Anionic Polymerization. 8. Effect of Polar Modifiers on Uptake of Styrene and the Rate of Lithium Morpholinide Initiated Butadiene/Styrene Copolymerization

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ABSTRACT: Copolymerization of butadiene and styrene in hexane with lithium morpholinide has been examined. A tapered block was obtained regardless of polymerization temperatures. Addition of small amounts of ethers and amines to the butadiene–styrene copolymerization randomizes the distribution of these styrene units in the polymer chain. In addition, the vinyl content of the butadiene portion of the copolymer was determined to be high in the presence of polar modifiers. The range of the vinyl content is between 11 and 95%, depending on the modifier used. Kinetic studies for the copolymerization have also been performed at 30, 40, 50, and 60 °C. It was found that the rate of copolymerization increased as the polymerization temperature increased. With the introduction of polar modifiers, one would expect to see rate enhancement. Detailed results for the copolymerizations are discussed.

Introduction

The copolymerization of dienes and styrene with alkyllithium as catalyst has been extensively studied in recent years.[1–3,14] The effect of modifiers, particularly ethers and amines, on the alkyllithium-intiated diene–styrene copolymerization is also well-known.[1,3] In general, copolymerization of butadiene and styrene with *n*-butyllithium in hexane produces a tapered block copolymer. This result is due to the fact that butadiene is consumed more rapidly than styrene in the copolymerization. The copolymerization character is changed if a small amount of polar solvent or modifier is used. The resulting copolymer exhibits an essentially random sequence of butadiene and styrene units.[2–4]

Recently, we have studied the homopolymerization of butadiene with lithium morpholinide in hexane.[5] The results indicated that lithium morpholinide is an effective initiator for the polymerization of butadiene and that the polymerization process is markedly affected by the presence of additives, such as THF and amines. It was also found that the systems studied have many similarities to polymerization of dienes using alkyllithium initiators. However, the effect of additives, particularly ethers and amines, on the kinetics of polymerization of butadiene and styrene with lithium morpholinide is not known. It is, therefore, of interest to know whether similarities to the alkyllithium-initiated copolymerization also exist.

This paper will detail the general phenomena associated with the use of lithium morpholinide as a copolymerization initiator. We will also discuss the effect of additives, such as ethers and amines, on the kinetics of the copolymerization process.

Experimental Section

A. Preparation of Lithium Morpholinide. Lithium morpholinide was prepared by the reaction of *n*-butyllithium with morpholine in hexane. The *n*-butyllithium (349 mmol) in hexane was added to the morpholine–hexane solution (382 mmol of morpholine, 400 mL of hexane) slowly because of the exothermic nature of the reaction. The lithium morpholinide precipitated from the solution and was isolated by filtration. The product was then washed four times with a total of 2 L of hexane. The material was dried in a vacuum oven at room temperature and then suspended in hexane solution for use as a polymerization initiator. A GC–mass spectroscopic method was used to verify the purity of this material. A titration[24] was used for determination of total alkalinity.

B. Polymerization Procedure. The copolymerizations were performed with a butadiene/styrene/hexane blend. This blend was prepared by a procedure described in our earlier paper.[5]

Modifiers, such as THF (tetrahydrofuran), TMEDA (tetramethylethylenediamine), glyme (1,2-dimethoxyethane), DPE (1,2-dipiperidinoethane), and triethylamine, were purified by distillation. These modifiers were mixed with the lithium morpholinide.

All the copolymerizations were carried out in a 1-gal stainless steel reactor. Butadiene/styrene blend (130 g of 80/20 BD/styrene in 950 mL of hexane) was charged to the reactor under nitrogen pressure. Lithium morpholinide (0.011 34 mol) or lithium morpholinide and modifier (0.011 34 mol of lithium morpholinide and 0.37 mol of modifier) was then added to the blend by means of a hypodermic syringe. The reaction mixture was allowed to stir at a constant temperature. Samples were taken periodically. Polymers were isolated by coagulation in methanol. The polymer was then dried in an oven at 40 °C and 60–70-mm pressure and weighed. Polymers were purified before analyzing by infrared and NMR spectroscopy.[25–27]

Results and Discussion

Lithium morpholinide was chosen as an initiator for butadiene–styrene copolymerization because of its built-in oxygen atom. It was felt that the presence of oxygen in the initiator might lead to a copolymer with unusual properties.

