotacticity with a large increase in heterotactic triads relative to the lithium system.

One surprising result was that just the magnesiate initiator itself would initiate methyl methacrylate without the use of DPE to modify the basicity and steric bulk of the initiator. In this case as well, high yields and fairly narrow molecular weight distributions were obtained. The tacticity showed little change compared with the R_3MgNa/DPE case. Once again, there was no control of molecular weight; very high values were obtained relative to predicted values.

Table 20 summarized the molecular weight, yield and tacticity data results for the sec-butyllithium/DPE control and the two polymerizations using R_3MgNa, with and without DPE. Clearly, one important negative factor was the loss in molecular weight control.

Two positive features of this initiating system were that high yields and narrow molecular weight distributions were obtained even without modification with DPE. This was indicative of a weakly basic, sterically bulky initiating species which prevented attack across the ester carbonyl. This side reaction, if occurring, would lead to low yields and broad molecular weight distributions.

E. Difunctional Butadiene Polymerizations Modified with Dibutylmagnesium

Proton NMR and FTIR were used to quantitate the amount of 1,4- and 1,2- addition along the polybutadiene backbone. In all cases, high 1,4-microstructures were obtained (about 87% to 90%) and were comparable to the amounts observed with no magnesium present regardless of the ratio of lithium to magnesium.

TABLE 20

Summary of Methyl Methacrylate Polymerizations in THF at $-78°C$

	sec-butyl Li + DPE	R_3Mg Na + DPE	R_3Mg Na
M_n	92,200	277,600	308,300
MWD	1.16	1.40	1.37
Yield	100%	90%	81%
Tacticities			
% syndiotactic	74%	56%	53%
% heterotactic	24%	38%	40%
% isotactic	2%	6%	7%

Percent conversion versus polymerization time was determined using the gravimetric technique discussed earlier. These results show that for lithium to magnesium ratios of ≥2, polymerization rates were essentially unchanged relative to the control polymerization where just the difunctional initiator was used with no added dibutylmagnesium. However, very slow polymerization rates and low conversions were observed at higher concentrations of magnesium (lithium to magnesium ratio of about 1). Figure 44 illustrates the effect of added magnesium on the conversion versus time behavior.

These results indicate that at low magnesium concentrations, the basicity of the initiation site was relatively uneffected because initiation rates still proceeded at a rapid rate. However, initiation and propagation rates became very slow at high concentrations of magnesium (1 to 1 with lithium) and indicated that the initiation site was not basic enough to effectively initiate butadiene.

The molecular weight dependence on the amount of added magnesium was also studied. Figure 45 clearly illustrates that the polybutadiene molecular weight decreased as the magnesium content increased as evidenced by GPC results. One explanation of these results was that polyfunctional initiator species (functionality of greater than 2) were formed after addition of dibutylmagnesium which would produce branched polymers that have lower elution volumes than the corresponding linear species of equal molecular weight. This explanation seems unlikely at this time. However, only one peak was observed in the GPC which indicates only one type of initiating species.

Figure 44. Percent Conversion for Polybutadiene as a Function of the Lithium to Magnesium Ratio in Cyclohexane at 50°C

Figure 45. Molecular Weight of Polybutadiene as a Function of the Lithium to Magnesium Ratio in Cyclohexane at 50°C

The more likely explanation is that the functionality of the initiator decreased (become less than 2) as magnesium was added. The concentration of monofunctional species increased with increased magnesium concentration and would account for the lowering of the molecular weight. Combined functionality and molecular weight measurements might clarify the situation.

VIII. Conclusions

The conclusions based on the utilization of the trialkylsodium magnesiate for the polymerization of cyclic and vinyl monomers were based, in most cases, on controlled experiments using sec-butyllithium as the initiator. In general, the magnesiate initiator was:

1. Reasonably effective in polymerizing monomers with a variety of polarities.

2. A fairly "universal" initiator in that both polar and nonpolar monomers could be polymerized without further modification.

3. A sterically bulky and weakly basic anion which helps to limit deleterious side reactions.

In particular the magnesiate initiator was:

4. Able to polymerize styrene and isoprene but at only reasonably slow initiation and propagation rates.

5. Able to prepare polyisoprene with higher 1,4- microstructure than expected for polymers prepared using a sodium counterion alone.

