Studies Related to the Alternating Copolymerization of Substituted Stilbenes

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Abstract

Stilbene containing polymers are a group of interesting and versatile polymers. The pendent phenyl ring along the polymer backbone can impart unusual rigidity to the polymer backbone due to steric repulsion. By functionalizing stilbene, a variety of functional groups and ionic groups can be precisely placed along the polymer chain with tunable charge density. Therefore, stilbene containing polymers are potentially rod-like polyelectrolytes with controllable charges and charge density. They are the basis of a novel group of rigid synthetic polyelectrolytes and can be used for furthering our knowledge of rigid polyelectrolytes.

A novel series of methyl substituted stilbenes were synthesized and copolymerized with maleic anhydride. A conversion-time study was undertaken to understand the methyl substituent effect on copolymerization rates. Methyl substituted stilbene-maleic anhydride copolymer compositions were determined by quantitative ^{13}C 1D NMR. SEC measurements showed the weight average molecular weights of these copolymers vary from 3 000 to over 1 000 000 g/mol. No glass transition temperature or crystalline melting temperature was observed between 0 ^{o}C and 250 ^{o}C by DSC. TGA showed that these polymers have 5% weight loss around 290 ^{o}C.

Precursors to a polycation and a polyanion based on functionalized stilbenes and maleimides have been prepared: poly(di-*t*-butyl-(*E*)-4,4'-stilbenedicarboxylate-*co*-*N*-(4-(*t*-butoxycarbonyl)phenyl)maleimide) and poly(*N,N,N',N'*-tetraalkyl-4,4'-di-aminostilbenes-*co*-*N*-4-(*N',N'*-dimethylaminophenyl)-maleimide). These copolymer precursors were characterized by ^{1}H NMR, SEC, TGA, and DSC. The ^{1}H NMR spectrum indicated the rigidity of copolymer backbones. SEC measurements showed the weight average molecular weights of these copolymers vary from 5 000 to 11 700 g/mol. No glass

transition temperature or crystalline melting temperature was observed between 0 °C and 175 °C by DSC for poly(di-*t*-butyl-*(E)*-4,4'-stilbenedicarboxylate-*co*-*N*-(4-(*t*-butoxy-carbonyl)phenyl)maleimide). TGA showed that this polymer has 5% weight loss around 210 °C and 26% weight loss on the first stage of decomposition which corresponds to elimination of *t*-butyl functional group in the copolymer.

The homopolymerization of EMS-III via free radical polymerization, anionic polymerization and cationic polymerization was attempted. However, no polymer was obtained from any of these polymerization methods. In anionic polymerization, the solution changed to red upon the addition of the initiator *sec*-bu-Li, indicating the successful addition of the *sec*-bu-Li to EMS-III. However, the initiated monomer did not propagate to form homopolymer.

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1.1. Introduction of Stiff Chain Polyelectrolytes

Polyelectrolytes are polymers containing a high level of ionizable groups. In polar solvents, like water, these ionizable groups dissociate into either positively charged ionic groups or negatively charged ionic groups. Polyelectrolytes have high charge density which differs from ionomers, which are defined as polymers with a low level of ionizable groups (usually no more than 15 percent). Polyelectrolytes play key roles in nature and find broad applications in industrial processes and daily life, like gene and drug delivery,[1-15] waste water purification,[16-27] surface modification for improved adhesion, etc.[1,28-31] Their properties depend on many variables, such as the nature of the chargeable groups, the origin of the polyelectrolyte chains (natural or synthetic), and the backbone's intrinsic flexibility or rigidity.

A large amount of research has been done to understand the structure-property relationships of polyelectrolytes.[32-34] However, this relationship is still not well understood. For flexible chain polyelectrolytes, changing ionic strength results in both electrostatic forces and chain conformation change simultaneously. And both electrostatic forces change and chain conformational change can lead to the macroscopically observed polyelectrolyte behavior change. As a result, the different parameters related to the observations on polyelectrolyte behavior change cannot be determined individually. For conformationally rigid, rod-like polyelectrolytes, however, since the rigid conformation doesn't change with the ionic strength, all effects observed on changing ionic strength can be attributed to electrostatics. If this special aspect of polyelectrolyte behavior of rod-like systems can be understood, it should be much easier to describe flexible polyelectrolytes when conformational changes have to be taken into account. Therefore rod-like polyelectrolytes are considered to be ideal model systems for developing a better understanding of polyelectrolytes in solution.[35]

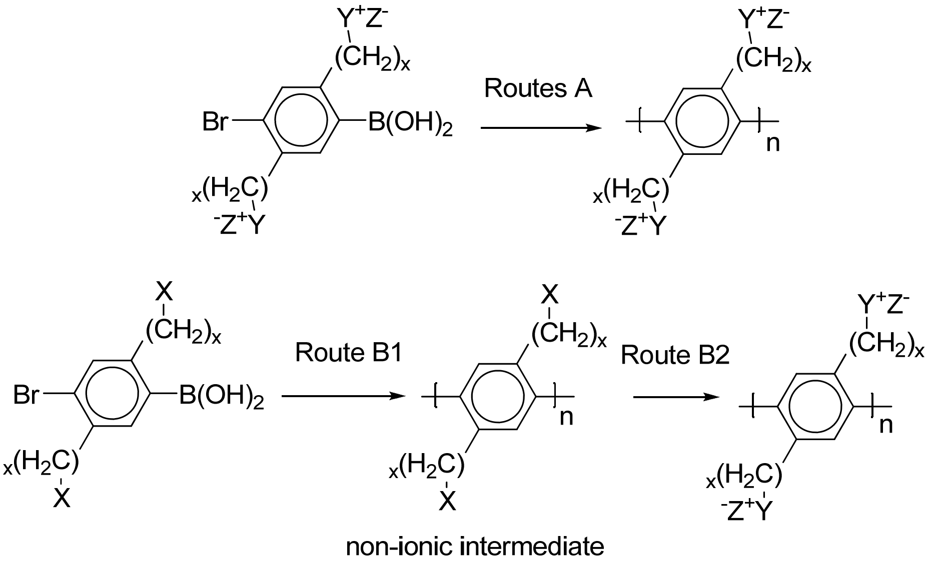
Some biological rigid polyelectrolytes have been known for a long time, such as DNA,[36-39] xanthan,[40-43] the ferredoxin virus,[44,45] and the tobacco mosaic virus.[46,47] However, when the ionic strength is very low or temperature is high the helical conformation and thereby the rod-like shape are lost. Moreover, the charge density which is the number of ionic groups per unit length cannot be changed on these biopolymers. Therefore, the development of well-defined synthetic rod-like polyelectrolytes is important to analyze quantitatively intermolecular interactions, the correlation of the counterions with the macroion, and structure formation in solution depending on ionic strength, temperature, and polyelectrolyte concentration.[48] In the early 1990s, there were publications on some synthetic rod-like polyelectrolytes, like poly(p-phenylene-benzobisoxazoles) and poly(p-phenylene-benzobisthiazoles).[49-52] During the past 15 years, a lot of attention has been focused on the synthesis of substituted rod-like poly(p-phenylene) (PPP) polyelectrolytes prepared via Suzuki Pd-catalyzed aryl-aryl coupling reactions because the resulting polymers are intrinsically rod-like and inert to hydrolysis and other side reactions. A major problem with this poly(p-phenylene) (PPP) system is their solubility as the density of charged functional groups along the backbone change. At the same time, various researchers also successfully made and studied other types of rod-like polyelectrolytes, such as poly(p-phenylene ethynylenes), polyfluorene and sulfonated poly(aramides). Another approach has been to prepare dendronized polymers with pendent dendrons along the polymer backbone. This type of polymer uses steric repulsion from pendent dendrons to stiffen the polymer backbone to the point that it is fully stretched. The dendronized polymers are considered to have good potential to form both flexible and rigid polyelectrolytes by varying the dendrons' structure, size, and attachment density along the backbones.[53] Recently, a new series of rigid charged polymers based on substituted stilbenes have been synthesized via free radical polymerization.[54] Both anionic and cationic alternating copolymers based on substituted stilbenes have been synthesized. My current work will be mainly focused on this area.

1.2. Synthesis of Rigid Polyelectrolytes

1.2.1. The synthetic routes leading to rod-like poly(p-phenylene) (PPP) polyelectrolytes

The most reported rod-like polyelectrolytes have been based on poly(p-phenylene) (PPP). The advantages behind this widely-used rigid polyelectrolytes system can be generally stated in three aspects listed below[48]: a. intrinsically stiff due to all-para-linked phenylene backbones; b. it is inert to side reactions; c. prepared via flexible Suzuki Pd-catalyzed coupling reaction.

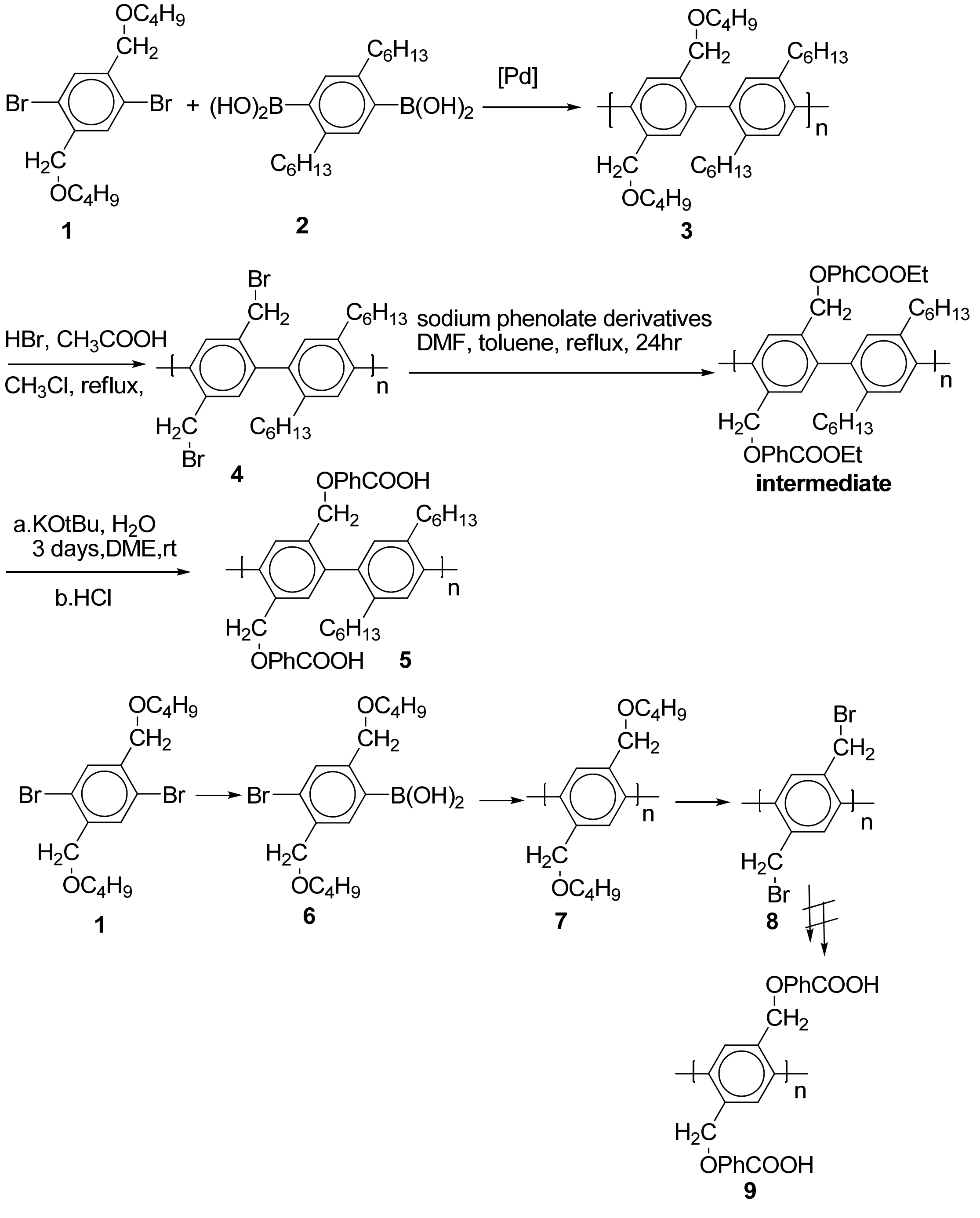
Since the Suzuki coupling reaction has tolerance of functional groups in the monomers, two synthetic routes can be applied here: precursor strategies (Routes B) and direct routes (Routes A), shown in scheme 1.1.[55] However, the direct routes A, i.e. the ionic functionalities are already available on the monomers, have been shown to be problematic. This is due to the difficulties in characterization of ionic polymers, such as molecular weight, molecular weight distribution, molecular structure, etc.. Instead the precursor strategies routes B were selected because the non-ionic intermediates in the polycondensation process (B1) can be fully characterized by the conventional techniques of polymer analysis,[55] which means the molecular information of the backbone of the ionic polymers can be determined without complication due to the ionic groups. As shown in Scheme, polycondensation process (B1) and macromolecular substitution step (B2) lead to the desired PPP polyelectrolytes.



Scheme 1.1: General presentation of direct routes and precursor strategies leading to PPP polyelectrolytes

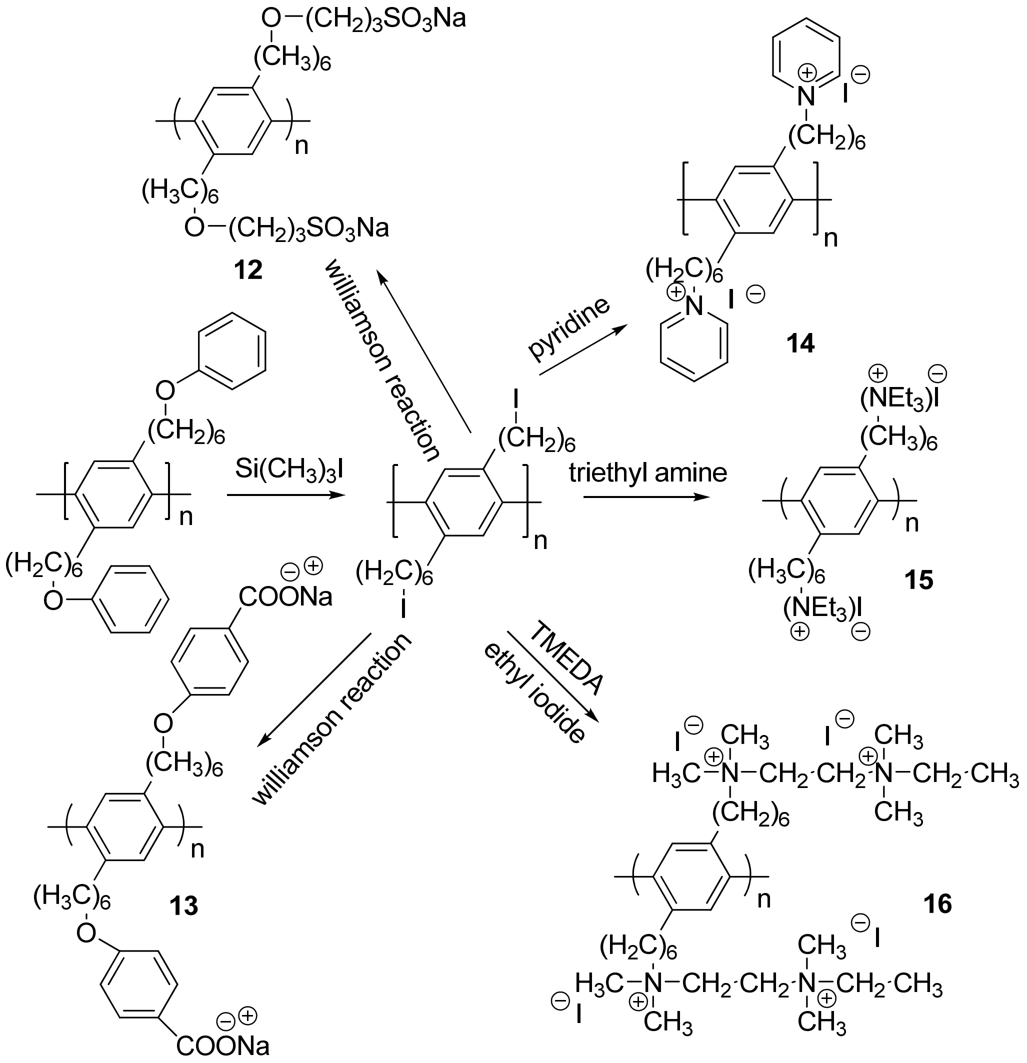
1.2.1.1. PPP polyelectrolytes via ether intermediates

Rau first developed the synthetic routes of carboxylated poly(p-phenylene)s, which are shown in Scheme 1.2.[55] The Suzuki Pd-catalyzed synthesis of precursor 3 was achieved via step-growth polymerization of monomer 1 and 2.[56] The ether group on precursor 3 later was quantitatively transformed into bromomethylene pendent group in the 2,5-positions of every alternate phenylene repeating unit. The soluble precursor yielded is designated as 4 in the scheme. Followed by a Williamson reaction,[57] the bromomethylene groups were transferred into ester intermediate PPP derivative 5. The corresponding p-carboxyphenoxymethylene-substituted PPP 5 was obtained by hydrolysis of the ester group in the intermediate.[58] However, it was shown that p-carboxyphenoxymethylene-substituted PPP 5 was not soluble in water or aqueous bases due to relatively low density of charged functional groups pendent along the backbone and also to intermolecular hydrophobic interactions caused by the nonpolar alkyl side chains. As an alternative route,[55] the precursor 7 was therefore made from AB type monomer 6 via a successful step-growth polymerization. However, it was not possible to transform bromomethylene groups in precursor 8 to p-carboxyphenoxymethylene functionalities due to the poor solubility of the short side chains along the backbone in precursor 8.