On the basis of preliminary work in our earlier paper,[5] it was clear that the butadiene–styrene copolymer could be obtained in good yield (>95%) at low polymerization temperature. The conversion to the copolymer decreased as the polymerization temperature increased. It was found that the decrease in conversion to the copolymer resulted in lower styrene contents.[5] This result is consistent with the results published by Adams and associates[6] on the thermal stability of living polymer–lithium systems. In Adams' paper, it was concluded that the formation of lithium hydride from poly(styryllithium) and poly(butadienyllithium) did occur at higher temperature in hydrocarbon solvent. The thermal stability of poly(styryllithium) in cyclohexane was found to be poorer than the stability of poly(butadienyllithium). From these results, it appears that the decrease in the styrene content in lithium morpholinide initiated copolymerization at higher temperatures might be associated with the formation of lithium hydride.

Since the reversal of activity of butadiene with respect to styrene in alkyllithium systems has been observed,[7] it would be of interest to determine whether the inversion phenomenon also occurs in case of the lithium morpholinide system. In addition, it would also be of interest to

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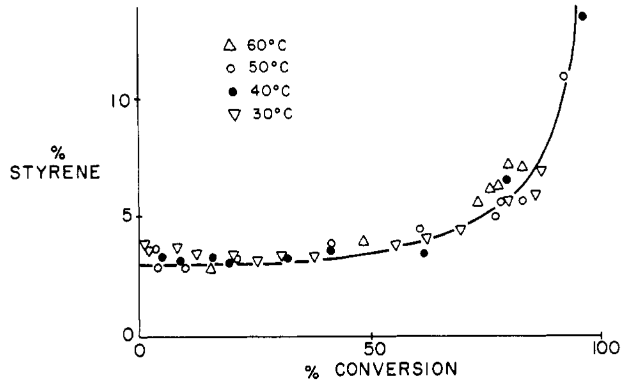


Figure 1. Copolymerization of BD/St with lithium morpholinide in hexane.

know whether the temperature has any effect on the rate of polymerization in this system. For these reasons, we have studied the copolymerization of butadiene and styrene at 30, 40, 50, and 60 °C in hexane. At 30 °C polymerization temperature, the curve for percent bound styrene vs. percent conversion (Figure 1) is characteristic of a tapered block butadiene–styrene copolymerization. Initially, only a small amount of styrene (~3%) is polymerized. The butadiene polymerization dominates the initial stage of the copolymerization to the virtual exclusion of styrene. The remaining styrene is polymerized after all the butadiene monomer is consumed. This result is identical with the result for the alkyllithium-initiated copolymerization. Thus, the order of reactivity in the copolymerization with lithium morpholinide initiator is butadiene > styrene.

At this stage, it would be of interest to know what molecular characteristics cause butadiene to be polymerized more readily than styrene. Unfortunately, no conclusive evidence is available at this time. However, it can be speculated that butadiene is more effective than styrene at "solvation" or coordination of the carbon–lithium bond of the polymer–lithium. Steric factors may also play an important role. Since butadiene is a smaller molecule than styrene,[3] butadiene would be expected to polymerize at a faster rate. Such interpretations have been suggested by Kuntz,[3,9] Forman,[10] and Szwarc[11] in the alkyllithium-initiated copolymerizations. The work of Oliver and associates[15,16] further supports the concept of preferential solvation. They observed the interaction between the lithium and the double bond of the model compound (3-butenyl)lithium by ^{7}Li NMR, UV, and IR spectroscopy. Similar results were also reported by Glaze.[17]