6. Able to prepare poly(methyl methacrylate) in high yields with higher syndiotactic content than typical organolithium polymerizations.

IX. Suggested Future Studies

Suggestions for continued work in this area include the following.

1. Detail the structure of the initiation site and the actual initiating species and counterion.

2. Study the feasibility of using the trialkylsodium magnesiate initiator for the preparation of poly(methyl methacrylate) homopolymers at elevated temperatures at or above $0°C$.

3. Attempt to polymerize acrylates with the trialkylsodium magnesiate initiator.

4. Explore the utility of using the less basic nature of these anions as a more effective and versatile route to functional termination of polymer chains.

X. Bibliography

1. C.W. Kamienski, United States Patent (to Lithium Corp.), 3,646,231 (1972); 3,766,280 (1973).

2. W.H. Glase and C.R. McDaniel, J. Organomet. Chem., 51, 23 (1973).

3. C.W. Kamienski and J.F. Eastham, J. Organomet. Chem., 8, 542 (1967).

4. C.W. Kamienski and J.F. Eastham, J. Organomet. Chem., 34, 116 (1969).

5. W. Navis-Smith, J. Organomet. Chem., 64, 25 (1974).

6. C.W. Kamienski, United States Patent (to Lithium Corp.), 3,755,478 (1973).

7. W. Schlenk, Chem. Ber., 64, 736 (1931).

8. W. Schlenk and W. Schlenk, Chem. Ber., 62, 920 (1929).

9. E.C. Ashby and W.E. Becker, J. Am. Chem. Soc., 85, 118 (1963).

10. A.W. Duff, et al., J. Organomet. Chem., 293, 271 (1985).

11. E. Wiers, J. Organomet. Chem., 2, 314 (1964); 4, 101 (1965).

12. G. Wittig, F.J. Meyer, and G. Lange, Liebigs Ann. Chem., 571, 167 (1951).

13. R.D. Allen, T.E. Long, and J.E. McGrath, Polymer Bull., 15, 127 (1986).

14. L.M. Seitz and T.L. Brown, J. Am. Chem. Soc., 89, 1602 (1967).

15. G.E. Goates and J.A. Heslop, J. Chem. Soc., A, 514 (1968).

16. G. Fraenkel and J. W. Cooper, J. Am. Chem. Soc., 93, 7228 (1971).

17. D.B. Malpass and J.F. Eastham, J. Org. Chem., 38, 3718 (1873).

18. C.W. Kamienski and J.F. Eastham, United States Patent (to Lithium Corp.), 3,742,077 (1968); 3,766,280 (1973); 3,822,219 (1974); 3,847,883 (1974).