Scheme 1.2: Synthesis of carboxylated PPP polyelectrolytes

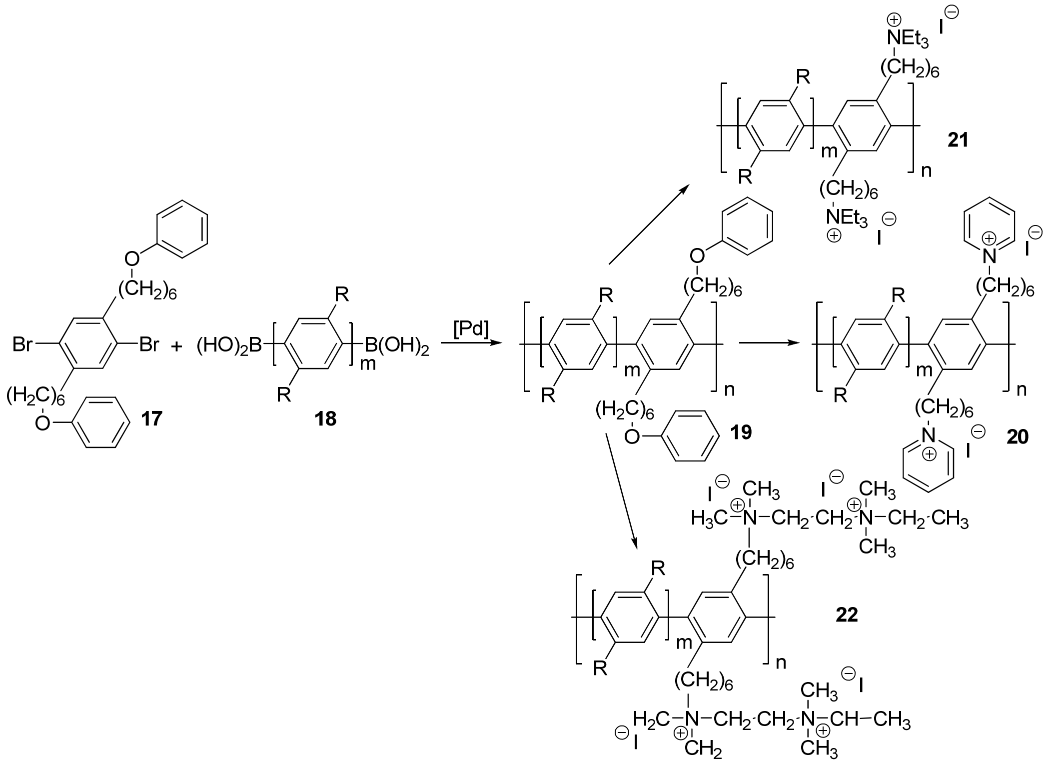
The explanation of this phenomenon is that the interior of cylinder-like cationic polyelectrolytes is covered by a dense, homogeneous shell of hydrophilic ionic side chains which prevent chain aggregation.[59] In the case of anionic polyelectrolytes such as 12 and 13, however, no sufficiently dense and homogeneous shell covering the interior of the polyelectrolyte due to the long n-alkyl spacers may lead to the insolubility in water.



Scheme 1.3: Synthesis of PPP polyelectrolytes via 6-phenoxyhexyl-substituted precursor

1.2.1.2. PPP polyelectrolytes via amino intermediates

All PPP polyelectrolytes reported so far have high density of charged functional groups. To fully understand rigid rod-like polyelectrolytes, PPP polyelectrolytes with low density of charged functional groups are required as well. An attempt based on this idea, shown in scheme 1.4,[59] however turned out to be a failure: polyelectrolytes 20-22 were insoluble in water. Similar PPP polyelectrolytes were reported to be insoluble in water too or soluble only as well-defined aggregates.[60-64]



Scheme 1.4: Attempted synthesis of PPP polyelectrolytes with low density of functional groups

From this unsuccessful attempt, it is concluded that PPP polyelectrolytes need a very dense and homogeneous hydrophilic shell extended from the nonpolar interior of the backbone for good solubility in water like PPP 15 and PPP 16. Low density and poor homogeneity of the hydrophilic shell can lead to occurrence of intramolecular side-chain segregation, i.e. hydrophilic and hydrophobic areas segregation on the polyelectrolytes' outer shell. According to the experimental evidence, segregation and thereby aggregation or precipitation of the polyelectrolytes via hydrophobic interactions occur when only every second phenylene repeating unit bear charged functional groups meaning a wide spacing of charged groups (Figure 1.1), such as 20-22.[55]

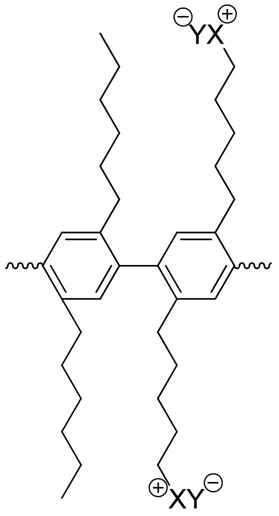
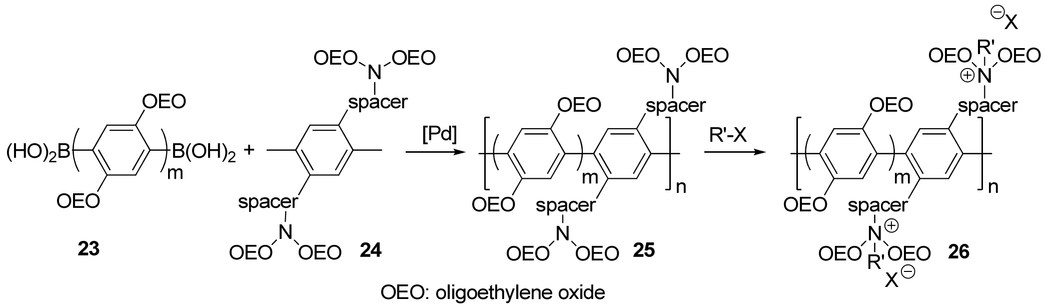


Figure 1.1: Presentation of models which lead to segregation in solutions

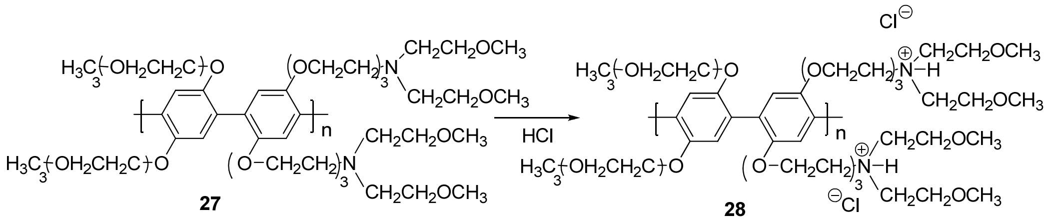
Therefore, non-ionic building blocks that are hydrophilic enough to prevent aggregation were suggested to synthesize water-soluble PPP polyelectrolytes with low charge density. A new strategy was started by Traser, shown in scheme 1.5. The core step of this new strategy is the attachment of oligoethylene oxide (OEO) side chains to the main chain of the PPPs.[65] These substitutions should allow (1) avoidance of the hydrophobic side chains and, (2) efficient prevention of hydrophobic interactions of the nonpolar backbone of the PPPs. However, the change from alkyl to OEO substituents has negative effects for the precursor strategy because ether cleavage step cannot be used in the presence of OEO side chains. The most convenient way to avoid ether cleavage as a macromolecular substitution step is to use tertiary amines as the precursor functionalities and to generate the polyelectrolyte via treatment of the tertiary amines precursor with low-molecular weight alkyl halides (scheme 1.5).[8]



OEO: oligoethylene oxide
spacer: (a) $-CH_2-$; (b) $-(CH_2)_6-$; (c) -OEO
R': H, n-alkyl, OEO
X: Cl, Br, I

Scheme 1.5: Synthesis of cationic PPP polyelectrolytes via water-soluble amino-functionalized precursors

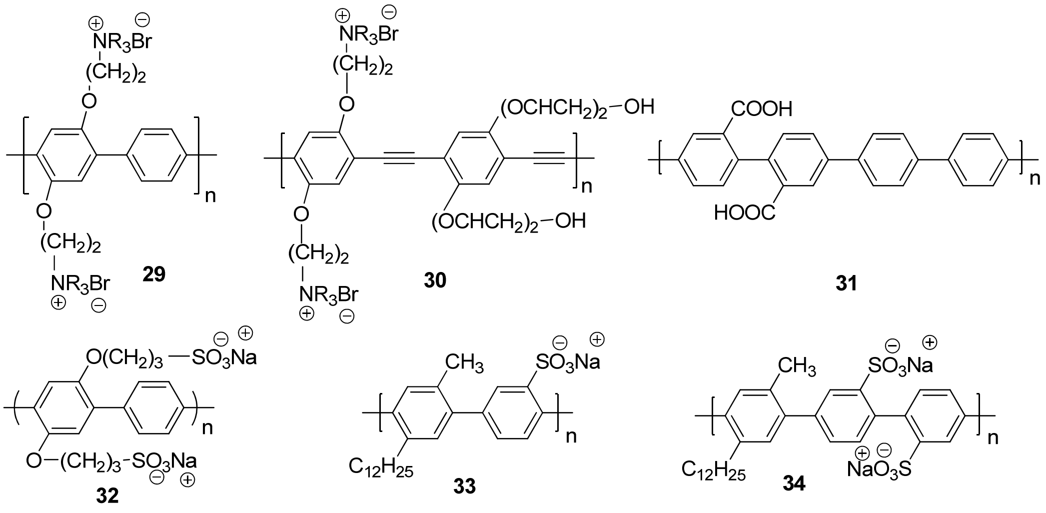
The positive side-effect of the new strategy is a clearly simplified and accelerated polyelectrolyte synthesis: the time-consuming ether cleavage is not needed anymore and thus the monomers are quickly available. Moreover, it was found, by extensive model investigations, the Pd-catalyzed polycondensation process was not affected by the polar, potentially coordinating, side chain. Using this new strategy, the first uncharged but water-soluble precursor PPPs such as 27 was obtained (Scheme 1.6).



Scheme 1.6: Synthesis of water-soluble polyelectrolytes from precursor PPPs

1.2.1.3. Further approaches to rigid, rod-like polyelectrolytes

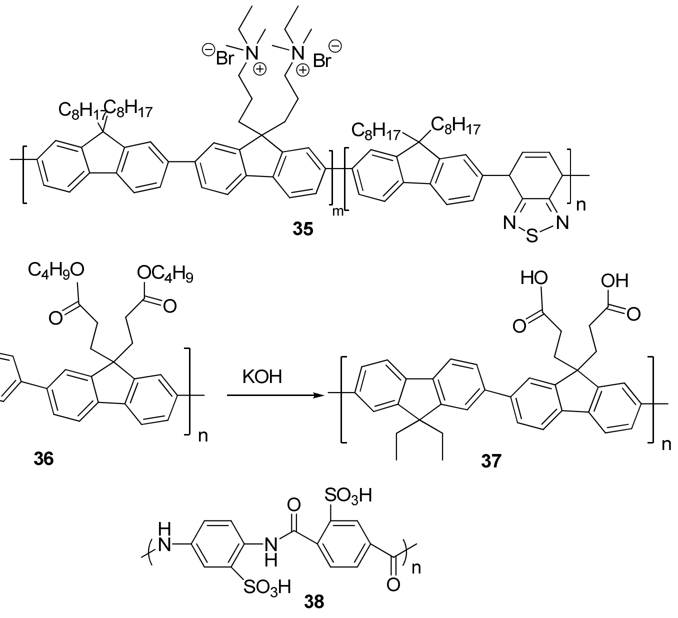
In addition to the work presented on the PPP polyelectrolytes above, other research was directed towards the synthesis of rod-like polyelectrolytes. Reynolds' group synthesized water-soluble cationic PPPs such as 29.[66] These polymers were developed with regard to their potential application as luminescent materials.[20] In 2000, Swager et al. reported a series of similar polyelectrolytes,[33,67] poly(p-phenylene ethynylenes), such as 30. These polymers were investigated as active components for chemosensors (Scheme 1.79). In respect to anionic polyelectrolytes, Wallow and Novak reported in 1991 a series of carboxylated PPPs such as 31 which have good solubility in aqueous bases.[68-70] In 1994, Reynolds' group first developed synthetic routes for sulfonated PPPs such as 32[71,72] via step-growth polymerization in direct synthetic routes. Later, Wegner et al. developed precursor synthetic routes of sulfonated PPPs such as 33 and 34.[60-64] Due to their long aliphatic side chains, these polymers form well defined cylindrical micelles in solution, which provides a lot of information on the association behavior of rod-like polyelectrolytes consisting of hydrophilic and hydrophobic sub-units. In this case, the studies offer an important supplement for the entire polyelectrolytes system studies.[55]



Scheme 1.7: New PPP polyelectrolyte structures

Beside development of new synthetic routes for PPP polyelectrolytes, other different rigid-rod polyelectrolytes structures have also been investigated. Conjugated polyfluorene polyelectrolytes have been mainly developed with regard to their potential application in optoelectronics such as light-emitting diodes (LEDs), photovoltaics, and sensors.

Both anionic charged and cationic charged polyfluorene have been reported, such as 35[73] and 37[74] (Scheme 1.8). To synthesize 37, Brookins et al. in 2007 reported a base-free Suzuki coupling reaction,[74] where cesium fluoride and tetrabutylammonium fluoride were used to activate boronic acids. Based on this technique, a carboxylic acid-functionalized polyfluorene was converted from butyl carboxylate-functionalized polyfluorene 36. In 2004, fully sulfonated poly(aramides), 38, were successfully prepared by application of the Yamazaki-Hifashi polycondensation technique from 2,5-diaminobenzene sulfonic acid and sulfoterephthalic acid in the presence of triphenyl phosphate, pyridine, and lithium chloride in N-methylpyrrolidone as the solvent.[75,76] Based on fully sulfonated poly(aramides) 37, an effective method of determination of charge and molecular weight of rigid-rod polyelectrolytes was reported by Boehme et al. in 2007.[77]



Scheme 1.8: New polyelectrolyte structures

1.2.2. Synthesis of rigid dendronized polymers

Dendronized polymers are another type of potential rigid polyelectrolytes. Conformation of dendronized polymers can vary from random-coil to fully stretched linear rod just by proper substitution with large dendrons. Rigid-rod polyelectrolytes can therefore be obtained by modification of pendent dendrons with functional groups. Synthesis routes of dendronized polymers are currently classified into (a) attach-to route and (b) macromonomer route. In the attach-to route, the polymer backbone is synthesized with anchor groups for attaching dendrons. The concentration of these anchor groups can be varied. The anchor groups on the polymer backbone later are used to attach a dense sequence of dendrons. In the macromonomer route, however, the classical dendrimers are synthesized first as monomers and then are polymerized into dendronized polymers. It is concluded so far that the macromonomer route is superior to the attach-to route since higher molecular weights can be obtained.[53] The polymerization process of the macromonomer approach is categorized into (a) radical polymerization (b) step-growth polymerization. Figure 1.2[53] shows examples of reported macromonomer structures with protected functional groups which can be converted to charged function groups in aqueous solutions. Both Frechet's group and Schluter's have reported synthetic routes of potentially anionic and cationic dendronized polymers[78,79].