O'Driscoll and Kuntz,[12] on the other hand, suggested that classical copolymerization kinetics is sufficient to explain the copolymerization results. They believe that the crossover reaction between styryllithium and the diene is responsible for the unusual phenomenon of the copolymerization. These results have been confirmed by many investigators.[18–21] The crossover rate constant between styryllithium and butadiene is rapid compared to the other three rate constants. The individual reaction steps can be summarized as follows:

$$\mathrm{BLi} + \mathrm{B} \xrightarrow{K_{\mathrm{BB}}} \sim\!\mathrm{BBLi}$$

$$\mathrm{BLi} + \mathrm{S} \xrightarrow{K_{\mathrm{BS}}} \sim\!\mathrm{BSLi}$$

$$\mathrm{SLi} + \mathrm{B} \xrightarrow{K_{\mathrm{SB}}} \sim\!\mathrm{SBLi}$$

$$\mathrm{SLi} + \mathrm{S} \xrightarrow{K_{\mathrm{SS}}} \sim\!\mathrm{SSLi}$$

Here B and S represent the butadiene and styrene, respectively. K_{BB} and K_{SS} represent the rate constants of homopolymerization of butadiene and styrene, respectively, K_{BS} represents the crossover rate constant between BLi and S, and K_{SB} represents the crossover rate constant between SLi and B. The order of the rate constants based on several papers[18–21] is $K_{\mathrm{SB}} \gg K_{\mathrm{SS}} > K_{\mathrm{BB}} > K_{\mathrm{BS}}$. Both explanations for the unusual reactivity of butadiene and styrene in alkyllithium polymerizations in hydrocarbon solvents can also be applied in the lithium morpholinide copolymerization.

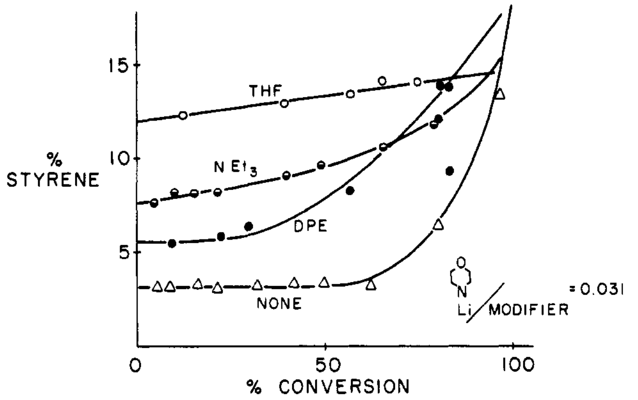


Figure 2. Styrene uptake in lithium morpholinide initiated BD/St copolymerization.

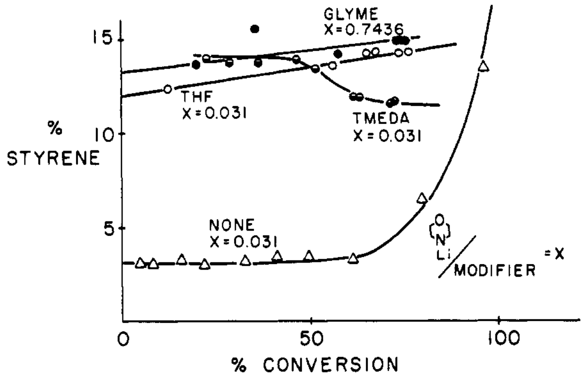


Figure 3. Styrene uptake in lithium morpholinide intiated BD/St copolymerization.