19. T. Ikematu and Y. Hattori, European Patent, 61,902 (1982).

20. B.C. Roest, H.A.J. Schepers, and J. Zwart, German Patent (to Stamicarbon N.V.), 2,138,307 (1972).

21. H.L. Hsieh and I.W. Wang, <u>Proc. IUPAC, I.U.P.A.C.</u>, <u>Macromol. Symp.</u>, 28th, 103 (1982).

22. H.L. Hsieh and I.W. Wang, <u>Macromolecules</u>, <u>19</u>, 299 (1986).

APPENDIX

What follows is a copy of the computer program that was used to

calculate kinetic data if values for the rate constants are inputed by

the operator. This program was prepared by Dr. David Hewitt and was

translated into Fortran from a Basic program that was shown in Reference

173 of Part I.

```
1000   DIM Ak(20),A0(20),C(20),C0(20),C$(80)[20],C1$(80)[20],
       P$(50)[20],D(50)
1001   DIM S3(80),Jre(20,4),S4(20,30),D1(20),R$(20)[100],M(80)
1010   INTEGER I,J,K,N,R
1020   GOSUB Clear_screen
1030   GOSUB Help
1040   R=20
1050   A1=30
1060   C1=20
1070   S1=5
1080   D1=.7
1090   Rs=30
1100   Ni=1
1110   Np=10
1120   !       ZERO JRE, S3, S4
1130   FOR I=1 TO R
1140   FOR J=1 TO 4
1150   Jre(I,J)=0
1160   NEXT J
1170   NEXT I
1180   FOR I=1 TO S1
1190   S3(I)=0
1200   FOR J=1 TO A1
1210   S4(I,J)=0
1220   NEXT J
1230   NEXT I
1240   !    TAKE IN COMPOUND NAMES, REACTIONS
1250   GOSUB Clear_screen
1260   PRINT "Enter reaction as:      wA  +  xB  -> yC  + zD"
1270   PRINT "If only one reagent or product press <ENTER> at 2nd
       request - "
1280   PRINT "press <ENTER> at 1st reagent request to end input"
1290   PRINT
1300   FOR I=1 TO R
1310   PRINT I;
1320   FOR J=1 TO 4
1330   IF J<3 THEN LINPUT "REAGENT ?",C$(4*(I-1)+J)
1340   IF J>2 THEN LINPUT "PRODUCT ?",C$(4*(I-1)+J)
```

```
1350   PRINT TABXY((J-1)*16+5,I+5),C$(4*(I-1)+J)
1360   IF J=2 THEN 1450
1370   IF J=4 THEN 1460
1380   IF J=1 AND C$(4*(I-1)+J)="" THEN
1390   R=I-1
1400   GOTO 1500
1410   ELSE
1420   PRINT TABXY((J-1)*16+18,I+5),"+"
1430   GOTO 1460
1440   END IF
1450   PRINT TABXY((J-1)*16+18,I+5),"->"
1460   NEXT J
1470   NEXT I
1480   J=J-1
1490   I=I-1
1500   N1=4*(I-1)+J
1510   INPUT "Do you wish to correct any entries (Y/N)?",A$
1520   IF A$<>"Y" THEN 1670
1530   INPUT "Enter number of reaction to correct",Nc
1540   PRINT Nc;"   ";
1550   FOR K=1 TO 4
1560   IF K<3 THEN
1570   LINPUT "REAGENT ?",C$((Nc-1)*4+K)
1580   ELSE
1590   LINPUT "PRODUCT ?",C$((Nc-1)*4+K)
1600   END IF
1610   PRINT C$((Nc-1)*4+K);
1620   IF K=1 OR K=3 THEN PRINT " + ";
1630   IF K=2 THEN PRINT " -> ";
1640   NEXT K
1650   PRINT
1660   GOTO 1510
1670   !     GET M VALUES
1680   FOR I=1 TO N1
1690   M$=""
1700   K=1
1710   IF C$(I)="" OR C$(I)[K,K]>"9" THEN 1760
1720   IF C$(I)[K,K]<"." THEN 1760
1730   M$=C$(I)[1,K]
1740   K=K+1
1750   GOTO 1710
1760   IF M$<>"" THEN M(I)=VAL(M$)
1770   IF M(I)<=0 THEN M(I)=1
1780   NEXT I
1790   !     CHECK FOR STEADY STATE COMPOUNDS
1800   GOSUB Clear_screen
1810   N=1
1820   FOR I=1 TO R
```