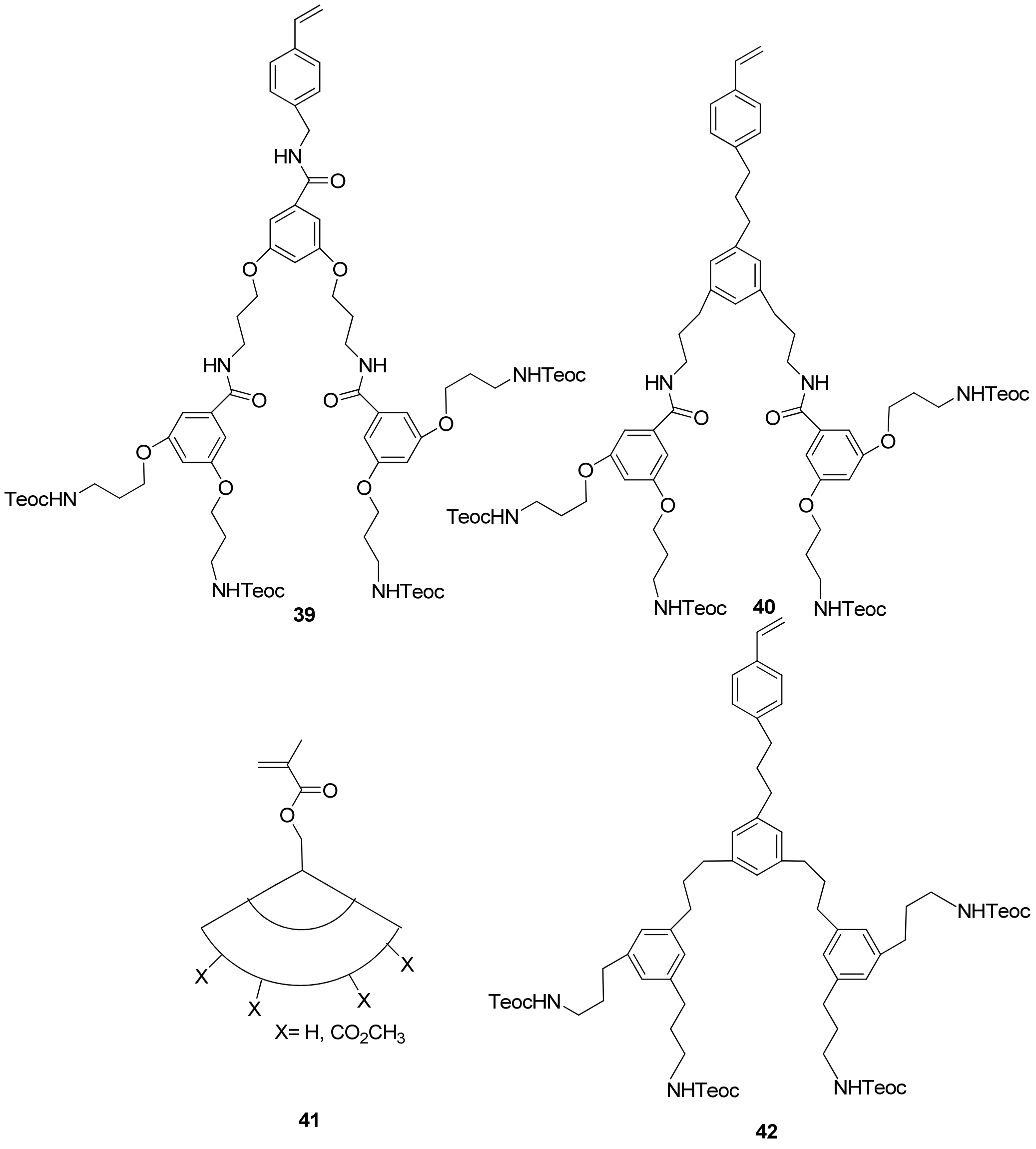


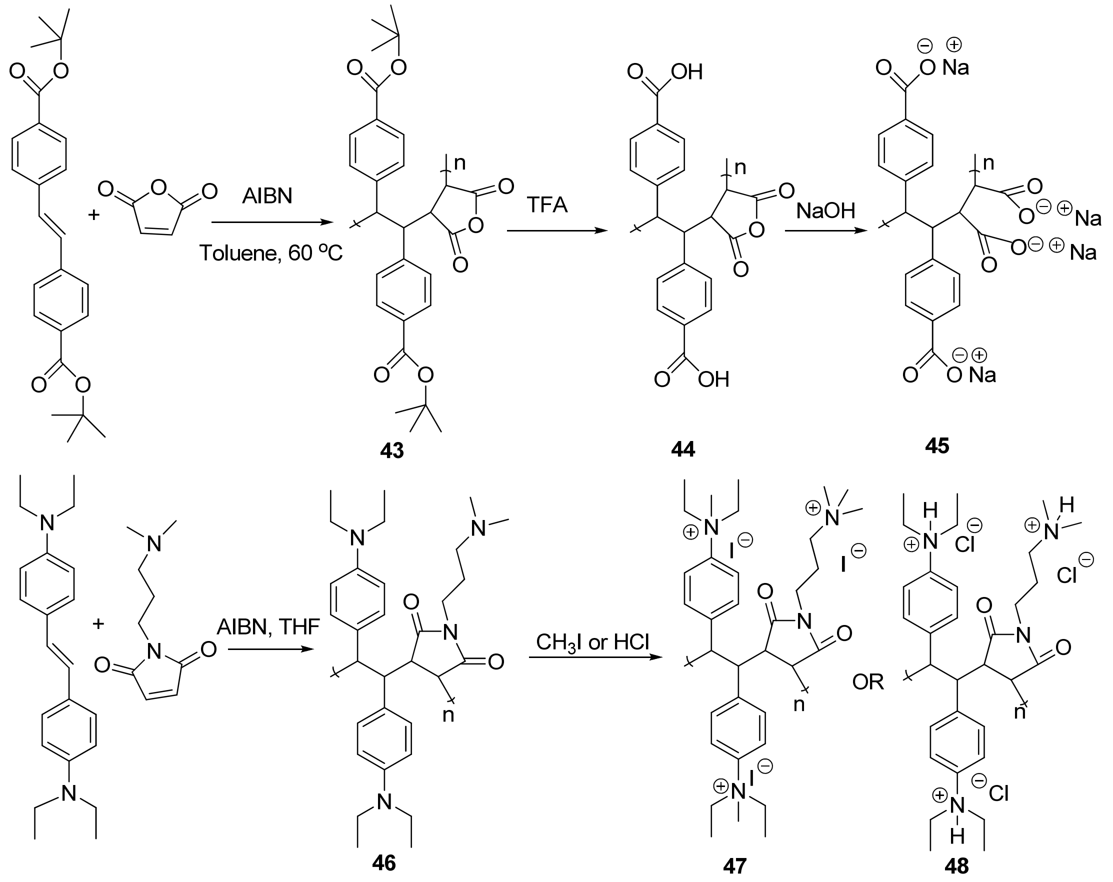
Figure 1.2: Reported macromonomer structures. Teoc = (trimethylsilyl)ethoxycarbonyl

1.2.3. Synthesis of rigid linear polymers via free radical polymerization

Free radical polymerization is known to be tolerant of many kinds of functional groups along the backbones, which allows incorporation of functional monomers into a (co)polymer via free radical polymerization.[80]

Recently, synthetic routes of rigid polyampholytes based on *N,N,N',N'*-tetraalkyl-4,4'-diaminostilbenes (TDAS) and maleic anhydride (MAH) via free radical alternating copolymerization were reported by Turner and Mao.[81] Based on this technique, anionic and cationic polyelectrolytes based on the alternating copolymer of substituted stilbenes have also been reported by Turner and Mao,[82] shown in scheme 1.9 those are expected to be rod-like copolymers. After precursor alternating copolymer 43 was obtained via free radical copolymerization, the *t*-butyl ester groups were cleaved by trifluoroacetic acid (TFA) to yield intermediate 44. And the remaining anhydride groups were undisturbed. The anhydride was hydrolyzed to obtain the anionic polyelectrolyte 45 which was proved to be soluble in water. Precursor 46 of cationic polymer was synthesized in the similar way. Followed by the treatment of hydrochloric acid solution or iodomethane solution, the amine groups attached to the main chain of 46 can be easily converted into quaternary ammonium groups and thus polycations 47 and 48 were readily prepared.

Molecular weight distributions were obtained using SEC. The chain rigidity was supported by dynamic light scattering studies. The hydrodynamic radius (R_h) of the polymer 46 remained almost the same at different temperatures. Moreover, the hydrodynamic radius (R_h) of polymer 46 was identical to that of the hydrolyzed, highly charged form of polymer 47, which suggests that the neutral polymer chain is already fully extended and thus is rigid.



Scheme 1.9: General presentation of synthetic routes of linear anionic and cationic polyelectrolytes via free radical polymerization

1.3. Characterization and Special Properties of Polyelectrolytes

1.3.1. Chain rigidity of polyelectrolytes

Several polymer determination techniques can be used to probe the stiffness of a polymer chain.

For rigid chain conformation, usually it is qualitatively observed that in a solution ^{1}H NMR spectrum the peaks of the hydrogen atoms on the main chains are broadened and almost invisible and the peaks of the hydrogen atoms on the side chains are also very broad. This is in agreement with severely restricted rotation of the polymer backbone, indicating the rigidity of the polymer chains.

The effect of temperature on the hydrodynamic radius (R_h) obtained by dynamic light scattering can be used as a probe of chain stiffness. The R_h of a rigid polyelectrolyte should remain almost constant as the temperature of the solution is varied. Moreover, R_h of rigid polyelectrolytes dissolved in dilute aqueous acid, where the polymers were hydrolyzed and highly charged, was same as the R_h of un-hydrolyzed form of the polymer dissolved in organic solvents, indicating the rigidity of the neutral initial precursors.[82] Another way to measure the stiffness of the polymer backbone is using multi-angle laser light scattering (MALLS).[78] Generally, the polymer conformation is related to the exponent v in the power dependence of the following equation[78] concerning z-average root-mean-square (RMS) radius ($R_{g,z}$) to the weight-average molecular weight (M_w).[83-85]

$$R_{g,z} \propto M_w^{\ v} \tag{1.1}$$

The theoretical value v for a rigid rod polymer equals 1.[78] By comparing the experimental values v to the theoretical value v, the stiffness of the polymer backbone can be determined.

The most direct measurement of the rigidity of polyelectrolytes is to determine the persistence length. Stiffness is reflected in the persistence length, l_p, the distance over which the spatial orientations of monomers are not mutually independent, i.e. the orientation of monomer segments 'persist' from one monomer to the next.[86] The persistence length can be estimated from the relationship between molar mass, M, and root-mean-square radius of gyration, R_g. Both M and R_g can be readily measured by size exclusion chromatography with multi-angle laser light scattering (SEC-MALLS). The equation relating R_g,M and l_p is Eq. (1.2):[86]

$$R_g^{\ 2} = \frac{l_p M}{3M_L} - l_p^{\ 2} + \frac{2l_p^{\ 3} M_L}{3M} - \frac{2l_p^{\ 4} M_L^{\ 2}}{M^2}(1 - e^{-\frac{M}{l_p M_L}}) \tag{1.2}$$

Where the persistence length l_p and the molar mass per unit contour length M_L can be obtained by a least-squares non-linear regression fit of the data to Eq. (1.2)[87-90].

1.3.2. Viscosity investigations

For flexible chain polyelectrolytes, both intramolecular electrostatic interactions and intermolecular electrostatic interactions exist in the dilute solutions. The famous "polyelectrolyte effect" observed in the Huggins plot, that η_{sp}/c_p increases as c_p decreases in dilute salt-free solutions, has been extensively discussed in the literature.[32,91-93] There are some statements that attribute the whole polyelectrolyte effect to conformational changes, i.e. increasing intramolecular coulomb repulsion due to coil expansion at decreasing ionic strength. Equations have also been proposed to model the observed increase of η_{sp}/c_p with decreasing c_p. However, this model does not explain the decrease of η_{sp}/c_p at very low c_p. Therefore, other concepts have been developed by Cohen, Priel and Rabin to better explain the effect[94-97]: it is assumed that the dilution of polyelectrolytes starts at a high ionic concentration. Hence, in the initial dilution steps, the Debye screening length, defined as the length over which charges are screened, increases much faster than the average distance between each macromolecule chain, shown in Figure 1.3.[9] As a result, the intermolecular electrostatic repulsion increases, leading to the expansion of the macromolecule chains and thus the increase of η_{sp}/c_p upon the initial dilution of salt-free solutions. On further dilution, the ionic strength is more and more dependent on self-dissociation of water and dissolved gasses:[50] at very low polyelectrolyte concentration, the concentration of dissociated counterions becomes lower than that of dissociation of water and the residual ionic impurities (such as dissolved CO_2) and the ionic strength remains constant upon further dilution.[98] Accordingly, the screening length increases less efficiently than the average distance between each macromolecule chain. The electrostatic interaction of polyelectrolytes decreases finally and thus η_{sp}/c_p reduces.[9] Therefore, it is of great importance to develop polymer structures that allow the investigation only of the effects of electrostatic interactions on the solution properties of polyelectrolytes.

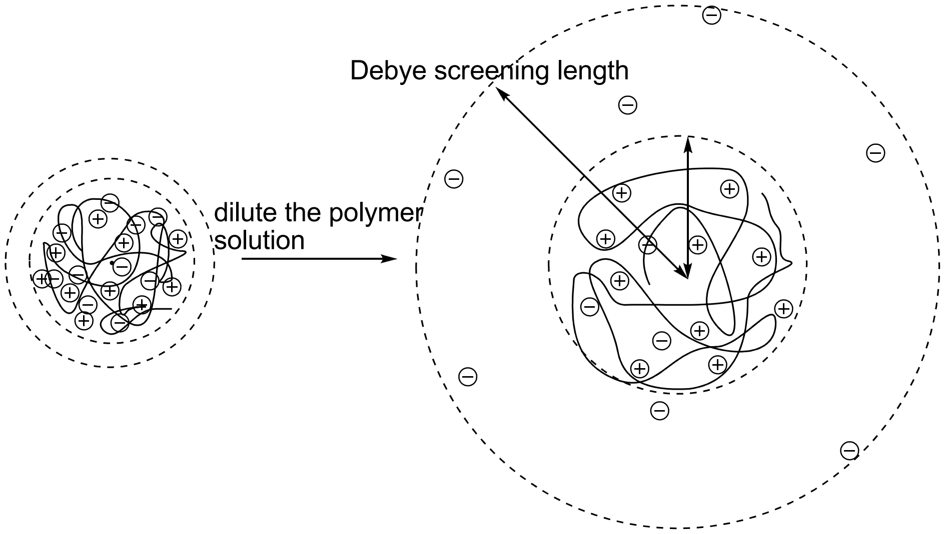


Figure 1.3: Presentation of changes of the Debye screening length (outer length) and the polyelectrolyte's chain conformation (inner circle) on decrease of ionic strength in salt-free solutions

1.4. Research Objectives

The following three chapters will introduce research on the polymerization behavior of methyl substituted stilbenes area. By being located on the different positions of benzene ring, The methyl substituents are believed to impact copolymerization behavior of stilbene monomers with maleic anhydride differently: methyl group on the ortho position can disturb the conjugation between the ethylene and phenyl ring by twisting the phenyl ring out of the plane and therefore slows down the copolymerization rate with maleic anhydride. On the other hand, the methyl group on the para position is electron donating, which increases the copolymerization rate with maleic anhydride. In chapter 2, conversion versus time data were obtained, the copolymerization rates for methyl substituted stilbenes with maleic anhydride will be compared, and the methyl substituent impact on copolymerization behavior will be discussed. The alternating copolymer structure will be confirmed by quantitative ^{13}C NMR. Copolymers will be also characterized by TGA, DSC, and ^{1}H NMR.

There is a need for more examples of rigid polyelectrolytes and for structures that can be more easily synthesized while maintaining functional groups along the backbone. Stilbene can be readily functionalized and the incorporation of stilbene can be expected to have a large effect on chain dimensions due to steric repulsion of the pendent phenyl ring along the chain.

N-Substituted maleimides have been found to homopolymerize via free radical polymerization[99] and the resulting homopolymers were reported to have stiff chains with high glass transition temperatures. *N*-substituted maleimide copolymers have a strong tendency to be alternating due to the strong electronegativity of the maleimide double bond. The incorporation of maleimide and its derivatives in our free radically prepared copolymers system are anticipated to improve the chain rigidity and to introduce unique solution and other physical properties.

In chapter 3, synthesis and characterization of a series of functionalized stilbenes and n-phenylmaleimides will be introduced. Preliminary work on copolymerization of these functionalized stilbenes and *N*-phenylmaleimides will be presented, such as data from ^{1}H NMR, SEC, DSC and TGA.

It’s been known for years that (*E*)-stilbene cannot undergo homopolymerization readily.[100-102] Possible reasons for this failure could arise from the large energy barrier which results from the stability of the monomer and an unstable high-energy transition state caused by steric hindrance. Adding one methyl group on the ortho position of the phenyl ring is expected to disturb the conjugation of stilbene monomer and thereby make the monomer less stable because the phenyl ring on which the methyl group is located will twist out of the plane due to steric hindrance. Meanwhile, the methyl substituent will lead to less stable transition state compared to unsubstituted stilbene. In chapter 4, the methyl substituent impact on the molecular structure change and reactivity change of 2-methylstilbene will be furthered discussed and attempted homopolymerization of 2-methylstilbene will be described.

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Chapter 2. FREE RADICAL COPOLYMERIZATION OF METHYL SUBSTITUTED STILBENES WITH MALEIC ANHYDRIDE

2.1. Abstract

Stilbene-maleic anhydride is a well-known donor-acceptor comonomer pair which undergoes free radical copolymerization to form an alternating copolymer. Neither stilbene nor maleic anhydride homopolymerizes due to steric hindrance caused by the substituents around the ethylene double bond. The methyl substituents on the phenyl ring of stilbene can change the reactivity of stilbene by changing the resonance stability of the propagating radical and steric hindrance in propagation step and thereby change the copolymerization rate of stilbene with maleic anhydride. A series of methyl substituted stilbenes were synthesized and copolymerized with maleic anhydride. Conversion versus time study was undertaken to understand the methyl substituent effect on copolymerization rates. Methyl substituted stilbene-maleic anhydride copolymers were determined by quantitative ^{13}C 1D NMR to be alternating copolymers. SEC measurements show that the weight average molecular weights of these copolymers vary from 3 000 to over 1 000 000 g/mol. No glass transition temperature or crystalline melting temperature was observed between 0 °C and 250 °C by DSC. TGA shows that these polymers have 5% weight loss around 290 °C.

2.2. Introduction

1,2-Disubstituted ethylenes such as maleic anhydride and (*E*)-stilbene (*trans*-stilbene) usually exhibit very little or no tendency to undergo homopolymerization mainly due to kinetic considerations. The approach of the propagating radical to a monomer molecule is sterically hindered.[1] However, (*E*)-stilbene-maleic anhydride readily undergo free radical copolymerization to form an alternating copolymer because (*E*)-stilbene is a strong electron donor and maleic anhydride is an electron acceptor.[2-8] Stilbene-maleic anhydride copolymer was first reported by Wagner-Jauregg[2] in 1930 and appeared insoluble in xylene. Lewis and Mayo[3] found that a gel formed in chloroform during the copolymerization of (*E*)-stilbene with maleic anhydride and the yield for the copolymer was up to 60%. Later insoluble and crosslinked stilbene-maleic anhydride copolymer was also reported by Hallensleben[4] via radical copolymerization. Tanaka and Vog,[1,5] however, argued that high molecular weight led to insolubility, not crosslinking. More recently the copolymer has been studied by Rzayev et al.,[6] Edbon et al.,[7] and McNeill et al.[8] Rzayev et al. investigated the formation of a stilbene-maleic anhydride charge-transfer complex based on copolymerization in methyl ethyl ketone initiated with benzoyl peroxide at 80 ^{o}C.[6] Stilbene-maleic anhydride copolymer composition and molecular weight distribution have been investigated by Edbon et al. who obtained the copolymer from the free radical copolymerization experiment in methyl ethyl ketone at 60 ^{o}C using 2,2'-azo-bis-isobutyronitrile as initiator. They found the copolymer composition rich in maleic anhydride with a broad molecular weight distribution and attributed these effects to phase separation during the copolymerization.[7] McNeill et al. have conducted a thorough investigation of the alternating structure of stilbene-maleic anhydride copolymer and thermal degradation process and found no evidence for crosslinking based on TGA data or IR spectrum.[8]

We have interest in substituted stilbene alternating copolymers because these structures are anticipated to have potentially rigid backbones due to steric repulsion of the pendent phenyl groups along the main chain. In addition the rich chemistry available for substituted stilbenes makes the preparation of a variety of functional stilbene derivatives possible. Copolymerization of these monomers can enable the precise placement of functional and ionic groups along these rigid polymer backbones.[9,10] In this study we prepared several methyl substituted (*E*)-stilbene monomers and observed significant difference in the rates of polymerization with maleic anhydride depending on the position of the methyl groups on the phenyl ring.

To the best of our knowledge, there has been no work on preparation of copolymers of methyl substituted (*E*)-stilbenes with maleic anhydride and characterization of the properties of these novel structures.