Addition of small amounts of ethers and tertiary amines to the lithium morpholinide initiated copolymerizations reduces or eliminates block formation. At the ratio 0.031:1 of lithium morpholinide to THF, an almost uniform random copolymer of butadiene and styrene was observed. As can be seen in the styrene–conversion curve of Figure 2, the rate of styrene polymerization is increased when THF is used as a modifier. It is obvious that styrene is being consumed faster in the presence of THF than in the absence of modifier. The uniformity of the copolymer probably could have been further improved by increasing the amount of THF. The use of amines, such as triethylamine ($\mathrm{NEt_3}$) and 1,2-dipiperidinoethane (DPE), as modifiers also improves the randomization of the copolymer. However, these amines are much less effective than THF. The order of the randomization effectiveness of the modifiers in this system is THF > $\mathrm{NEt_3}$ > DPE. Other modifiers, such as glyme and TMEDA, have also been studied at 40 °C (Figure 3). In the case of glyme, it was found that the copolymerization could not be carried out beyond 50% conversion when one used a 0.031:1 ratio of lithium morpholinide to glyme as an initiator. It was, therefore, necessary for us to carry out the copolymerization using additional lithium morpholinide. At a 0.7436:1 ratio of lithium morpholinide to glyme, an almost uniformly random copolymer of butadiene and sty-

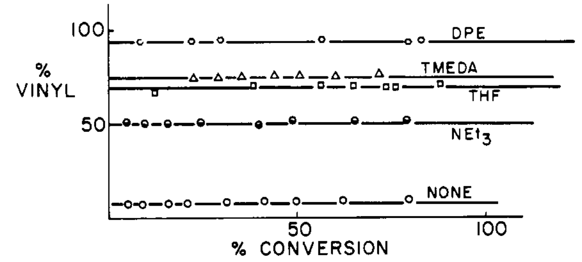


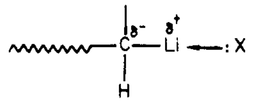
Figure 4. 1,2 content of BD portion of BD/St copolymer (40 °C in hexane).

rene was obtained. The reason for the need for an excess of lithium morpholinide in this system is unknown. It is believed that the loss of live ends and low conversion could be associated with the reaction between carbon–lithium or nitrogen–lithium bond and glyme. In the case of TMEDA it was found that the styrene is being taken up at a constant rate (14%) until 50% conversion to copolymer is achieved (Figure 3). From then on, the styrene content in the copolymer slowly decreased. The decrease in styrene content continues until about 60% conversion to copolymer is reached. From 60–70% the styrene content again remains constant. However, it only levels off at 11% styrene. At present, we are not able to offer a good explanation for this effect. More work along these lines is needed in order to understand the mode of action of these two modifiers.

At this time, it is appropriate to consider the microstructure of the copolymers, since the presence of polar compounds not only increases the rate of styrene polymerization in alkyllithium systems but also changes the ratio of the geometrical isomers in the diene portion of the polymer. It is believed that a similar phenomenon may also be observed in case of the lithium morpholinide initiator.

As can be seen in Figure 4, the vinyl content of the butadiene portion of the copolymer is consistently higher in the presence of polar modifiers than in the absence of modifier. At a 0.031:1 ratio of lithium morpholinide to modifier, the vinyl content of the butadiene portion of the copolymer changes from 50 to 95% as one changes polar modifiers from NEt_3 to DPE. The vinyl content of the copolymer was also found to be constant regardless of the conversion. This effect has been reported by Hsieh for the alkyllithium initiator system.[22]

The reason for the increase in vinyl content of the butadiene portion of the copolymer in the presence of polar modifiers is believed to be associated with complex formation between carbon–lithium and modifiers as shown below:



$$\sim\sim\sim\sim\!-\!\underset{\underset{H}{|}}{\overset{|}{C}}{}^{\delta^-}\!-\!Li^{\delta^+} \leftarrow :X$$

The X is a modifier, such as an amine or an ether. The result of electron donation by the modifier, X, is an enhancement of the ionic character of the carbon–lithium bond. An increase in ionic character in the copolymerization results in an increased amount of vinyl structure. Such an explanation has been suggested for the n-butyllithium-intiated butadiene polymerization.[1]

In addition to the effects on styrene uptake, the overall rate of copolymerization is also increased when polar modifier is used in the alkyllithium-intiated butadiene–styrene copolymerization.[3] Attempts to explain this in terms of preferential complexation of the diene monomer at the active polymerization site[7] and appropriate ion pair–monomer rate constants[12] have failed due to the lack of solid evidence for the state of association of the carbon–lithium bond. It is, therefore, of interest to know whether the same phenomenon holds for the lithium morpholinide system. This initiator, with built-in oxygen as a modifier, is insoluble in hexane, while n-butyllithium initiator is soluble in hexane.