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```
1830    FOR J=1 TO 4
1840    IF C$(4*(I-1)+J)="" OR Jre(I,J)<0 THEN 2060
1850    X$=C$(4*(I-1)+J)
1860    GOSUB Remove_numbers
1870    PRINT X$
1880    INPUT "Steady state (Y/N)?",A$
1890    IF A$<>"Y" THEN 2060
1900    Jre(I,J)=-N
1910    Ns=Ns+1
1920    FOR I1=1 TO R
1930    FOR J1=1 TO 4
1940    X$=C$(4*(I-1)+J)
1950    GOSUB Remove_numbers
1960    Y$=X$
1970    X$=C$(4*(I1-1)+J1)
1980    GOSUB Remove_numbers
1990    IF X$=Y$ THEN
2000    Jre(I1,J1)=-N
2010    S3(N)=S3(N)+1
2020    END IF
2030    NEXT J1
2040    NEXT I1
2050    N=N+1
2060    NEXT J
2070    NEXT I
2080    !     ASSIGN JRE VALUES FOR NON-STEADY STATE COMPOUNDS
2090    FOR I=1 TO R
2100    FOR J=1 TO 4
2110    IF Jre(I,J)<>0 OR C$(4*(I-1)+J)="" THEN 2240
2120    Jre(I,J)=N
2130    FOR I1=I TO R
2140    FOR J1=1 TO 4
2150    X$=C$(4*(I-1)+J)
2160    GOSUB Remove_numbers
2170    Y$=X$
2180    X$=C$(4*(I1-1)+J1)
2190    GOSUB Remove_numbers
2200    IF X$=Y$ THEN Jre(I1,J1)=N
2210    NEXT J1
2220    NEXT I1
2230    N=N+1
2240    NEXT J
2250    NEXT I
2260    !     READ CATALYSED REACTION SPECS
2270    GOSUB Clear_screen
2280    GOTO 2380
2290 Catalyst: !_____
2300    PRINT
2310    PRINT "          i.e. the reaction should have appeared as"
2320    PRINT "                    A           -> B"
```

```
2330    PRINT
2340    PRINT "                    although it will be treated as"
2350    PRINT "                 A + cat    -> B + cat"
2360    PRINT
2370    RETURN
2380    INPUT "Are there any catalysed reactions (Y/N)?",A$
2390    IF A$<>"Y" THEN 2600
2400    FOR I=1 TO R
2410    NEXT I
2420    INPUT "Enter number of catalysed reaction",Cr
2430    INPUT "Enter name of catalyst",A$
2440    Ca=0
2450    FOR I=1 TO R
2460    FOR J=1 TO 4
2470    X$=C$(4*(I-1)+J)
2480    GOSUB Remove_numbers
2490    IF A$=X$ THEN Ca=ABS(Jre(I,J))
2500    C$((Cr-1)*4+2)=A$
2510    I=4
2520    J=4
2530    NEXT J
2540    NEXT I
2550    IF Ca=0 THEN
2560    PRINT A$;" does not appear in your reaction scheme"
2570    GOTO 2430
2580    ELSE
2590    END IF
2600    !    ASSIGN S4(K,I) VALUES TO STEADY STATE COMPOUNDS
2610    FOR I=1 TO Ns
2620    A=0
2630    FOR J=1 TO R
2640    FOR K=1 TO 4
2650    IF Jre(J,K)=-I THEN
2660    A=A+1
2670    S4(I,A)=J
2680    IF K>2 THEN S4(I,A)=-S4(I,A)
2690    END IF
2700    NEXT K
2710    NEXT J
2720    NEXT I
2730    !
2740    !    ENTRY POINT FOR RUNNING AGAIN
2750    !
2760    !
2770    !READ IN INITIAL CONCENTRATIONS - C0(I)
2780    GOSUB Clear_screen
2790    PRINT "Enter Initial Concentrations"
2800    FOR I=1 TO R
2810    FOR J=1 TO 4
2820    C1$(ABS(Jre(I,J)))=C$(4*(I-1)+J)
```