2.3. Experimental Section

2.3.1. Materials

(*E*)-Stilbene (EMS-I, Aldrich, 96%), maleic anhydride (MAH, Aldrich, ≥99.0%), 2-methylbenzyl chloride (Aldrich, 99%), 4-methylbenzyl chloride (Aldrich, 98%), *o*-tolualdehyde (Aldrich, 97%), benzaldehyde (Aldrich, ≥99%), potassium tert-butoxide solution 1.0 M in tetrahydrofuran (KOtBu, Aldrich), triethylphosphite (Aldrich, 98%), 2,2′-azobisisobutyronitrile (AIBN, Aldrich, 98%) were all purchased from Aldrich and used as received. Tetrahydrofuran (THF, Fisher, HPLC grade) and hexane (Fisher, HPLC grade) and methylene chloride (Fisher, HPLC grade) were used as received. Water was deionized before use.

2.3.2. Characterization

^{1}H NMR spectra and ^{13}C NMR spectra of monomers were determined at 25 °C in $CDCl_3$ at 400 MHz with a Varian Inova spectrometer or 500 MHz with a Jeol Eclipse +500 spectrometer. Quantitative ^{13}C 1D NMR spectra for determination of copolymer compositions were recorded of solution in $CDCl_3$ on a Varian Unity spectrometer at 400 MHz with proton decoupling and nuclear Overhauls enhancements suppressment. 10 s recycle delays between pulses allow full relaxation of the carbon spins. Temperature is set at 50 ^{o}C. Number of pulses is 500. Pulse width is 16.5 μs (corresponding to a nuclear tip angle of 90^o). IR spectra were recorded with a MIDAC M2004 FT-IR spectrophotometer in the reflection mode on powders. Melting points of monomers were measured on BUCHI Melting Point B-540 instrument.

Thermogravimetric analysis (TGA) was conducted under nitrogen, from 25 ^{o}C to 600 ^{o}C at a heating rate of 10 ^{o}C / min using a TA Instrument TGA Q5000. Glass transition temperatures (T_g) were determined using a Perkin-Elmer Pyris 1 DSC at heating rate of 10 ^{o}C/min and cooling rate of 20 ^{o}C in a nitrogen atmosphere.

Molecular weights of the synthesized polymers were determined using a Waters size exclusion chromatograph equipped with a Waters 1515 isocratic HPLC pump, a Viscotek 270 viscosity detector, and a Waters 2414 differential refractive index detector operating at 880 nm and 35 ^{o}C and a Waters 717 plus autosampler, a Wyatt miniDAWN multiangle laser light scattering (MALLS) detector operating a He-Ne laser at 690 nm. The d_n/d_c values were determined using the Wyatt Astra V software package. SEC measurements were performed at 40 °C in THF at a flow rate of 1.0 mL/min.

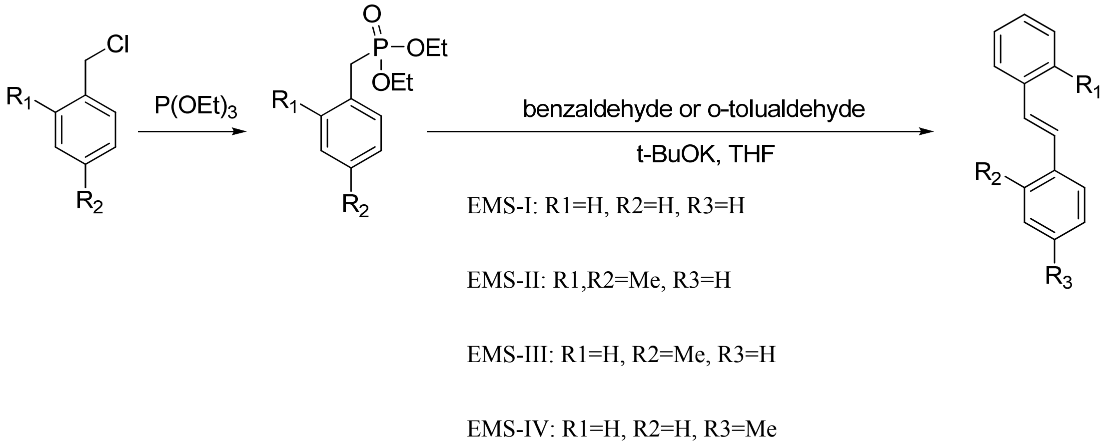
2.3.3. Synthesis of methyl substituted *(E)*-stilbenes (EMSs)

The Wittig-Horner reaction of an aldehyde with a phosphorus ylide is employed to synthesize the EMSs11 (Scheme 2.1).

A typical procedure to prepare (*E*)-2,2'-dimethylstilbene (EMS-II) is as follows: 2-methylbenzyl chloride (16.40 g, 117.01 mmol) was heated with excess triethylphosphite (77.77 g, 81 mL, 468.04 mmol) at 160 ^{o}C for 24 h. The remaining triethylphosphite was then removed by vacuum distillation at 80 ^{o}C (0.2 mmHg) to afford 2-methylbenzyl diethylphosphonate. Yield: 95%, 26.90 g. To a solution of 2-methylbenzyl diethylphosphonate (27.47 g, 113.50 mmol) and *o*-tolualdehyde (13.62 g, 113.50 mmol) in dry THF (50 mL) cooled in an ice bath was added KO^{t}Bu (1.0 M in THF, 120 mL) dropwise over 20 min. The solution was stirred at room temperature for 24 h. Then the solution was poured into 500 mL of water. The product precipitated from the solution was collected by filtration and washed with water and vacuum dried overnight to yield a white crystalline solid. Yield: 80%, 18.89 g. There was no detectable Z isomer by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.63 (d, 2H), 7.20-7.25 (m, 8H), 2.43 (s, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ ppm: 136.9, 135.9, 130.5, 128.1, 127.7, 126.3, 125.7, 20.1. Mp: 82-84 ^{o}C (Lit.[12]: 83-84 ^{o}C).

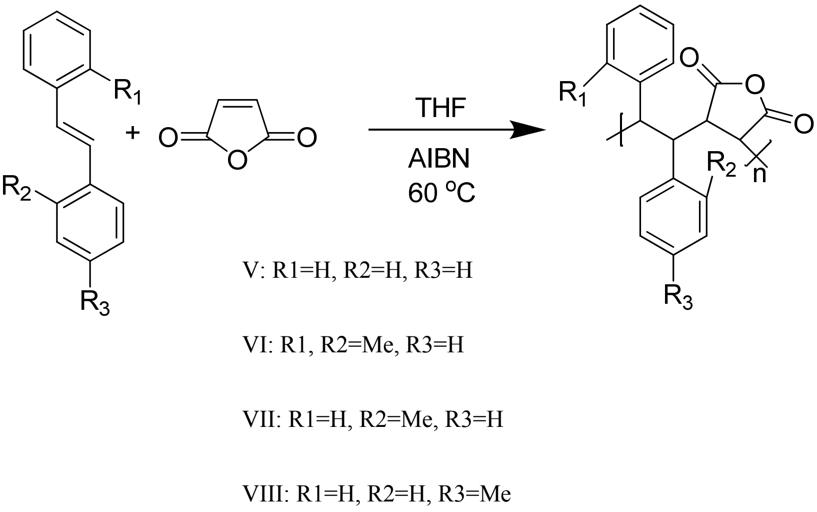
(*E*)-2-Methylstilbene (EMS-III) was synthesized via condensation of 2-methylbenzyl diethylphosphonate (15.00 g, 61.98 mmol) and benzaldehyde (6.57 g, 61.98 mmol) under the same Wittig-Horner reaction conditions as EMS-II. After condensation, the solution was poured into water. The oily product was extracted with methylene chloride, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (hexane) yielded a clear oil. Yield: 87%, 9.70 g. There was no detectable Z isomer by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.59 (d, 1H), 7.52 (d, 2H), 7.29-7.40 (m, 3H), 7.27 (d, 1H), 7.15-7.25 (m, 3H), 7.00 (d, 1H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ ppm: 137.8, 136.5, 135.9, 130.5, 130.1, 128.8, 127.72, 127.68, 126.68, 126.67, 126.3, 125.5, 20.0. Mp: 30-31 °C (Lit.[13]: 30 °C). Bp: 212 °C at atmospheric pressure.

(*E*)-4-Methylstilbene (EMS-IV) was synthesized via condensation of 4-methylbenzyl diethylphosphonate (12.00 g, 49.59 mmol) and benzaldehyde (5.26 g, 49.59 mmol) under the same Wittig-Horner reaction conditions as EMS-II, where 4-methylbenzyl diethylphosphonate was synthesized from 2-methylbenzyl chloride with excess triethylphosphite. After the condensation reaction, the solution was poured into water. The product precipitated from the solution was collected by filtration, and washed with water and vacuum dried overnight to yield a white solid. Yield: 86%, 7.68 g. There was no detectable Z isomer by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 7.03-7.60 (m, 11H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ ppm: 137.6, 134.7, 129.5, 128.7, 127.8, 127.5, 126.54, 126.50, 21.4. Mp: 121-122 °C (Lit.[14]: 118-120 °C).



Scheme 2.1: Synthesis of (*E*)-methyl substituted stilbenes

The EMSs, MAH, and THF were mixed with the initiator, AIBN, in a 50-mL septum sealed glass bottle equipped with a magnetic stirrer. All of the copolymerization experiments contained an equimolar ratio of EMSs and MAH except for the copolymer composition study. The initiator concentration was 1 wt. % based on monomer in all polymerizations. For instance, EMS-II (2.08 g, 10.00 mmol), MAH (0.98 g, 10.00 mmol) and THF (13.75 mL) were mixed with AIBN (0.0306 g) in a 50-mL septum sealed glass bottle equipped with a magnetic stirrer. The mixture was degassed by purging with argon for 10 min and polymerized at 60 °C (Scheme 2.2). The reaction duration varies in the conversion versus time study and for the copolymer composition study is 24 h. Copolymers were recovered by precipitation into hexane in the conversion versus time study and purified by reprecipitation from THF into hexane in the copolymer composition study. All polymers were dried under vacuum at 60 °C overnight before characterization. Two peaks associated with the anhydride groups of the copolymers ($1841\ \text{cm}^{-1}$ and $1775\ \text{cm}^{-1}$) were clearly observed in the IR spectrum. Copolymer VI and copolymer VII were soluble in THF, whereas copolymer V and copolymer VIII had poor solubility in THF.



V: R1=H, R2=H, R3=H

VI: R1, R2=Me, R3=H

VII: R1=H, R2=Me, R3=H

VIII: R1=H, R2=H, R3=Me

Scheme 2.2: Alternating copolymerization of (*E*)-methyl substituted stilbenes with maleic anhydride

2.4. Results and Discussion

Copolymerization conversions in the conversion versus time study were measured for different time durations but with a constant overall monomer concentration (20 wt. %) in THF solvent at 60 ^{o}C using AIBN. Conversion equals the weight of a polymer divided by the total weight of monomers and then times 100%. Polymers were isolated by carefully precipitating the polymerization solution into hexane. NMR analysis of the polymer showed no residual unreacted monomer. As shown in Figure 2.1, the copolymerization rates in the first stage linearly increase in the following order: EMS-IV-MAH > EMS-I-MAH > EMS-III-MAH > EMS-II-MAH. As the time duration is approaching 24 h, the increase of copolymerization rates for all the copolymers slows down and finally levels off as the comonomers are depleted in concentration. In order to understand the order of the copolymerization rates, the following aspects are considered: a. the methyl substituent on para position of EMS-IV is inductively electron donating, which leads to a more reactive stilbene radical than EMS-I radical and thus faster cross-propagation with MAH than EMS-I. Therefore, the copolymerization rate of EMS-IV with MAH is faster than EMS-I with MAH; b. steric hindrance arising from the ortho methyl substituent on the phenyl ring and a vinyl proton causes the phenyl ring to rotate out of plane with the vinyl. It was reported[15,16] that the torsion angle around the C-Ph bond for EMS-II is larger than for EMS-I, where the torsion angle is defined as the angle θ around the C-Ph bond in the C=C-C-C linkage (shown in Figure 2.2). This enlargement of the torsion angle around C-Ph bond leads to less conjugated EMS-II which results in a more reactive stilbene radical but less stable transition state. Therefore the effect of this rotational vibration along C-Ph bond on copolymerization rate is complicated; c. the ethylene double bond is less accessible due to steric hindrance from the ortho methyl substituent on the aromatic ring, which slows down the cross-propagation and the copolymerization rates of EMS radicals towards MAH monomer in the order of EMS-II < EMS-III < EMS-I.

In the copolymer composition study, copolymerization was targeted to 10% conversion with different monomer feed ratios in THF at 60 ^{o}C at unchangeable monomer concentration and initiator concentration. All copolymers were reprecipitated from THF into hexane in order to get rid of monomer residues. The compositions of the copolymers were determined by comparing the relative intensities of the signals arising from the carbonyl carbons of MAH units and the aromatic carbons of EMS units on ^{13}C NMR spectrum shown in Figure 2.3.[9] It can be found from Table 2.1 that EMSs-MAH copolymers have an approximately equimolar composition irrespective of the initial monomer feed ratios indicating their alternating copolymer structure, also shown in Figure 2.4. Note that for EMS-IV having 0.65 and 0.75 in monomer feed ratio, the copolymer composition is richer in EMS-IV units. Integration inaccuracy is within ±5%.

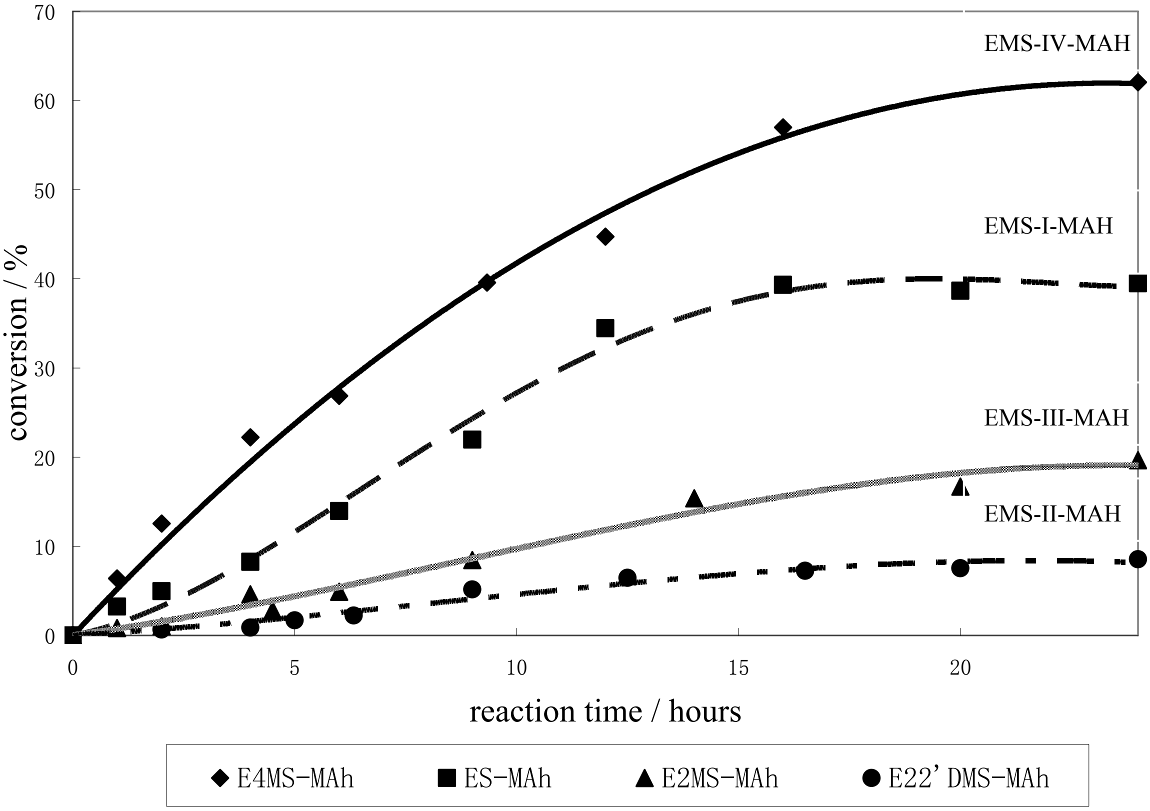


Figure 2.1: Conversion vs. time plots for comparison of copolymerization rates of methyl substituted *(E)*-stilbenes with maleic anhydride

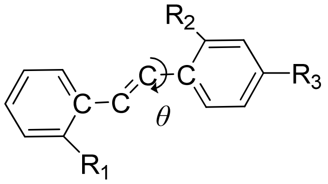


Figure 2.2: Torsion angle θ

It is interesting to notice from Table 2.1 that conversions of the copolymerization increase with decrease of EMS in the feed ratios. In radical copolymerization of EMS-I with MAH,[9] Edbon et al. also observed that rates of copolymerization increased as the amount of EMS-I in the feed was decreased and concluded that low reactivity of EMS-I towards the 2-cyano-2-propyl radical generated from AIBN[17-19] was responsible. It is very likely in our system that reactivities of EMSs towards 2-cyano-2-propyl radical are also low so that conversions of the copolymerization go up with the decrease of EMS feed ratios.