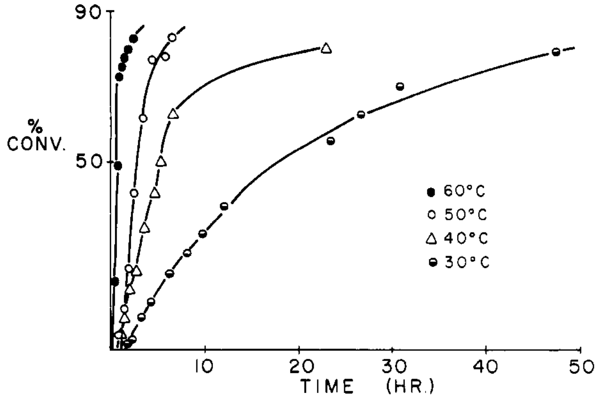


Figure 5. Rates of BD/St copolymerization with lithium morpholinide.

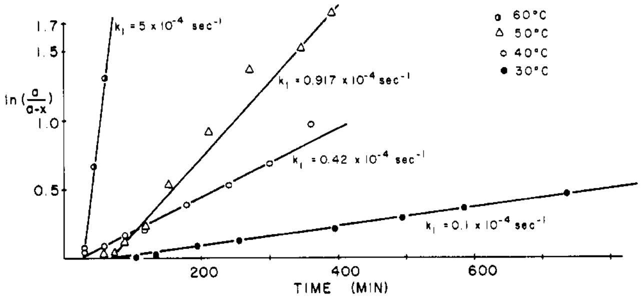


Figure 6. Rates of lithium morpholinide initiated BD/St copolymerization.

The copolymerization of butadiene–styrene with lithium morpholinide was carried out heterogeneously in hexane. Four polymerization temperatures have been chosen for this study. These temperatures are 30, 40, 50, and 60 °C. In all of the copolymerization studies, the same butadiene–styrene blend (80/20 by weight) and the same lithium morpholinide concentration (1.75 mmol/100 g of monomer) were used.

From the conversion–time curve (Figure 5), it was found that the rate of copolymerization increased sharply with the increase of polymerization temperature. As expected, the S-shaped conversion curves do not go through the origin. This is due to the nature of the heterogeneous initiator. It is generally known that the rate of initiation in the heterogeneous system is directly related to the size of the insoluble heterogeneous initiator particles. It is, thus, expected that the large size of the initiator particles causes the longer induction period. On the other hand, the induction period decreases as the polymerization temperature is increased. This result is expected, since the rates of both initiation and propagation increase as the polymerization temperatures increase. This is probably due to the fact that a soluble monomer–initiator complex is produced at higher temperatures, thereby reducing the induction period. Such an explanation has also been suggested by Tait[13] in the lithium diethylamide initiated isoprene polymerization.

Rate studies were examined and compared by another method. Figure 6 shows first-order plots with respect to monomer concentration for lithium morpholinide initiated butadiene–styrene copolymerization at 30, 40, 50, and 60

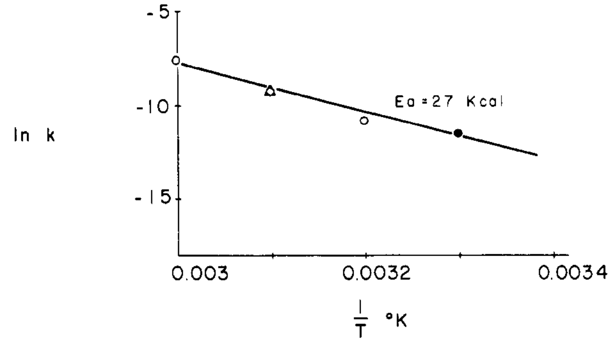


Figure 7. Arrhenius plot for lithium morpholinide initiated BD/St copolymerization.