```
2830   NEXT J
2840   NEXT I
2850   N=N-1
2860   FOR I=1 TO N
2870   PRINT USING "D.DDDE,    ,#";C0(I)
2880   X$=C1$(I)
2890   GOSUB Remove_numbers
2900   PRINT "     ";X$
2910   INPUT "New concentration ",C0(I)
2920   PRINT TABXY(30,I+2);
2930   PRINT USING "D.DDDE";C0(I)
2940   NEXT I
2950   !    READ IN RATE CONSTANTS
2960   GOSUB Clear_screen
2970   PRINT "Reaction                                      Old rate
       New rate"
2980   FOR I=1 TO R
2990   PRINT I
3000   FOR J=1 TO 4
3010   PRINT TABXY((J-1)*12+5,I+2),C$(4*(I-1)+J)
3020   PRINT TABXY((J-1)*12+13,I+2);
3030   IF J=1 OR J=3 THEN PRINT "+"
3040   IF J=2 THEN PRINT "->"
3050   NEXT J
3060   PRINT TABXY(50,I+2);
3070   PRINT USING "D.DDE";A0(I)
3080   INPUT "Enter New Rate",A0(I)
3090   PRINT TABXY(70,I+2);
3100   PRINT USING "D.DDE";A0(I)
3110   NEXT I
3120   !    READ IN CALCULATING PARAMETERS
3130   FOR I=1 TO N
3140   C(I)=C0(I)
3150   Ak(I)=A0(I)
3160   NEXT I
3170   GOSUB Clear_screen
3180   PRINT "        CALCULATION PARAMETERS"
3190   PRINT
3200   PRINT Rs;" Maximum steady state iterations"
3210   INPUT "New Maximum?",Rs
3220   PRINT TABXY(50,4);Rs
3230   PRINT T0;" Initial time"
3240   INPUT "New initial time?",T0
3250   PRINT TABXY(50,5);T0
3260   PRINT Dt;" Time increment"
3270   INPUT "New time increment?",Dt
3280   PRINT TABXY(50,6);Dt
3290   PRINT Ni;" Number of increments per print"
3300   INPUT "New number of increments per print?",Ni
3310   PRINT TABXY(50,7);Ni
```

```
3320    PRINT Np;" Number of print intervals"
3330    INPUT "New number of print intervals?",Np
3340    PRINT TABXY(50,8);Np
3350    !      PRINT TABLE HEADINGS
3360    GOSUB Clear_screen
3370    PRINT "        Printout Details"
3380    PRINT "Indicate concentrations you require printed"
3390    FOR I=1 TO N
3400    X$=C1$(I)
3410    GOSUB Remove_numbers
3420    PRINT TABXY(1,15);"
                                  "
3430    PRINT TABXY(1,15);X$;"      ";P$(I)
3440    INPUT "Print (Y/N) ?",P$(I)
3450    NEXT I
3460    GOSUB 5460
3470    PRINT
3480    FOR I=1 TO R
3490    PRINT I;
3500    FOR J=1 TO 4
3510    PRINT TAB((J-1)*15+5),C$(4*(I-1)+J);
3520    IF (J=1 OR J=3) AND C$(4*(I-1)+J+1)<>"" THEN PRINT " + ";
3530    IF J=2 THEN PRINT TAB(J*15),"->";
3540    NEXT J
3550    PRINT TAB(70);
3560    PRINT USING "D.DDDE";Ak(I)
3570    NEXT I
3580    PRINT
3590    PRINT "Steady state iterations ";Rs
3600    PRINT "Print cycles             ";Np
3610    PRINT "Time increment           ";Dt
3620    PRINT "Increments per print     ";Ni
3630    PRINT
3640    IF Print$="Y" THEN GOSUB 5510
3650    PRINT
3660    IF Ns<>0 THEN
3670    PRINT "Steady state - ";
3680    FOR I=1 TO Ns
3690    X$=C1$(I)
3700    GOSUB Remove_numbers
3710    PRINT X$;"    ";
3720    NEXT I
3730    PRINT
3740    END IF
3750    PRINT "Time     ";
3760    FOR I=1 TO N
3770    X$=C1$(I)
3780    GOSUB Remove_numbers
3790    IF P$(I)="Y" THEN PRINT USING "AAAAAAAAA,X,#";X$
```