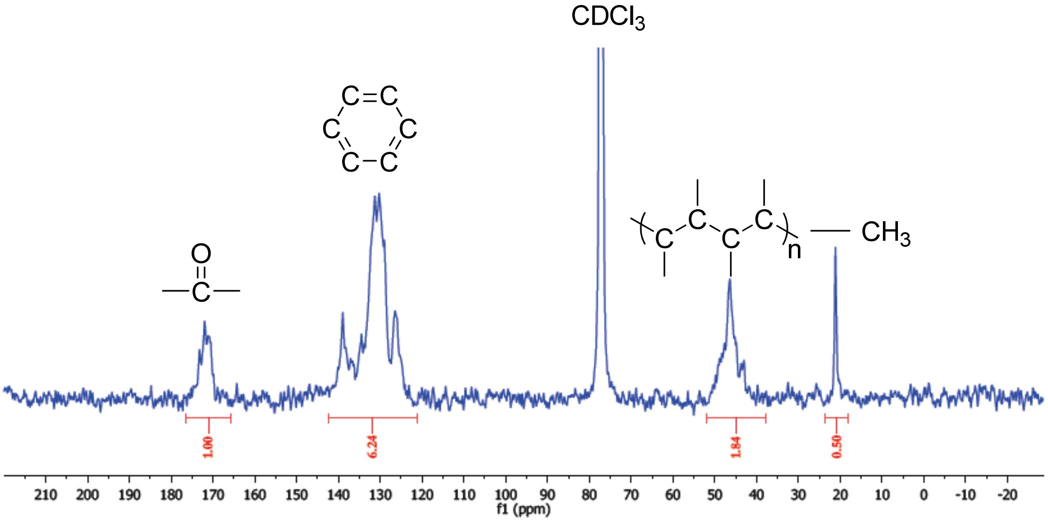


Figure 2.3: A typical 400 MHz ^{13}C 1D NMR spectrum of a EMS-IV-MAH copolymer containing 0.50 mol fraction of EMS-IV in $CDCl_3$

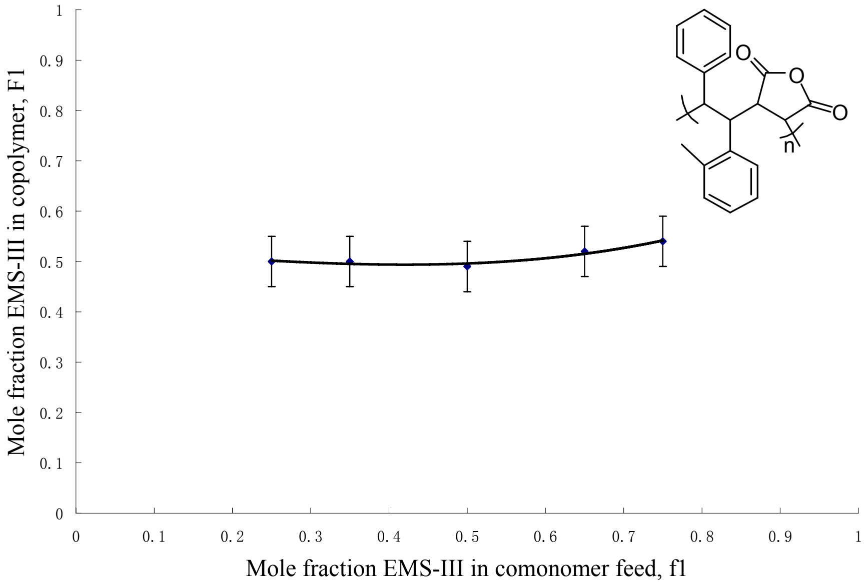


Figure 2.4: Variations of mole fractions in comonomer feed and copolymer compositions for EMS-III

Table 2.1: Compositions, polymerization time, conversions and molecular weights for EMSs-MAH copolymers

Mol fraction EMSs			Poly-meri-zation time (h)	Conversion (%)	M_n g/mol	M_w g/mol	SEC Trace
	In feed	In copolymer ^{13}C NMR					
EMS-II	0.25	0.43±0.05	24	20	2 700	3 500	unimodal
	0.35	0.51±0.05	24	18	——	——	——
	0.50	0.50±0.05	24	8.5	2 500	3 200	unimodal
	0.65	0.47±0.05	24	8.3	——	——	——
	0.75	0.52±0.05	24	3.0	3 500	4 000	unimodal
EMS-III	0.25	0.50±0.05	12	21	4 000	5 500	unimodal

	0.35	0.50±0.05	12	14	——	——	——
	0.50	0.49±0.05	12	12	4 500	6 300	unimodal
	0.65	0.52±0.05	12	10	2 900	4 400	unimodal
	0.75	0.54±0.05	12	4.8	3 700	5 000	unimodal
EMS-IV	0.25	0.46±0.05	2	20(peak1)	7 340 000	10 900 000	bimodal
				(peak2)	6 800	9 900	
	0.35	0.50±0.05	2	13(peak1)	4 860 000	5 670 000	bimodal
				(peak2)	18 000	23 200	
	0.50	0.52±0.05	2	13(peak1)	3 440 000	4 440 000	bimodal
				(peak2)	11 300	15 600	
	0.65	0.61±0.05	2	4.8(peak1)	2 810 000	3 880 000	bimodal
				(peak2)	12 500	18 400	
	0.75	0.63±0.05	2	3.5(peak1)	3 880 000	5 500 000	bimodal
				(peak2)	9 000	14 600	

The molecular weights of these EMSs-Maleic anhydride copolymer were obtained from the SEC traces shown in Table 2.1. These molecular weights are based on the use of both the light scattering (L.S.) detector which is more sensitive to relatively high molecular weights and refractive index (R.I.) detector. For EMS-II-MAH copolymers and EMS-III-MAH copolymers, SEC traces given by two detectors are unimodal, but not for EMS-IV-MAH copolymers. As shown in Figure 2.5, the SEC trace given by R.I. detector on the right is bimodal and the higher molecular weight peak grows in height significantly and the lower molecular weight peak shrinks in height relatively in the L.S. trace on the left. This significant change on height arises from the sensitivity difference of the two detectors. However, both traces show that the molecular weight distributions of the copolymers of EMS-IV with MAH are bimodal. The number-average molecular weight data and the weight-average molecular weight data of EMS-II-MAH copolymer, EMS-III-MAH copolymer and EMS-IV-MAH copolymer are provided in Table 2.1, where the molecular weight for EMS-II-MAH copolymer is found to be below 5 000 g/mol, and for EMS-III-MAH copolymer below 10 000 g/mol. The low molecular weights of these copolymers are most likely due to the steric effect of the ortho methyl substituent in the transition state which slows down the propagation step. The table also provides two sets of molecular weight information for bimodal trace of EMS-IV-MAH copolymer, respectively. The molecular weight for peak 1 is over 1 000 000 g/mol and for peak 2 is around 10 000 g/mol which is still relatively high compared to the molecular weights of EMS-II-MAH copolymer and EMS-III-MAH copolymer. It is interesting to note that Edbon et al. [9] also observed bimodality SEC traces and over 1 000 000 g/mol high molecular weights for EMS-I-MAH copolymers. Edbon et al. concluded that phase separation arising from crosslinking and gelation were probably the reasons for polymodality. However, McNeill et al.[10] later stated that they found no evidence for crosslinking based on TGA data or IR spectrum. Based on our observations of EMS-IV-MAH copolymer system, it has poor solubility in THF, that is the THF solutions get turbid quickly as copolymerization progresses and THF solutions do seem to be more viscous after 24 h copolymerization. Therefore, it is more likely that high molecular weights and broad molecular weight distributions are due to a “gel effect” during the process of copolymerization: in the polymer solution, the polymer chain precipitates as the molecular weight increases so that the phase separation occurs. In the insoluble phase, the small monomer molecules can diffuse in and propagate, but the termination step is depressed due to the high viscosity, which leads to the very high molecular weights. Other possible reasons for broad molecular weight distributions are chain transfer to EMS-IV, and the copolymerization of EMS-IV-MAH in absence of the initiator AIBN. However, these reasons can be excluded because the SEC traces of EMS-II-MAH and EMS-III-MAH copolymers are unimodal under the same conditions.

There was no glass transition temperature or crystalline melting temperature observed between 0 °C and 250 °C for all the copolymers (measured by DSC). And the copolymers are thermally stable up to 290 °C (measured by TGA). Furthermore, the aromatic hydrogen atoms and hydrogen atoms on the polymer backbone show very broad peaks in the ^{1}H NMR spectrum. These observations are consistent with a stiff polymer backbone with restricted motions.

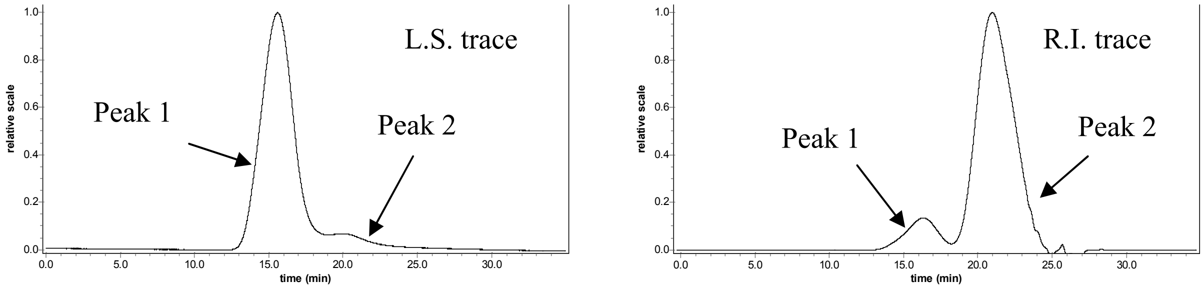


Figure 2.5: SEC traces of EMS-IV-MAH copolymers obtained at 60 °C for 24 h. Trace on the right was obtained from R.I. detector, trace on the left was from L.S. detector

2.5. Summary

A series of EMSs-MAH copolymers were synthesized and characterized. The copolymerization rates were impacted by the position of the methyl substituent. EMS-IV-MAH copolymer has the highest copolymerization rate, followed by EMS-I-MAH, EMS-III-MAH, EMS-II-MAH, respectively. Alternating structures of the copolymers were confirmed by quantitative ^{13}C 1D NMR. The EMS-IV-MAH copolymer has broad molecular weight distributions and high molecular weights which was attributed to a “gel effect” during the course of the copolymerization. All copolymers showed no thermal transition between 0 °C and 250 °C on DSC trace. No glass transition temperature or crystalline melting temperature and the broad peaks on NMR spectrum all indicate the chain rigidity of these copolymers.

2.6. Acknowledgments

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Chapter 3. RIGID POLYELECTROLYTES WITH DIFFERENT CHARGES AND CHARGE DENSITIES

3.1. Abstract

Precursors to a polycation and a polyanion based on functionalized stilbenes and maleimides have been prepared: poly(di-*t*-butyl-(*E*)-4,4'-stilbenedicarboxylate-*co*-*N*-(4-(t-butoxycarbonyl)phenyl)maleimide) (poly(TDAS II-*co*-APMI)) and poly(*N,N,N',N'*-tetraalkyl-4,4'-diaminostilbenes-*co*-*N*-4-(*N',N'*-dimethylaminophenyl)-maleimide) (poly-(TBSC-*co*-BCPMI)). The precursors were characterized by ^{1}H NMR, SEC, TGA, and DSC. The ^{1}H NMR spectrum indicated the rigidity of copolymer backbones. SEC measurements showed the weight average molecular weights of these copolymers vary from 5 000 to 11 700 g/mol. No glass transition temperature or crystalline melting temperature was observed between 0 ^{o}C and 175 ^{o}C by DSC for poly(di-*t*-butyl-(*E*)-4,4'-stilbene-dicarboxylate-*co*-*N*-(4-(*t*-butoxycarbonyl)phenyl)maleimide). TGA showed that this polymer has 5% weight loss around 210 ^{o}C and 26% weight loss on the first stage of decomposition which indicates the presence of *t*-butyl functional group in the copolymer.

3.2. Introduction

Polyelectrolytes are widely applied in industrial processes and daily life, e.g. drug delivery,[1,2] waste water purification,[3] surface modification for improved adhesion.[4] Their properties depend on many variables, such as the nature of the chargeable groups, the origin of the polyelectrolytes chains (natural or synthetic), and the backbone's intrinsic flexibility or rigidity.

In nature, materials make use of self-assembly to achieve a variety of functional behavior which is often impossible to replicate in today's synthetic materials and this self-assembly behavior of biological molecules has attracted considerable scientific attention and understand. Therefore much research has been focused on the self-assembly of polyelectrolytes, such as making polyelectrolyte microcapsules by layer-by-layer self-assembled techniques.[1,2] In order to better manipulate the self-assembly process of polyelectrolytes, being able to tailor make polymers with controllable molecular structures and precise functional groups, to generate charge in sequential or gradient fashion, and to tune charge density along polymer backbones is very important.[5] Free radical polymerization processes are known for being tolerant to functional groups and control of the molecular parameters of free radical polymers such as molecular weight distribution and architecture6 and therefore is used for our study.

In this chapter, our objective is to prepare a series of water soluble polyanions and polycations based on substituted stilbenes and substituted phenylmaleimides. By varying the diversity and number of functional groups on monomers, the type of charges as well as charge densities of polyelectrolytes can be precisely controlled. A rod-like polymer chain is also expected due to the incorporation of both stilbenes and phenylmaleimides units into polymer backbone. We believe that these precisely controlled polyelectrolytes will have interesting self-assembly properties.

3.3. Experimental Section

3.3.1. Materials and Characterization

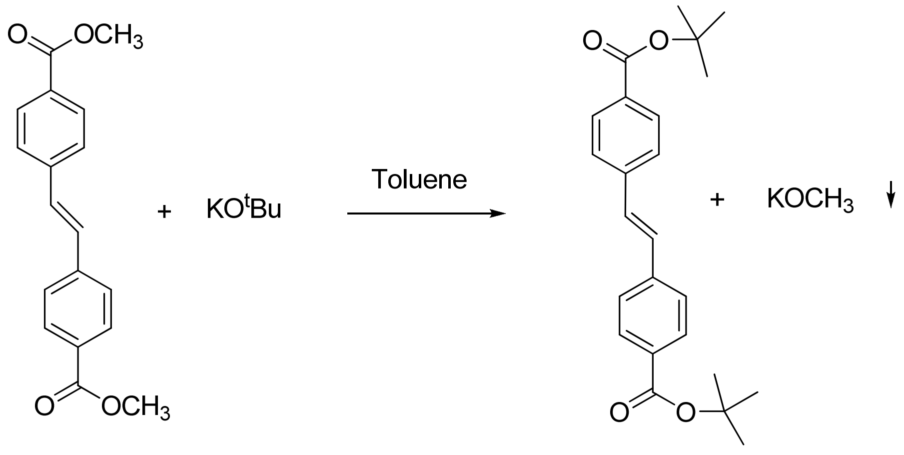
All reagents were purchased from Aldrich and were used as received. ^{1}H NMR spectra and ^{13}C NMR spectra of monomers were determined at 25 °C in $CDCl_3$ at 400 MHz with a Varian Inova spectrometer or 500 MHz with a Jeol Eclipse +500 spectrometer. Melting points of monomers were measured on BUCHI Melting Point B-540 instrument.

Thermogravimetric analysis (TGA) was conducted under nitrogen, from 25 ^{o}C to 600 ^{o}C at a heating rate of 10 ^{o}C/min using a TA Instrument TGA Q5000. Glass transition temperatures (T_g) were determined using a Perkin-Elmer Pyris 1 DSC at heating rate of 10 ^{o}C /min and cooling rate of 20 ^{o}C in a nitrogen atmosphere.

Molecular weights of the synthesized polymers were determined using a Waters size exclusion chromatograph equipped with a Waters 1515 isocratic HPLC pump, a Viscotek 270 viscosity detector, and a Waters 2414 differential refractive index detector operating at 880 nm and 35 ^{o}C and a Waters 717 plus autosampler, a Wyatt miniDAWN multiangle laser light scattering (MALLS) detector operating a He-Ne laser at 690 nm. The d_n/d_c values were determined using the Wyatt Astra V software package. SEC measurements were performed at 40 °C in THF at a flow rate of 1.0 mL/min.

3.3.2. Synthesis of di-*t*-butyl-(*E*)-4,4'-stilbenedicarboxylate(TBSC)

The ester interchange method was used to convert the methyl ester into the more soluble *t*-butyl ester.[7] Dimethyl-(*E*)-4,4'-stilbenedicarboxylate (MSC) is highly insoluble in most organic solvents. The ester interchange reaction was driven by the precipitation of potassium methoxide (KOMe) (Scheme 3.1). A typical procedure to prepare di-*t*-butyl-(*E*) -4,4'-stilbenedicarboxylate is as follows: KO^{t}Bu (1.0 M in THF, 10 mL) was slowly added to a suspension of MSC (0.77 g, 2.6 mmol) in toluene (15 mL) refluxing at 110 ^{o}C. After refluxing for 1 h, the reaction mixture was cooled down to room temperature and stirred overnight. Initial high temperature helps MSC dissolve in toluene to initiate the reaction and potassium methoxide is precipitated to drive the reaction to the completion. After that, the reaction solution was poured into 100 mL concentrated NH_4Cl aqueous solution. The organic layer was extracted and dried with $MgSO_4$. Crude product was obtained by evaporation of the solvent. The crude product was purified by column chromatography (hexane/ethyl acetate changes gradually from 97:3 to 94:6). A white solid was obtained. Yield: 70%, 0.7 g. ^{1}H NMR ($CDCl_3$, 400MHz) δ ppm: 7.99 (d, 4H), 7.56 (d, 4H), 7.21 (s, 2H), 1.61 (s, 18H). ^{13}C NMR ($CDCl_3$, 400MHz) δ ppm: 165.6, 140.9, 131.4, 130.0, 129.9, 126.5, 81.2, 28.3. Melting point: 170 ^{o}C. This compound thermally eliminates the *t*-butyl ester group when heated above 190 ^{o}C.