°C. As can be readily seen, a straight line was obtained regardless of the polymerization temperature. It is seen that the initial rate constant at 30 °C is approximately 0.1 × 10^{-4} s^{-1}. This result is close to the value of 0.3 × 10^{-4} s^{-1} reported by Kuntz[3] in the copolymerization of butadiene–styrene with *n*-butyllithium. As the polymerization temperature increases from 30 to 60 °C, the rate constants also increase from 0.1 × 10^{-4} to 5 × 10^{-4} s^{-1}. An Arrhenius plot for the copolymerization was also made based on 30, 40, 50, and 60 °C temperature data. This is shown in Figure 7. It was found that the energy of activation (E_a) for this copolymerization is about 27 kcal. This value is, indeed, very close to the value of 18–22 kcal for the *n*-butyllithium-initiated copolymerization.[23] This suggests that the mechanism of the copolymerization is similar for both the lithium morpholinide system and *n*-butyllithium systems. This result is reasonable because the propagating carbon–lithium chain end is the same for both systems. The presence of the built-in oxygen in the lithium morpholinide initiator is just not enough to change that rate of polymerization.

With the introduction of polar compounds as modifiers, one would expect to seen an enhancement of the rate of copolymerization. We have also studied the rate of copolymerization at 40 °C in the presence of several polar modifiers. These modifiers are THF, DPE, NEt_3, TMEDA, and glyme. The ratio of lithium morpholinide to modifier is always 0.031:1, with the exception of glyme (0.7436:1 lithium morpholinide to glyme is used).

In general, it was found that the reaction rate was accelerated by the presence of modifiers. As can be seen from Figure 8, the rate for the polymerization without modifier is 0.42 × 10^{-4} s^{-1}. The induction period is about 20–30 min. The first-order rate constant for the polymerization in THF is increased by sixfold (2.57 × 10^{-4} s^{-1}). The induction period is also reduced to almost zero. The increase in rate and decrease in induction period is expected, since the tetrahydrofuran leads to dissolution of the initiator with the production of a homogeneous polymerization system.

The variation in the overall rate of polymerization and induction period with other modifiers has also been studied in hexane. It was found that modifiers, such as DPE, TMEDA, and NEt_3, are less effective than THF in terms of increasing the rates of polymerization. In addition, the induction period with these modifiers is also longer than with THF with the exception of the use of glyme. This is shown in Figure 9.

Conclusion

The copolymerization of butadiene and styrene with lithium morpholinide has been studied in hexane. A tapered block copolymer was obtained regardless of polymerization temperature. It was found that a small amount

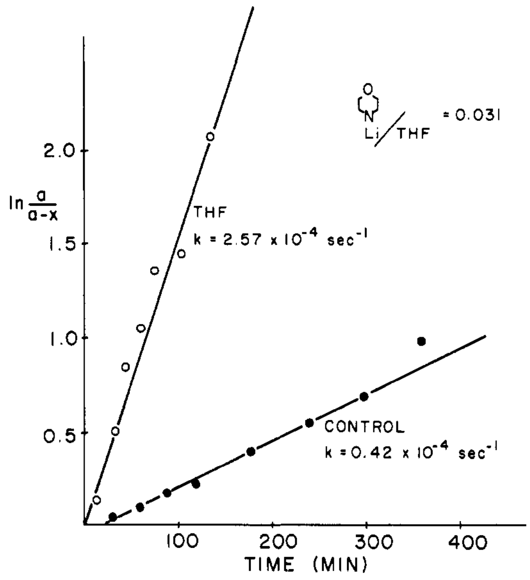


Figure 8. Rates of copolymerization with lithium morpholinide.