```
3800   NEXT I
3810   PRINT
3820   !    SET STEADY STATE CONCENTRATIONS
3830   T=T0
3840   FOR I=1 TO R
3850   FOR J=1 TO 4
3860   IF Jre(I,J)>=0 THEN 3880
3870   IF C(ABS(Jre(I,J)))=0 THEN C(ABS(Jre(I,J)))=1.E-10
3880   NEXT J
3890   NEXT I
3900   GOSUB 5220
3910   FOR I=1 TO R
3920   D1(I)=0
3930   Ak(I)=Ak(I)*Dt
3940   NEXT I
3950   FOR Ip=1 TO Np
3960   FOR It=1 TO Ni
3970   IF Ns<=0 THEN 4650
3980   FOR I8=1 TO Rs
3990   FOR N6=1 TO R
4000   N7=ABS(Jre(N6,1))
4010   N8=ABS(Jre(N6,2))
4020   IF N8<=0 THEN
4030   D(N6)=Ak(N6)*C(N7)^M(4*(N6-1)+1)
4040   ELSE
4050   IF C(N7)*C(N8)<>0 THEN D(N6)=Ak(N6)*(C(N7)^M(4*(N6-1)+1))*
       (C(N8)^M(4*(N6-1)+2))
4060   END IF
4070   NEXT N6
4080   I6=0
4090   FOR I9=1 TO Ns
4100   I7=S3(I9)
4110   Xnum=0
4120   D2=0
4130   FOR J9=1 TO I7
4140   Ks=S4(I9,J9)
4150   IF Ks>0 THEN
4160   Xnum=Xnum+D(Ks)
4170   GOTO 4230
4180   ELSE
4190   END IF
4200   IF Ks<0 THEN
4210   Ks=-Ks
4220   D2=D2+D(Ks)
4230   END IF
4240   NEXT J9
4250   F=Xnum/D2
4260   IF F=0 THEN
```

```
4270    F=1
4280    GOTO 4360
4290    END IF
4300    IF F<1 THEN
4310    F=(D1/F)+1-D1
4320    ELSE
4330    F=(D1*F)+1-D1
4340    F=1/F
4350    END IF
4360    IF C(I9)<1.E-100 THEN 4380
4370    C(I9)=C(I9)*F
4380    Fw=F-1
4390    !
4400    !OUTPUT TO MONITOR STEADY STATE CALCULATION CAN BE INSERTED
        HERE
4410    !
4420    !
4430    IF ABS(Fw)>.005 THEN I6=1
4440    NEXT I9
4450    IF C2>0 THEN
4460    Cs=0
4470    FOR I=1 TO Ns
4480    Cs=Cs+C(I)
4490    NEXT I
4500    F=C2/Cs
4510    FOR I=1 TO Ns
4520    C(I)=C(I)*F
4530    NEXT I
4540    END IF
4550    IF I6=0 THEN I8=Rs
4560    NEXT I8
4570    IF I6=0 THEN 4650
4580    !    OUTPUT ROUTINE
4590    PRINT "Steady state calculations did not converge"
4600    !
4610    !
4620    !
4630    !
4640    GOTO 5350
4650    !      END OF STEADY STATE
4660    FOR N6=1 TO R
4670    N7=ABS(Jre(N6,1))
4680    N8=ABS(Jre(N6,2))
4690    IF N8>0 THEN
4700    D(N6)=Ak(N6)*(C(N7)^M(4*(N6-1)+1))*(C(N8)^M(4*(N6-1)+2))
4710    ELSE
4720    D(N6)=Ak(N6)*C(N7)^M(4*(N6-1)+1)
4730    END IF
4740    NEXT N6
4750    IF Ip*It=1 THEN GOSUB 5220
```

```
4760    !    IF CR IS CATALYSED DO NOT DECREMENT CONCENTRATION
4770    IF (Ca*Cr)>0 THEN D(Cr)=C(Cr)*C(Ca)
4780    FOR N6=1 TO R
4790    IF D1(N6)>0 THEN
4800    Dlast=D(N6)
4810    D(N6)=1.5*D(N6)-.5*D1(N6)
4820    D1(N6)=Dlast
4830    ELSE
4840    D1(N6)=D(N6)
4850    END IF
4860    NEXT N6
4870    !    ADJUST CONCENTRATIONS
4880    FOR N6=1 TO R
4890    FOR I=1 TO 4
4900    IF Jre(N6,I)<=0 THEN 4970    -
4910    Ii=Jre(N6,I)
4920    IF I<3 THEN
4930    C(Ii)=C(Ii)-D(N6)*M(4*(N6-1)+I)
4940    ELSE
4950    C(Ii)=C(Ii)+D(N6)*M(4*(N6-1)+I)
4960    END IF
4970    NEXT I
4980    NEXT N6
4990    Ngchk=0
5000    FOR I=1 TO N
5010    IF C(I)<0 THEN Ngchk=-1
5020    NEXT I
5030    IF Ngchk>=0 THEN 5160
5040    !    OUTPUT ROUTINE
5050    PRINT "Calculation Error - NEGATIVE concentration"
5060    FOR I=1 TO N
5070    IF C(I)<0 THEN
5080    X$=C1$(I)
5090    GOSUB Remove_numbers
5100    PRINT X$,
5110    PRINT USING "SD.DDDE";C(I)
5120    END IF
5130    NEXT I
5140    !
5150    GOTO 5350
5160    T=T+Dt
5170    NEXT It
5180    GOSUB 5220
5190    NEXT Ip
5200    GOTO 5350
5210    !    OUTPUT ROUTINE
5220    IF T>=.01 OR T=0 THEN
5230    PRINT USING "DDDD.DD,X,#";T
5240    ELSE
5250    PRINT USING "D.DDE,X,#";T
```