Scheme 3.1: Synthetic route for di-*t*-butyl-*(E)*-4,4'-stilbenedicarboxylate

3.3.3. Synthesis of *N, N, N', N'*-tetraalkyl-4, 4'-diaminostilbenes (TDAS)

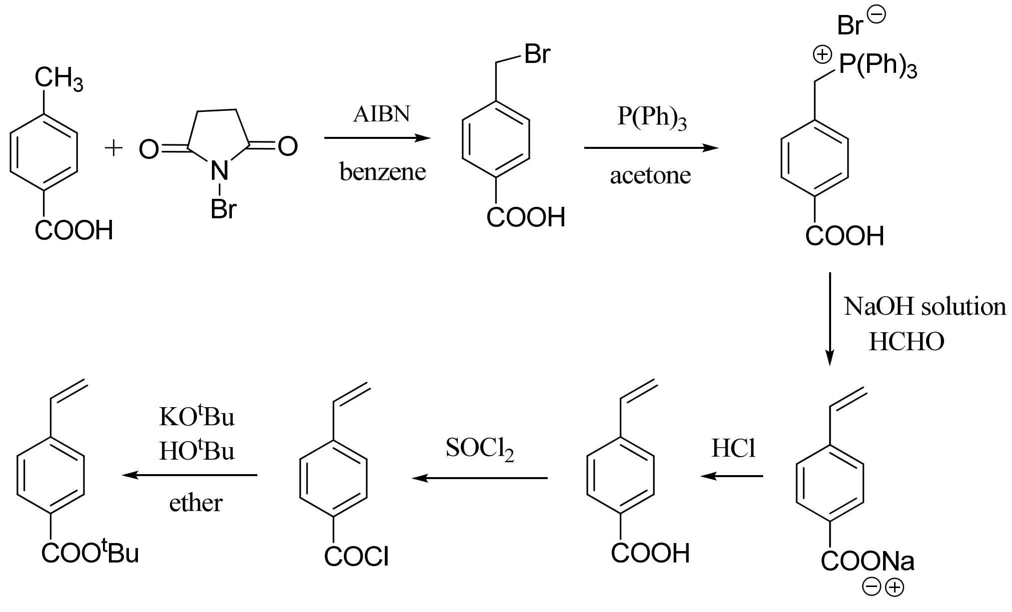
The Horner- Emmons condensation8 of an aldehyde with a phosphonate was employed to synthesize TDASs. *N, N, N', N'*-tetraalkyl-4, 4'-diaminostilbenes were prepared following a previously published procedure.[9]

N,N-Dimethyl-*N',N'*-dibutyl-4,4'-diaminostilbene (TDAS-I) was synthesized via the condensation of 4-N,N-dibutylaminobenzyl phosphonate (5.00 g, 14.08 mmol) with 4-N,N-dimethylamino –benzaldehyde (2.10 g, 14.08 mmol).[9] The crude product was purified by recrystallization from methanol. A yellow crystalline solid was obtained. Yield: 70% 3.45 g. ^{1}H NMR ($CDCl_3$, 400MHz) δ ppm: 7.32 (m, 4H), 6.82 (s, 2H), 6.70 (m, 4H), 3.25 (m, 4H), 2.95 (s, 6H), 1.60 (m, 4H), 1.40-1.30 (m, 4H), 0.95 (t, 6H). ^{13}C NMR ($CDCl_3$, 400MHz) δ ppm: 149.3, 147.2, 127.1, 126.8, 125.4, 124.9, 123.9, 112.7, 111.7, 50.8, 40.6, 29.4, 20.3, 14.0. Melting point: 87.1-87.4 ^{o}C.

N,N-Dimethyl-*N',N'*-diethyl-4,4'-diaminostilbene (TDAS-II) was synthesized via the condensation of 4-*N,N*-diethylaminobenzyl phosphonate (5.00 g, 16.72 mmol) with 4-*N,N*-dimethylaminobenzaldehyde (2.49 g, 16.72 mmol).[9] The crude product was purified by recrystallization from acetone. A yellow crystalline solid was obtained. Yield: 75%, 3.69 g. ^{1}H NMR ($CDCl_3$, 400MHz) δ ppm: 7.34 (m, 4H), 6.82 (s, 2H), 6.65 (m, 4H), 3.32 (q, 4H), 2.92 (s, 6H), 1.12 (t, 6H). ^{13}C NMR ($CDCl_3$, 400MHz) δ ppm: 149.5, 146.7, 127.2, 127.0, 126.9, 125.7, 124.9, 124.1, 112.7, 111.9, 44.4, 40.6, 12.7. Melting point: 155.4-155.8 ^{o}C.

3.3.4. Synthesis of *t*-butyl-4-vinyl benzoate (TBVB)

t-Butyl-4-vinyl benzoate was synthesized via a multistep process, as shown in Scheme 3.2. p-Carboxybenzyl bromide, p-carboxybenzyltriphenylphosphonium bromide, 4-vinylbenzoic acid, and 4-vinylbenzoyl chloride were prepared following a previously published procedure.[10-12]



Scheme 3.2: Synthetic routes for *t*-butyl-4-vinyl benzoate

Step A. p-Carboxybenzyl bromide was synthesized via free radical halogenation mechanism.[10] To a mixture of p-toluic acid (4.03 g, 29.41 mmol) and *N*-bromosuccinimide (5.28 g, 29.66 mmol) was added AIBN (0.003 g). Dry benzene (27 mL) was added and the suspension was stirred for 4 h under refluxing temperature. After the reaction solution was cooled down to room temperature, the precipitate was filtered out with suction, then extracted with hot water for 30 mins to dissolve succinimide as side product. The crude product was filtered out and recrystallized from methanol as a white solid and vacuum dried. Yield: 72%, 4.55 g. ^{1}H NMR (CD_3COCD_3, 400MHz) δ ppm: 7.99 (d, 2H), 6.82 (s, 2H), 7.57 (d, 2H), 4.68(s, 2H).

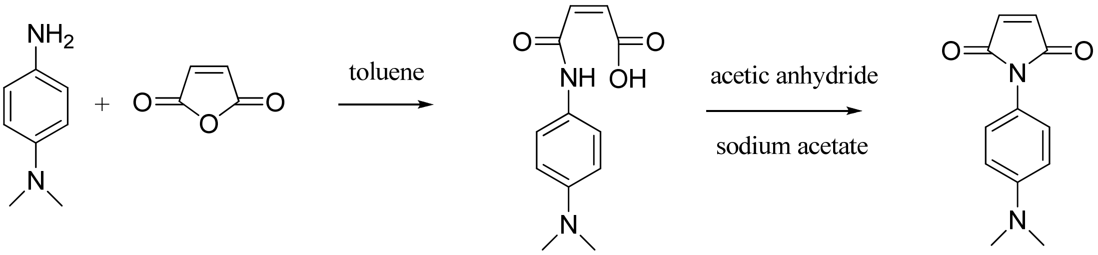
Step B. 4-Vinylbenzoic acid was prepared with p-carboxybenzyltriphenylphosphonium bromide and formaldehyde.[11] p-Carboxybenzyltriphenylphosphonium bromide was prepared following the previously published routes.[11] To a mixture of p-carboxybenzyltriphenylphosphonium bromide (36.20 g, 75.89 mmol) and 37% formaldehyde (150 mL) diluted with DI water (78 mL), sodium hydroxide aqueous solution (0.20 g/mL, 100 mL) was added dropwise. The mixture was stirred at room temperature for 60 mins. The precipitate was filtered out and washed with DI water. The filtrate was acidified with the diluted HCl solution till pH reached 1. 4-Vinylbenzoic acid was obtained as a white solid. Yield: 80%, 8.99 g. ^{1}H NMR (CD_3SOCD_3, 400MHz) δ ppm: 7.88 (d, 2H), 7.56 (d, 2H), 6.78 (dd, 1H), 5.95 (d, 1H), 5.38 (d, 1H).

Step C. 4-Vinylbenzoyl chloride was prepared as follows: The solution of 4-vinylbenzoic acid (1.37 g, 9.26 mmol) and thionyl chloride (2.72 mL, 37.04 mmol) was stirred in an ice-water bath initially and heated up to room temperature gradually for 4 h. Then the solution was heated up to 40 ^oC for another 1 h. Thionyl chloride in excess was stripped off by blowing argon and a clear light yellow liquid was obtained. ^{1}H NMR ($CDCl_3$, 400MHz) δ ppm: 8.01 (d, 2H), 7.46 (d, 2H), 6.72 (dd, 1H), 5.90 (d, 1H), 5.45 (d, 1H). ^{13}C NMR ($CDCl_3$, 400MHz) δ ppm: 167.8, 144.3, 135.3, 132.0, 131.8, 126.6, 118.5. *t*-Butyl-4-vinyl benzoate was prepared with 4-vinylbenzoyl chloride and potassium t-butoxide following the previously published routes.[12] Distillation gave a clear light green-colored liquid at 80 ^oC (0.2 mbar). Yield: 45% 0.85 g. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.92 (d, 2H), 7.39 (d, 2H), 6.69 (dd, 1H), 5.80 (d, 1H), 5.31 (d, 1H), 1.56 (s, 9H). ^{13}C NMR ($CDCl_3$, 400MHz) δ ppm: 165.6, 141.4, 136.1, 131.2, 129.7, 125.9, 116.1, 80.9, 20.1.

3.3.5. Synthesis of *N*-4-(*N’,N’*-dimethylaminophenyl)maleimide (APMI)

Step A. *N*-4-(*N’,N’*-Dimethyl)maleic monoanilide was synthesized as follows: a mixture of maleic anhydride (2.63 g, 26.84 mmol), *N*-4-amino-*N’,N’*-dimethylaniline (3.65 g, 26.84 mmol) and 32 mL Toluene was heated at 80 ^oC for 4 h. The precipitate was filtered out and washed with diethyl ether, and then vacuum dried to yield a red colored powder. Yield: 70%, 4.36g. ^{1}H NMR (CD_3SOCD_3, 400MHz) δ ppm: 7.40 (d, 2H), 6.66 (d, 2H), 6.42 (d, 1H), 6.23 (d, 1H), 5.31 (d, 1H), 2.81 (s, 6H).

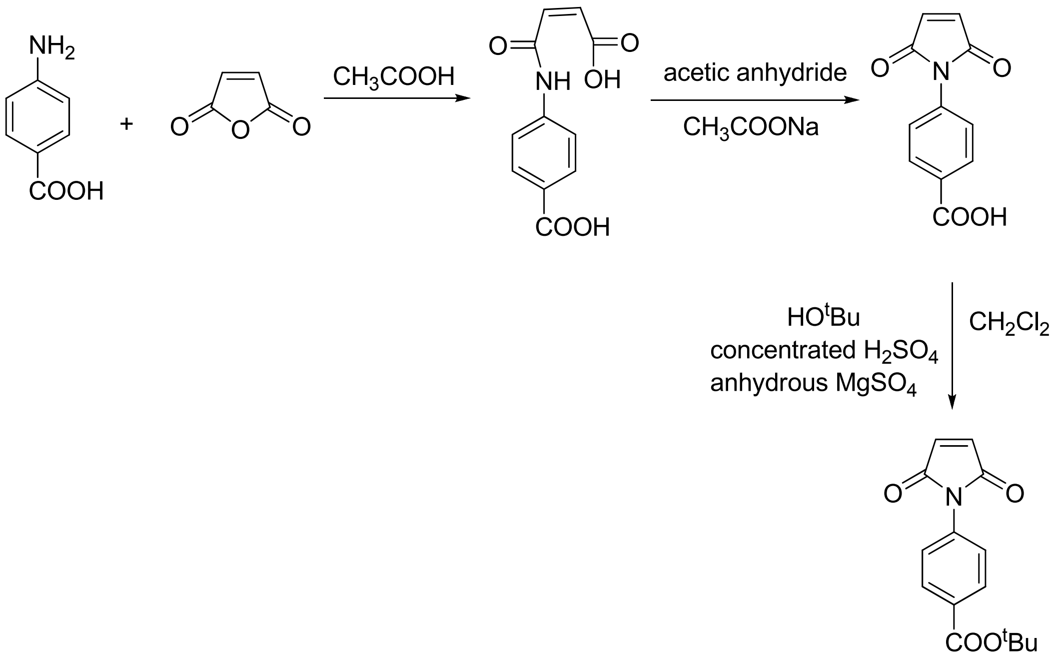
Step B. *N*-4-(*N’,N’*-dimethylaminophenyl)maleimide was synthesized as follows: to a 100 mL round bottomed flask connected with a reflux condenser with a drying tube attached was added *N*-4-(*N',N'*-dimethyl)maleic monoanilide (4.36 g, 18.63 mmol), acetic anhydride (17.0 g, 166.67 mmol), sodium acetate (0.76 g, 9.27 mmol). The mixture was stirred at 80 °C for overnight and poured into ice water. The solid was filtered out and purified by column chromatography (hexane: ethyl acetate = 4:1). An orange colored solid was obtained. Yield: 43%, 1.73 g. ^{1}H NMR ($CDCl_3$, 500MHz) δ ppm: 7.13 (d, 2H), 6.81 (s, 2H), 6.76 (d, 2H), 2.97 (s, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ ppm: 170.4, 150.4, 134.2, 127.4, 119.6, 112.6, 40.6. Melting point : 143.5 - 144.8 °C (lit.:[13] 151 – 153 °C).



Scheme 3.3: Synthesis of N-4-(N',N'-dimethylaminophenyl)maleimide

3.3.6. Synthesis of *N*-(4-(t-butoxycarbonyl)phenyl)maleimide (BCPMI)

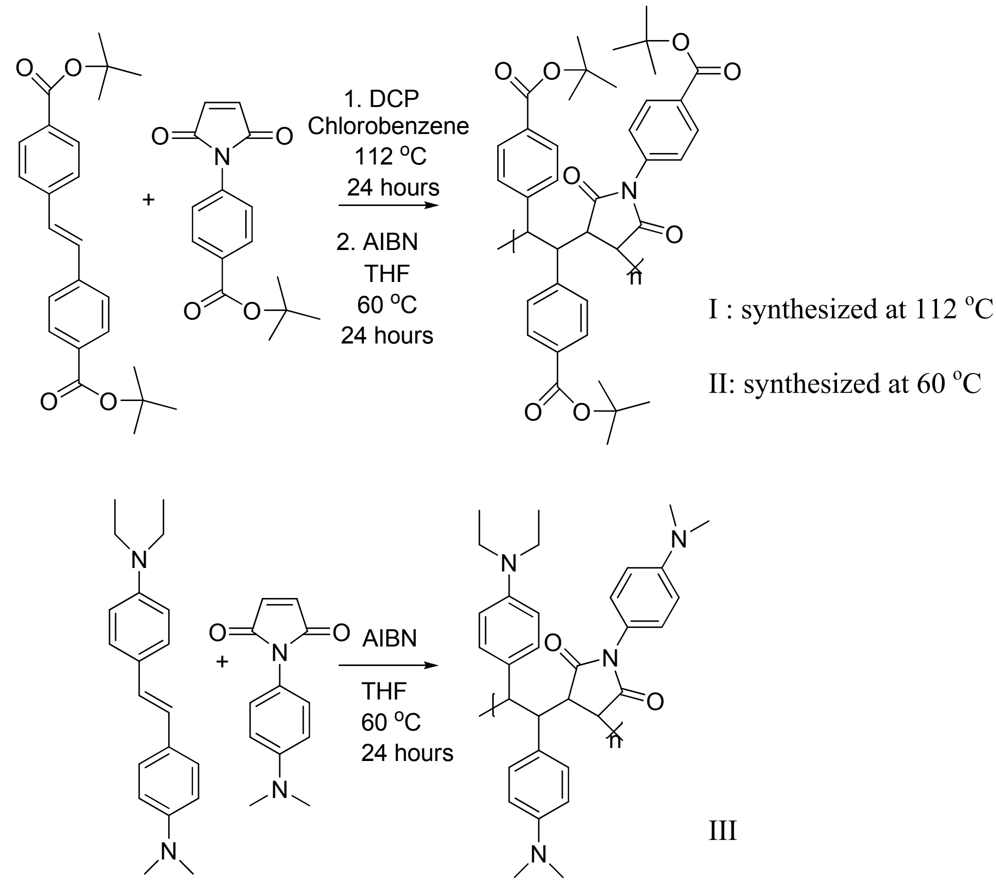
N-(4-(t-Butoxycarbonyl)phenyl)maleimide was synthesized via the multistep process, as shown in Scheme 3.4. 4-Maleimidobenzoic acid was prepared following a previously published procedure.[14] *N*-(4-(*t*-Butoxycarbonyl)phenyl)maleimide was synthesized as follows:[15] to a stirred suspension of anhydrous $MgSO_4$ (9.6 g, 80.00 mmol) and 60 mL CH_2Cl_2 was added concentrated H_2SO_4 (1.1 mL, 20.00 mmol). The mixture was stirred for 15 min. A mixture of HO^{t}Bu (7.4 g, 100.00 mmol) and 4-maleimidobenzoic acid (4.31 g, 19.86 mmol) dissolved in 30 mL CH_2Cl_2 was then added. The reaction flask was connected with a dry ice-acetone condenser and the mixture was stirred at room temperature for 18 h. The reaction was terminated by adding 200 mL 15% sodium bicarbonate solution. The organic layer was extracted, washed with brine and dried with anhydrous $MgSO_4$. The crude product was obtained by evaporation of the solvent and purified by column chromatography (hexane/ethyl acetate changes gradually from 10:1 to 5:1). Yield: 25%, 1.36 g. A yellow crystalline product was obtained after drying under vacuum for 24 h. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.08 (d, 2H), 7.45 (d, 2H), 6.87 (s, 2H), 1.59 (s, 9H). Melting point: 115-117 °C



Scheme 3.4: Synthesis of *N*-(4-(*t*-butoxycarbonyl)phenyl)maleimide

3.3.7. Polymerization

Copolymers I and III were prepared at 60 °C with 2,2′-azobisisobutyronitrile (AIBN) as initiator and THF as solvent. Copolymer II was prepared at 112 °C with dicumyl peroxide (DCP) as initiator and chlorobenzene as solvent. The substituted stilbenes, substituted maleimides, and solvent THF were mixed with an initiator in a 50-mL, septum sealed glass bottle equipped with a magnetic stirrer. For instance, a mixture of TBSC (3.80 g 10.00 mmol), BCPMI (2.73 g, 10.00 mmol), THF (29.35 mL), AIBN (0.0653 g) was sealed in a 50-mL, septum sealed glass bottle equipped with a magnetic stirrer and was degassed by purging with argon for 10 mins and polymerized for 24 h (Scheme 3.5). All of the copolymerizations contained an equimolar ratio of substituted stilbenes and substituted maleimides. The initiator concentration was 1 wt. % based on monomer in all polymerizations and the 20 wt. % monomer concentration remained the same. Copolymers were recovered by precipitating into hexane and were dried under vacuum at 60 °C overnight before characterization. Copolymer I and II were soluble both in THF and chloroform, whereas copolymer III had good solubility only in chloroform.



I : synthesized at 112 °C

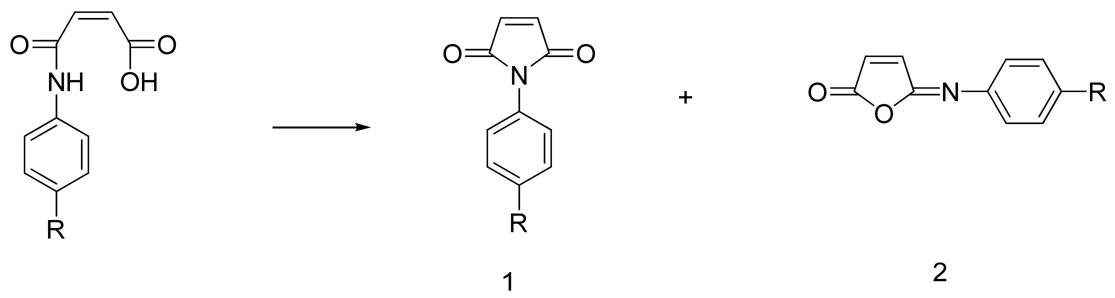
II: synthesized at 60 °C

III

Scheme 3.5: Copolymerization of substituted stilbenes with substituted maleimides.

3.4. Results and Discussion

Monomer *N*-4-(*N',N'*-dimethylaminophenyl)maleimide was prepared by dehydration of corresponding maleamic acid with acetic anhydride containing sodium acetate at temperature below 100 °C, which is a classical method for synthesis of *N*-arylmaleimides.[16,17] Dehydration of *N*-arylmaleamic acids can end up with two different ring closure routes to yield both *N*-arylmaleimides and *N*-arylmaleisoimides, as shown in Scheme 3.6. According to Sauers,[16] the presence of sodium acetate, the substituent on phenyl ring, reaction temperature as well as reaction duration can impact the ratio of *N*-arylmaleimides to *N*-arylmaleisoimides. In the presence of sodium acetate, *N*-arylmaleimides is favored. With decrease of electron density of the phenyl ring, increase of the reaction temperature and the reaction duration, the ratio of *N*-arylmaleimides to *N*-arylmaleisoimides is increased.[16] In the formation of *N*-4-(*N',N'*-dimethylaminophenyl)maleimide, the presence of sodium acetate, reaction temperature at 80 °C, and overnight reaction duration ensured 100% imide formation, which was measured by observing the absence of the isoimide olefinic proton peaks and the presence of the olefinic proton peak assigned to the imide in ^{1}H NMR spectra of the crude product.[16]



Scheme 3.6: Dehydration of *N*-arylmaleamic acids to yield *N*-arylmaleimides (1) and *N*-arylmaleisoimides (2)

There are many routes for preparation of *t*-butyl esters reported in literature:[15] the indirect reaction of a carboxylic acid chloride and *t*-butanol in pyridine,[18] the indirect reaction of a carboxylic acid chloride and an alkali metal *t*-butoxide,[19] and direct reaction of a carboxylic acid and t-butanol mediated by a carbodiimide.[20] The ethylene double bond of maleimide generally has a high reactivity toward nucleophiles, such as amine,[21] alcohol,[22] or thiol[23] via Michael addition reactions.[13] Therefore the direct reaction of 4-maleimidobenzoic acid and isobutylene in the presence of an acid catalyst[15] was adopted for preparation of *N*-(4-(*t*-butoxycarbonyl)phenyl)maleimide. Isobutylene was produced by the dehydration of *t*-butanol with concentrated sulfuric acid as catalyst.[15] The yield of the esterification step is quite low (25%) and probably due to poor solubility of 4-maleimidobenzoic acid in solvent CH_2Cl_2.

Polymers I and II were precipitated into hexane from THF and dried under vacuum at 60°C for 24 h to yield white powders. The ^{1}H NMR spectrum did not indicate any residual monomers. Moreover, the aromatic hydrogen atoms and hydrogen atoms on the polymer backbone were very broad peaks in the ^{1}H NMR spectrum which indicates the rigidity of the polymer backbones. By comparing the ^{1}H NMR spectrum of polymer I and poly(stilbene-alt-maleic anhydride), shown in Figure 3.1, a new resonance at 1.5 ppm in the ^{1}H NMR spectrum of polymer I is observed which indicates the presence of *t*-butyl functional group in the copolymer. As shown in Figure 3.2, the TGA trace of polymer I shows that this polymer has 5% weight loss at 210 °C and 26% weight loss on the first stage of decomposition starting around 190 °C which is consistent with the weight percent of *t*-butyl unit in the polymer chain and indicates the presence of the *t*-butyl functional group in the copolymer. As shown in Figure 3.3, the SEC trace shows a unimodal trace and the weight average molecular weight for polymer I is 11 700 g/mol and for polymer II is 5 600 g/mol. There was no glass transition temperature or crystalline melting temperature observed between 0 °C and 175 °C for polymer I.

Polymer III was precipitated into hexane from THF and dried under vacuum at 60 °C for 24 h to yield a brown colored powder. No sharp peak of monomer residue was observed in the ^{1}H NMR spectrum which indicates copolymerization of monomers. Moreover, the aromatic hydrogen atoms and hydrogen atoms on the polymer backbone show very broad peaks in the ^{1}H NMR spectrum which indicates the rigidity of the polymer backbones. The polymer dissolves in HCl solution when the pH is 5 or below. A turbid solution forms upon addition of NaOH solution. The SEC trace of the polymer shows a unimodal peak as shown Figure 3.4 and the weight average molecular weight is 8 300g/mol which is based on the use of a standard polystyrene calibration since it was necessary to run the SEC analysis in chloroform and absolute molecule weight detectors were not available on the instrument.

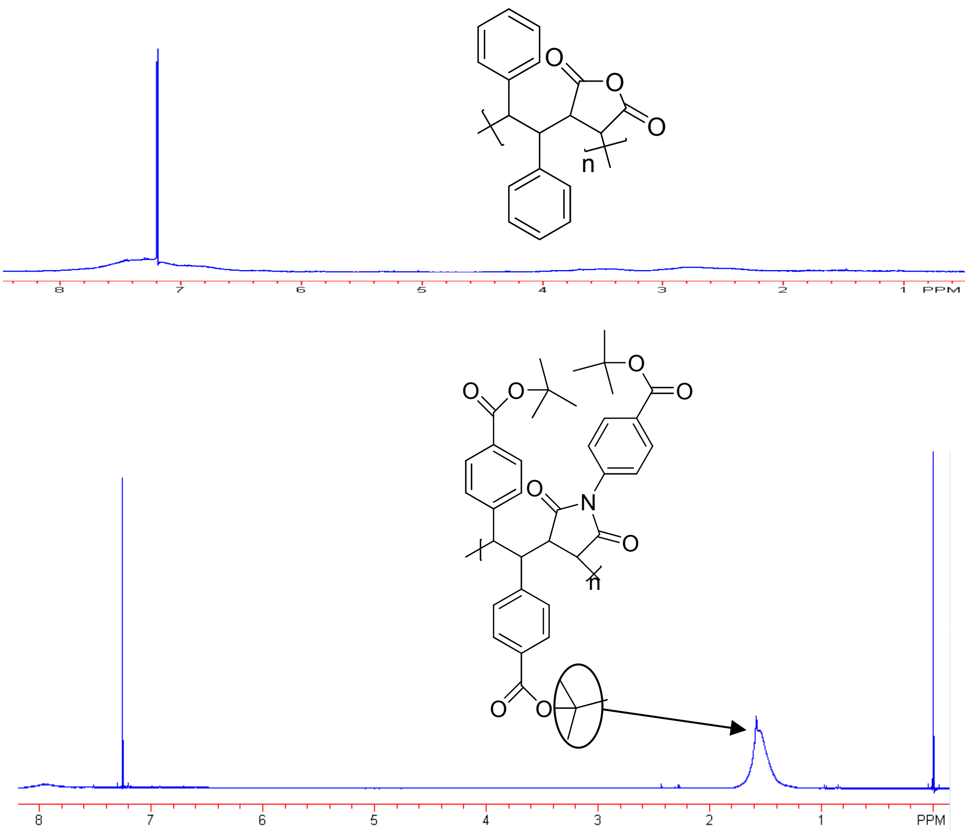


Figure 3.1: ^{1}H NMR spectrum of polymer I (bottom) and poly(stilbene-alt-maleic anhydride) (top)

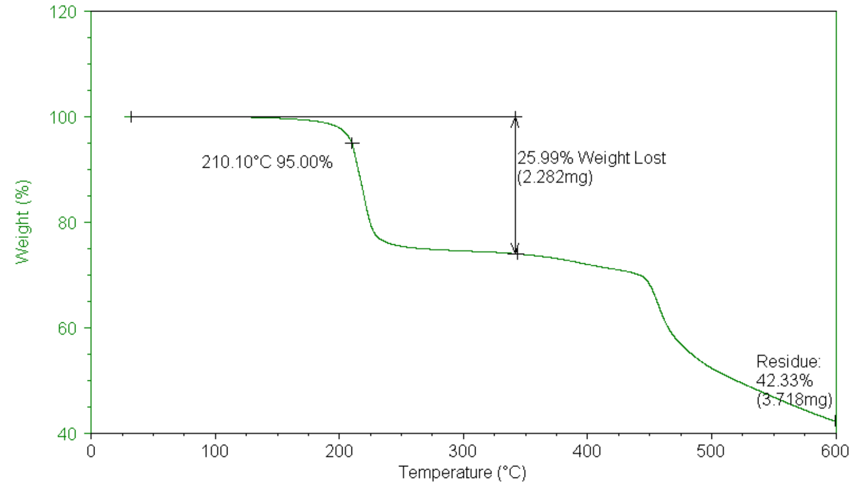


Figure 3.2: TGA trace of polymer I

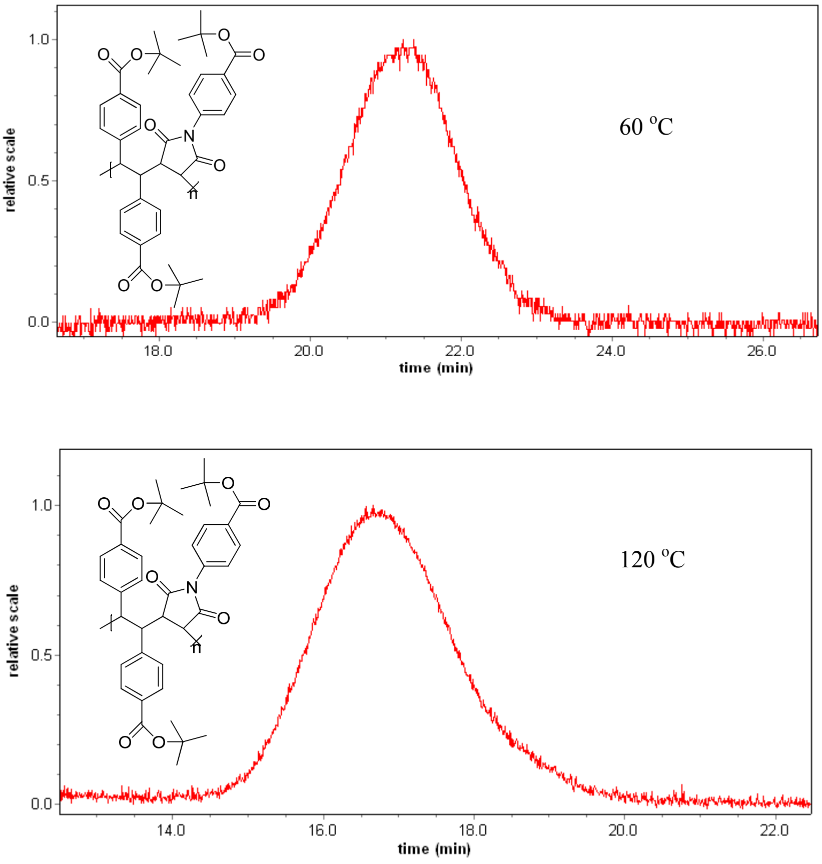


Figure 3.3: SEC traces of polymer I (bottom) and II (top)

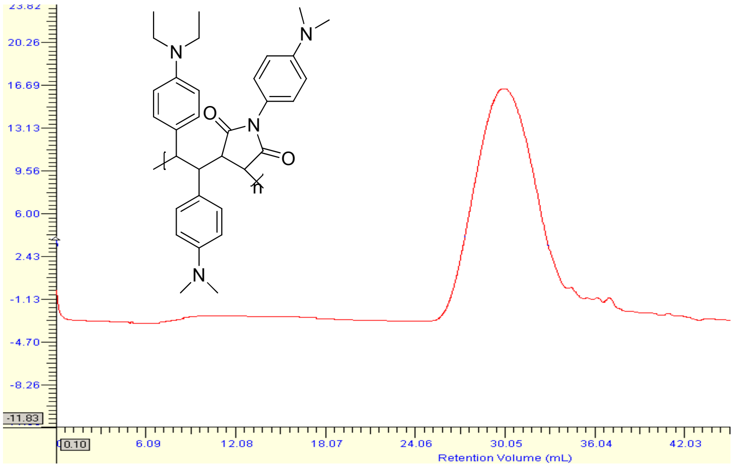


Figure 3.4: SEC trace of polymer III

3.5. Summary

In summary a series of substituted stilbene monomers and substituted maleimide monomers, TBSC, TBVB, APMI, BCPMI, were prepared. Poly(TDAS II-*co*-APMI) was synthesized both at 60 °C and 120 °C with different initiators and solvents. The noticeable molecular weight difference was observed for two polymers synthesized at different temperatures. Both ^{1}H NMR and TGA showed the t-butyl functional group was present in the copolymer backbone. Poly(TBSC-*co*-BCPMI) were synthesized at 60 °C and characterized by ^{1}H NMR and SEC. The weight average molecular weight was 8 700 g/mol. The polymer dissolved in HCl solution. A turbid solution reformed upon addition of NaOH solution.

3.6. Acknowledgements

This work was supported by Petroleum Research Fund of the American Chemical Society and teaching assistantship from Department of Chemistry at Virginia Tech. We thank Professor Timothy Long's group and Professor Judy Riffle's group for the help on the SEC, TGA, and DSC measurements. We also thank Eastman Chemical Company for general donation of Dimethyl-(*E*)-4,4'-stilbenedicarboxylate.

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Chapter 4. HOMOPOLYMERIZATION OF *(E)*-2-METHYLSTILBENE (EMS-III)

4.1. Abstract

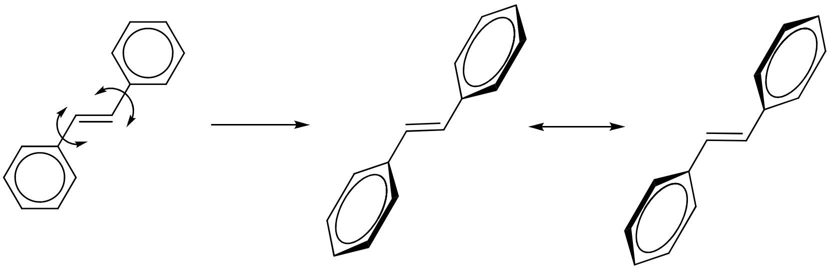
The homopolymerization of EMS-III via free radical polymerization, anionic polymerization and cationic polymerization was attempted. However, no polymer was produced from any of these polymerization methods. In anionic polymerization, the solution changed to red upon the addition of the initiator sec-bu-Li, indicating the successful addition of the sec-bu-Li to EMS-III. However, the initiated monomer did not propagate to form homopolymer.

4.2. Introduction

1,2-Disubstituted ethylenes such as maleic anhydride and stilbene usually exhibit very little or no tendency to undergo homopolymerization mainly due to kinetic considerations, that is the approach of the propagating radical to a monomer molecule is sterically hindered.[1] Even though it has been observed[2-5] that the ethylene bond interconnecting the two phenyl rings is shorter than the normal ethylene bond in the ethylene molecule, which was measured by X-ray diffraction and believed to give rise to pedal-like motion of (*E*)-stilbenes (shown in Scheme 4.1),[6] i.e. the C-Ph bonds on (*E*)-stilbene are twisted out of the plane and conformations of (*E*)-stilbenes are not strictly planar, (*E*)-stilbene is still very stable compound because the p-orbital from both phenyl rings and ethylene double bond still overlap with each other to form conjugated system. Therefore explanations for unsuccessful homopolymerization of (*E*)-stilbene[7-9] may lay in both kinetic and thermodynamic considerations: a. steric hindrance arising from the pendant phenyl substituent which increases the energy barrier in the transition state; b. stability of (*E*)-stilbene and steric interaction in the polymer radical chain. In some preliminary work the conversion of (*E*)-stilbene to poly(phenylmethylene) has been modeled and the heat of this reaction was calculated to be -22.5 kJ/mol,[10] which means this reaction is thermodynamically favored.

However, it is possible that stability of stilbene makes this polymerization process reversible at a low temperature, i.e. low ceiling temperature, which prevents (*E*)-stilbene from homopolymerizing.

In chapter 2, methyl substituted stilbenes were prepared and the methyl substituent effect on copolymerization with maleic anhydride were studied. In this chapter, the methyl substituent impact on homopolymerization process will be studied. We mainly focus on the homopolymerization study of (*E*)-2-methylstilbene (EMS-III). As mentioned, the methyl substituent can twist the phenyl ring out of the plane and makes stilbene less conjugated. For EMS-III as shown in Scheme 4.2, one methyl substituent further increases the energy barrier in the transition state. However, one phenyl ring is twisted out of the plane caused by steric hindrance between the ortho methyl substituent on the phenyl ring and the vinyl proton which is six bonds away from the proton on the methyl substituent whereas the other one remains planar, which might make EMS-III behave similar to styrene and enable it to homopolymerize.



Scheme 4.1: Pedal-like motion of (*E*)-stilbenes

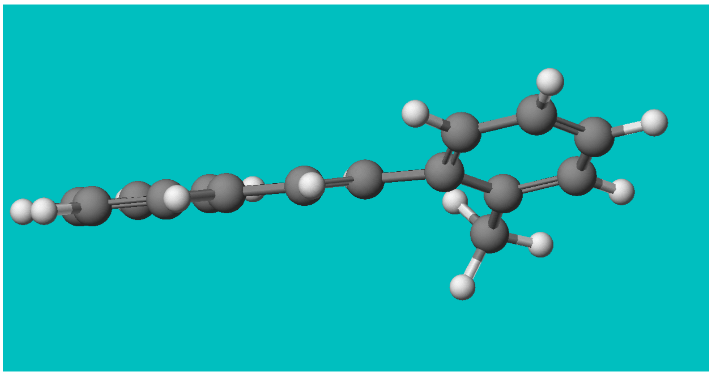


Figure 4.1: Predicted 3-D molecular structure of EMS-III

4.3. Experimental Section

4.3.1. Materials

All materials were purchased from Aldrich and used as received.