```
5260   END IF
5270   FOR I=1 TO N
5280   IF P$(I)="Y" THEN PRINT USING "D.DDDE,X,#";C(I)
5290   NEXT I
5300   PRINT
5310   RETURN
5320   !
5330   !    RESTART PROGRAM
5340   !
5350   PRINT "_____
             _____"
5360   PRINT
5370   PRINTER IS 1
5380   INPUT "Repeat same reaction scheme (Y/N)",A$
5390   IF A$="Y" THEN
5400   N=N+1
5410   GOTO 2770
5420   ELSE
5430   PRINT "Press <RUN> for another scheme"
5440   GOTO 6700
5450   END IF
5460   INPUT "Is hard copy required (Y/N)",Print$
5470   IF Print$="Y" THEN
5480  ·PRINTER IS 701
5490   END IF
5500   RETURN
5510   PRINT
5520   PRINT "Initial concentrations"
5530   FOR I=1 TO N
5540   X$=C1$(I)
5550   GOSUB Remove_numbers
5560   IF C0(I)<>0 THEN PRINT X$,C0(I)
5570   NEXT I
5580   RETURN
5590 Clear_screen: !
5600   FOR S=1 TO 18
5610   PRINT
5620   NEXT S
5630   PRINT TABXY(1,1)
5640   RETURN
5650 Remove_numbers:   !
5660   IF X$[1]>"9" OR X$="" OR X$[1]<"0" THEN RETURN
5670   X$=X$[2]
5680   GOTO 5660
5690   !
5700   !**********************************************************
       ***************
```

```
5710    !
5720    !RMCHSS
5730    !REACTION MECHANISM PROGRAM WITH STEADY STATE ROUTINES
5740    !FROM J.CHEM.ED. 1967, 44, 193
5750    !TRANSLATED FROM FORTRAN BY D.G. HEWITT
5760    !
5770    !PROGRAM ALLOWS UP TO 20 DIFFERENT REACTIONS INVOLVING UP
        TO 50
5780    !DIFFERENT REAGENTS.  EACH REACTION MAY HAVE UP TO 2
        STARTING MATERIALS
5790    !AND 2 PRODUCTS.
5800    !
5810    !ONE REACTION MAY BE CATALYSED - I.E. ONE OF THE REAGENTS IS
        NOT
5820    !CONSUMED DURING REACTION
5830    !
5840    !*********************************************************
        ***********
5850    !
5860    !VARIABLE DEFINITION TABLE
5870    !TO CHANGE CAPABILITY OF PROGRAM
5880    !    CHANGE DIMENSIONS OF -
5890    !     Ak(R),C(C1),C$(C1),C1$(C1),D(R),S3(S1),S4(S1,A1),
        Jre(R,4),D1(R)
5900    !
5910    !Ak(N)        RATE CONSTANT FOR REACTION N (LATER CONST*Dt)
5920    !C(K)         CONCENTRATION OF COMPOUND K
5930    !C$(K)        NAME OF COMPOUND K
5940    !D(N)         REACTION DECREMENT
5950    !D1           STEADY STATE CALCULATION DAMPING FACTOR
5960    !D1           VALUE OF D AT PREVIOUS INTERVAL
5970    !Dt           INCREMENT OF TIME
5980    !S1           MAXIMUM NUMBER OF STEADY STATE COMPOUNDS
5990    !S3(K)        NUMBER OF APPEARANCES OF STEADY STATE COMPOUND K
6000    !Jre(N,J)     C-ARRAY INDEX FOR REACTANTS AND PRODUCTS IN
        EQUATION N.  IT
6010    !             IS A NEGATIVE NUMBER FOR STEADY STATE COMPOUNDS,
        POSITIVE
6020    !             FOR ALL OTHERS
6030    !S4(K,I)      EQUATION NUMBER FOR THE Ith APPEARANCE OF STEADY
        STATE
6040    !             COMPOUND K.  POSITIVE IF K IS A PRODUCT,
        NEGATIVE IF K IS
6050    !             A REACTANT
6060    !A1           MAXIMUM NUMBER OF APPEARANCES
6070    !R            MAXIMUM NUMBER OF REACTIONS
6080    !Ca           INDEX NUMBER OF COMPOUND WHICH CATALYSES
        REACTION Cr
```