^{1}H NMR spectra and ^{13}C NMR spectra of monomers were determined at 25 °C in $CDCl_3$ at 400 MHz with a Varian Inova spectrometer or 500 MHz with a Jeol Eclipse +500 spectrometer.

4.3.2. Monomer synthesis

(*E*)-2-Methylstilbene (EMS-III) was synthesized in Chapter 2.

4.3.3. Free radical homopolymerization

EMS-III and THF were mixed together with an initiator AIBN in a 50-mL, septum sealed glass bottle equipped with a magnetic stirrer. The mixture was degassed by purging with argon for 10 mins and polymerized at 60 °C for 24 h (Scheme 2). The reaction solution was transferred into hexane dropwise by using pipette to isolate the polymer product from the monomer. However, no precipitation was observed during this process, which means EMS-III doesn't homopolymerize via free radical polymerization under these conditions.

4.3.4. Anionic homopolymerization

All the glassware (include stir bar, needles) were dried in oven overnight, and all the glassware were flame dried before using. The reaction flask was degassed by three freeze-thaw cycles, flame dried with N_2 flow till the flask became very bright and then cooled down to room temperature. Monomer EMS-III (2.065g, 10.64mmol) is transferred to the freeze-thaw flask using syringe. Then the solvent anhydrous cyclohexane (8 mL) was transferred to the freeze-thaw flask by two edged needle. After 3-cycle freeze-thaw of the reaction flask, the reaction flask was placed in an oil bath at 50 ^{o}C. The initiator sec-bu-Li is added by syringe (0.2 mL, 1.6 mol/L, 0.32 mmol) and the solution changed color to dark red. After 6 h, the reaction is terminated by adding 1 mL methanol. Red color disappears once upon the addition of methanol. Instead, the white turbid solution formed. There was nothing precipitated when trying to precipitate into methanol. A white viscous oil like product was obtained after the solvent was stripped off. Product was dried under vacuum at 60 ^{o}C for 24 h and from the ^{1}H NMR spectrum it showed that the product was the monomer EMS-III, which means EMS-III doesn't homopolymerize via anionic polymerization under these conditions.

4.3.5. Cationic homopolymerization

All the glassware (include stir bar, needles) were dried in oven overnight, and all the glassware were flame dried before using.

A two-necked flask was flame dried and purged with Ar. To the flask was added monomer EMS-III (0.5 g, 2.58 mmol), and 4.2 mL anhydrous methylene chloride with a syringe. The flask was cooled to -78 ^{o}C in a dry ice-acetone bath and the initiator boron trifluoride ethyl etherate (3.7 mg, 0.026 mmol) was added. After 3 h, 500 mL methanol was added and no precipitation was observed, which means EMS-III doesn't homopolymerize via cationic polymerization under these conditions.

4.4. Results and discussions

In anionic polymerization, the solution changed color to dark red after the initiator sec-bu-Li was added, meaning the anionic center was formed and EMS-III can be initiated. However, initiated EMS-III monomer did not propagate since no polymer was obtained in the end.

The methyl substituent might lead to more reactive stilbene radical, but also can increase steric hindrance in the transition state. The increase in steric hindrance cannot be overcome by the increase of stilbene radical reactivity since no homopolymer was obtained. It is possible that steric hindrance is the major basis for the failure of EMS-III to homopolymerize.

4.5. Summary

EMS-III could not homopolymerize via free radical polymerization, anionic polymerization and cationic polymerization, indicating that the increase in steric hindrance could not be overcome by the increase of stilbene radical reactivity since no homopolymer was obtained.

4.6. Acknowledgements

This work was supported by Petroleum Research Fund of the American Chemical Society and teaching assistantship from Department of Chemistry at Virginia Tech. We thank Renlong Gao's help on anionic polymerization.

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Chapter 5. CONCLUSIONS AND FUTURE RESEARCH

5.1. Conclusions

The methyl substituent effect on stilbene copolymerization rates is significant and copolymerization rates follow the order of EMS-IV-MAH > EMS-I-MAH > EMS-III-MAH > EMS-II-MAH. The methyl substituent on para position is electron-donating whereas the one on ortho position leads to steric hindrance and less resonance stability. Alternating structures of the copolymers were verified by quantitative ^{13}C 1D NMR. Broad molecular weight distributions and high molecular weights of EMS-IV-MAH copolymer were attributed to a "gel effect" during the course of copolymerization. No glass transition temperature or crystalline melting temperature observed between 0 °C and 250 °C by DSC and broad peaks on NMR spectrum both indicated the chain rigidity of these copolymers.

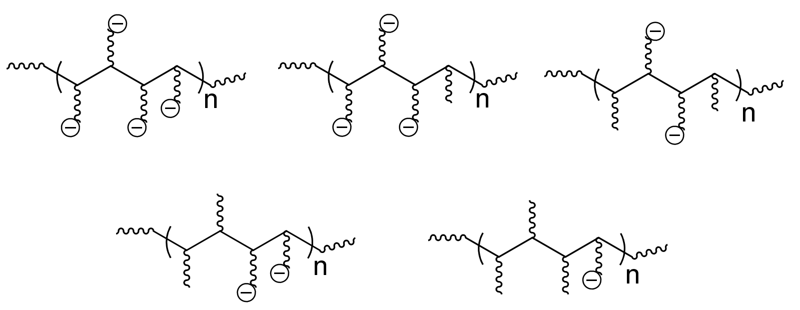
A series of substituted stilbene monomers and substituted maleimide monomers, TBSC, TBVB, APMI, BCPMI, were prepared. Poly(TDAS II-*co*-APMI) was synthesized both at 60 °C and 120 °C with different initiators and solvents. The noticeable molecular weight difference was observed for two polymers synthesized at different temperatures. Both ^{1}H NMR and TGA showed *t*-butyl functional group was present in the copolymer backbone. Poly(TBSC-*co*-BCPMI) was synthesized at 60 °C and characterized by ^{1}H NMR and SEC. The weight average molecular weight was 8 700 g/mol. The copolymer was soluble in chloroform. It also dissolved in HCl solution. A turbid solution reformed upon the addition of NaOH solution.

EMS-III could not homopolymerize via free radical polymerization, anionic polymerization and cationic polymerization, indicating that the increase in steric hindrance could not be overcome by the increase of stilbene radical reactivity since no homopolymer was obtained. In anionic polymerization, the solution changed to red upon the addition of the initiator *sec*-bu-Li, indicating the successful addition of the sec-bu-Li to EMS-III.

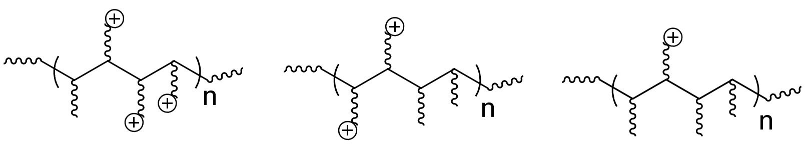
5.2. Future Research

Future research mainly focuses on synthesis of novel alternating copolymers containing functional groups that can be converted to ionic functional groups in solution. (*E*)-Stilbene, maleic anhydride and N-substituted maleimides are proposed to be the monomers to be functionalized and further polymerized. After polymerization and characterization, we will probe the rigidity of these macromolecules by determining the persistence length. We will follow up on the previous working: successfully synthesized various substituted stilbenes and N-substituted maleimides; synthesis of rigid anionic and cationic polyelectrolytes based on the alternating copolymers of substituted stilbenes; synthesis of rigid polyampholytes based on tetraalkyldiaminostilbenes and maleic anhydride;[1] synthesis and rod-coil block copolymers containing rigid polyampholyte segments using RAFT controlled free radical polymerization.[2] The preliminary work on substituted stilbene-N-substituted maleimide copolymer will be extended to new structures. To further explore special properties of rigid, rod-like polyelectrolytes system, such as solution rheology, absorption process, aggregation, like-charged attraction, etc. Currently, the work is focusing on synthesizing polyelectrolytes with controllable charges and charge density, i.e. by starting with different monomers, charged positions on the polyelectrolyte backbones can be controlled and varied. As shown in Scheme 5.1, a repeating unit can be fully charged or partially charged, depending on the different monomers used. We are trying to ascertain the “stiffness” of these copolymers and the affect of addition of the second phenyl group along the backbone.

Examples of specific polyelectrolytes are displayed in Figure 5.2 Polyanion 1 has negative charges on every carbon in the repeating unit. Polyanion 2 has negative charges on 3 carbons of every 4-carbon repeating unit. Polyanion 3 and 4 have negative charges on 2 carbons of every 4-carbon repeating unit. Polyanion 5 has negative charge only on 1 carbons of every 4-carbon repeating unit. Polycation 6 has positive charges on 3 carbons of every 4-carbon repeating unit. Polycation 7 has positive charges on 2 carbons of every 4-carbon repeating unit. Polycation 8 has positive charge on 1 carbon of every 4-carbon repeating unit.



Polyanions with controllable charge density



Polycations with controllable charge density

Scheme 5.1: General presentation of polyelectrolytes with different charge densities

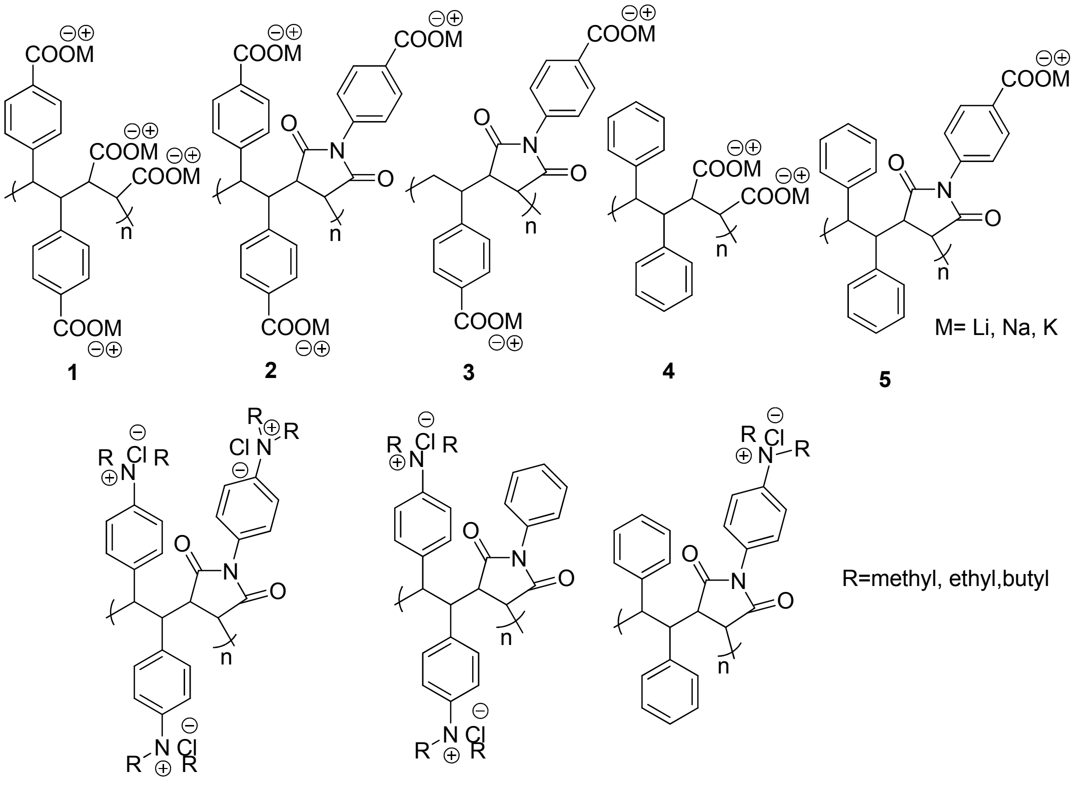
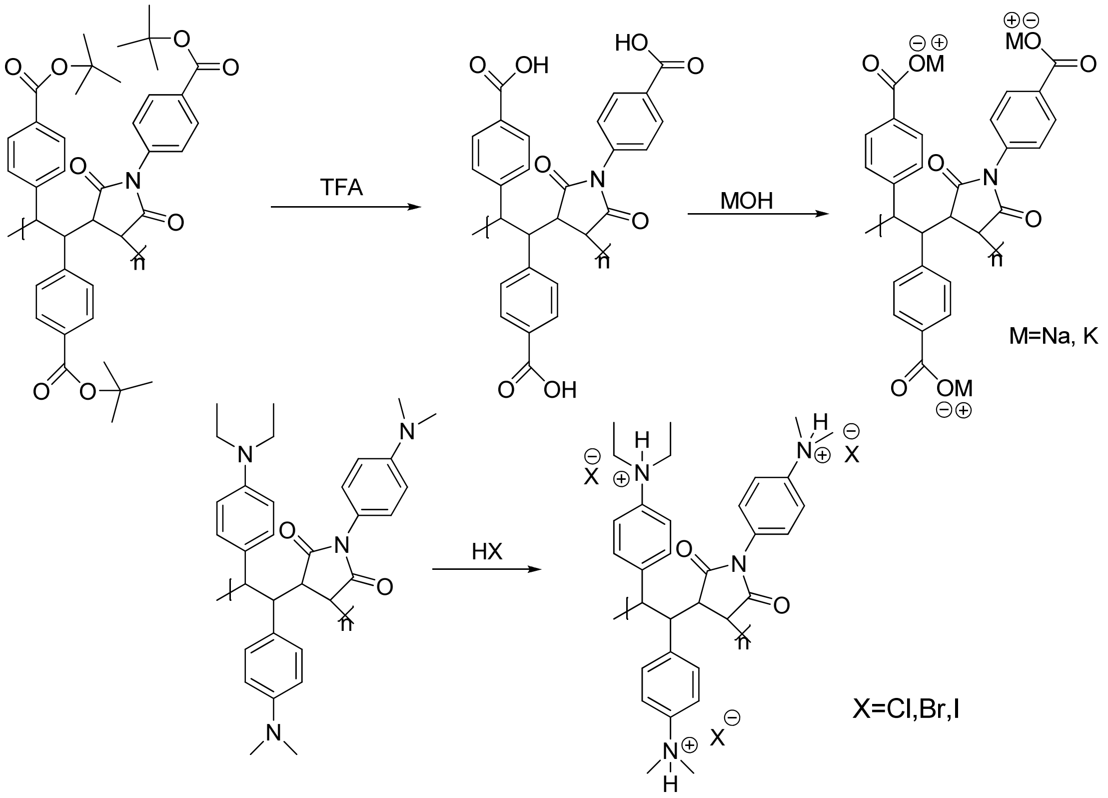


Figure 5.1: Examples of polycations and polyanions with different charge densities

To synthesize the above polymers, we started by synthesizing the following monomers, shown in Figure 5.2. Among these five monomers, synthetic routes of monomer 1, 3, and 4 have been reported.[1,3-5] The experimental procedures for synthesizing these monomers have been described in Chapter 3. ^{1}H NMR and ^{13}C NMR were used to characterize the structures of these monomers. Poly(di-*t*-butyl-(*E*)-4,4'-stilbenedicarboxylate-*c*o-*N*-(4-(*t*-butoxycarbonyl) phenyl)maleimide) and poly(N,N,N',N'-tetraalkyl-4,4'-diaminostilbenes-*co*-*N*-4-(*N',N'*-dimethylaminophenyl)maleimide) were also prepared and characterized by TGA, DSC, SEC, and ^{1}H NMR. No T_g or T_m was observed on DSC trace and the broad peaks on NMR spectrum was also observed. These observations all indicate the chain rigidity of these copolymers. In the future, the corresponding precursors of polycations and polyanions shown in Figure 5.1 will be synthesized and characterized by TGA, DSC, SEC, ^{1}H NMR, and the elemental analysis. The persistence length will be determined by SEC-MALLS,[6] SAXS, SANS.[7,8] The persistence length of polyanion 2 precursor will be compared with polyanion 3 precursor to evaluate the pendent phenyl group impact on the chain rigidity change. The precursors will be converted into water-soluble polyelectrolytes, as shown in Scheme 5.2. The solution properties of these polyelectrolytes will be studied, such as adsorption as a function of pH,[9] adsorption as function of polymer concentration,[9] lay-by lay self-assembly as a function of the persistence length,[10] morphology of the aggregated polyelectrolytes by DLS, TEM, AFM.[11]



Scheme 5.2: Example of the conversion of the polyanion and polycation precursors into water-soluble polyelectrolytes

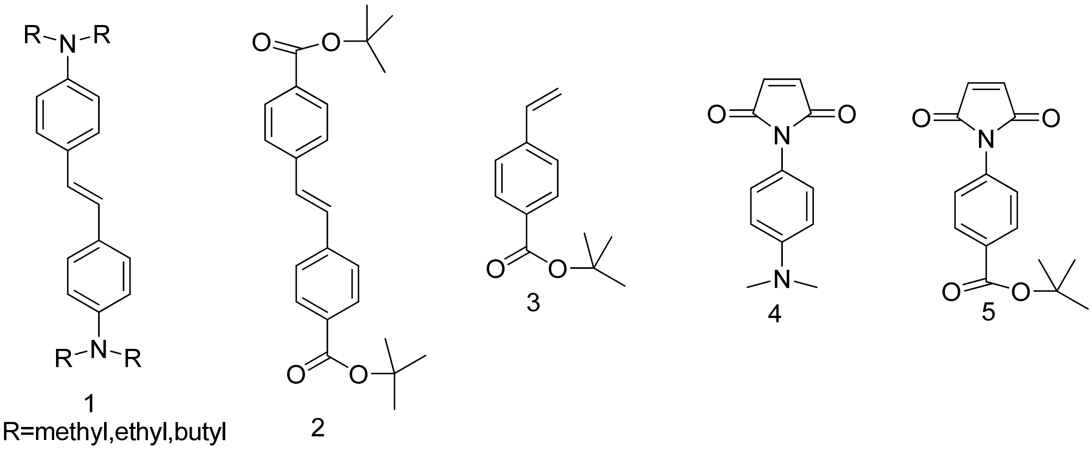


Figure 5.2: Targeted monomers for synthesizing polyanions and polycations

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