```
6090   !N1               TOTAL NUMBER OF COMPOUNDS
6100   !Ni               NUMBER OF ITERATIONS PER PRINT INTERVAL
6110   !Nr               NUMBER OF REACTIONS
6120   !T0               INITIAL TIME
6130   !Cr               REACTION CATALYSED BY Ca
6140   !Rs               NUMBER OF ITERATIONS ALLOWED IN STEADY STATE
       ADJUSTMENT
6150   !Ns               NUMBER OF STEADY STATE COMPOUNDS
6160   !T                CURRENT VALUE OF TIME
6170   !
6180 Help: !
6190   PRINT
6200   PRINT "                            RMCHSS"
6210   PRINT
6220   PRINT "Reaction mechanism simulation program with steady
       state option"
6230   PRINT
6240   PRINT
6250   INPUT "Do you require instructions (Y/N)?",A$
6260   IF A$<>"Y" THEN RETURN
6270   GOSUB Clear_screen
6280   PRINT "This program allows the kinetic analysis of complex
               reaction schemes"
6290   PRINT "of up to 20 different reactions including 50 different
               reagents."
6300   PRINT "It is used as follows:"
6310   PRINT
6320   PRINT "    1.  Enter the reactions as requested.  It is only
                    necessary to"
6330   PRINT "        enter the starting materials and products for
                    each reaction."
6340   PRINT "        Each reaction is permitted a maximum of TWO
                    starting"
6350   PRINT "        materials and TWO reagents.  If only one of
                    either is"
6360   PRINT "        desired simply press the ENTER key."
6370   PRINT
6380   PRINT "    2.  Identify those reagents (if any) which are
                    steady state."
6390   PRINT
6400   GOSUB Inkey
6410   PRINT "    3.  Identify a catalysed reaction.  It is possible
                    to have ONE"
6420   PRINT "        catalysed reaction - i.e. a reaction in which
                    one reagent"
6430   PRINT "        is not consumed.  The reagent which is to be
                    considered as"
```

```
6440 PRINT "       a catalyst must be mentioned in at least one
                   other reaction"
6450 PRINT "       It should NOT be entered at step 1 in the
                   reaction scheme."
6460 PRINT
6470 GOSUB Catalyst
6480 GOSUB Inkey
6490 PRINT "   4.  Enter the initial concentrations of reagents."
6500 PRINT
6510 PRINT "   5.  Identify those compounds for which you require
                   concentrations"
6520 PRINT "       to be printed."
6530 PRINT
6540 PRINT "   6.  Enter the printing and calculating parameters
                   - maximum"
6550 PRINT "       number of steady state iterations permitted,
                   time increment"
6560 PRINT "       number of increments between each
                   concentration printout,"
6570 PRINT "       and number of printouts."
6580 GOSUB Inkey
6590 PRINT
6600 PRINT "If you are still unclear on operation refer to"
6610 PRINT
6620 PRINT "       Journal of Chemical Education, 1967, 44, 193"
6630 PRINT
6640 GOSUB Inkey
6650 RETURN
6660 Inkey: !
6670 INPUT "Press any key to continue",A$
6680 GOSUB Clear_screen
6690 RETURN
6700 END
```

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