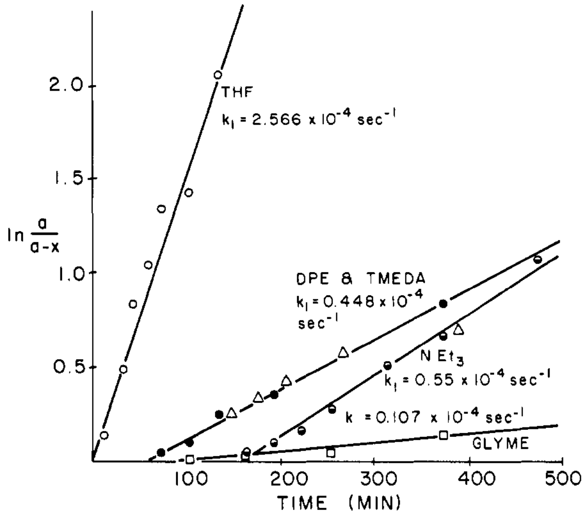


Figure 9. Rates of BD/St copolymerization.

of styrene (~3%) was incorporated into the copolymer through 60% conversion. The butadiene polymerization at this stage dominated the copolymerization. The remaining styrene was then polymerized after all the butadiene monomer was consumed. This result was also observed when one copolymerized butadiene and styrene with alkyllithium. It is believed that the diene monomer is capable of solvating the growing carbon–lithium more effective than styrene monomer. The net result is an increase in the rate of butadiene polymerization due to the increase of concentration of butadiene monomer in the vicinity of the growing chain ends. However, other explanations based on the classical copolymerization kinetics are also possible.

Addition of small amounts of ethers and tertiary amines to the butadiene–styrene copolymerization randomizes the distribution of these monomer units in the polymer chain. Tetrahydrofuran (THF) was found to be the most effective randomizing agent among all the modifiers studied. In addition, the vinyl content of the butadiene portion of the copolymer was determined to be high in the presence of polar modifiers. The vinyl content changed from 11 to 95%, depending on the type of modifier used.

The rate of copolymerization was also studied at several temperatures (30, 40, 50, and 60 °C). It was found that this rate increased as the polymerization temperature increased. The rate can also be increased if polar compounds are used as modifiers. The use of THF as a modifier also reduces the induction period usually associated with heterogeneous initiators, such as lithium morpholinide. The increase in copolymerization rate and decrease in induction period are believed to be related to a change from a heterogeneous to homogeneous polymerization upon dissolution of the initiator. Other additives, such as DPE, TMEDA, NEt_3, and glyme, do not reduce the induction period at the ratio 0.031:1 lithium morpholinide to modifier. These systems remain heterogeneous in nature. However, it is expected that the induction period would be eliminated if additional amounts of modifier were used in this system.

Finally, we have found that the presence of oxygen as a built-in modifier in the lithium morpholinide initiator does not give a copolymer with unusual properties. No randomization of styrene was observed in the butadiene–styrene copolymerization. As a result, the copolymerization with lithium morpholinide behaves like the alkyllithium system.

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Thermodynamic Properties of Moderately Concentrated Solutions of Linear Polymers[†]

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ABSTRACT: The osmotic pressure, light scattering, and vapor pressure of linear polymer solutions in the moderately concentrated region were studied for poly(α-methylstyrenes) having sharp molecular weight distributions and covering a wide range of molecular weight. The reduced osmotic pressure $\pi M/CRT$, where M is the molecular weight and C is the polymer concentration, was found to be a universal function of the degree of coil overlapping, which is defined by the ratio of polymer concentration C to a critical concentration C^*. In moderately concentrated solution, where C is larger than C^*, $\pi M/CRT$ is proportional to $(C/C^*)^{1.32_5}$, in good agreement with the scaling theory of des Cloizeaux.

Introduction

Many papers have been published to show that the thermodynamic and viscoelastic properties of linear polymer solutions show different behavior in three concentration regions. In dilute solutions, the thermodynamic properties are determined by the excluded-volume effect working between segments, and polymer coils in good solvents may be approximately regarded as hard spheres with respect to intermolecular interactions.[1,2] Many theoretical and experimental works have been published on the thermodynamic properties of dilute solutions. In concentrated solutions, polymer coils overlap so extensively that the excluded-volume effect of polymer coils disappears and the segments are uniformly distributed over the solution.[3] The thermodynamic properties of concentrated solutions are well explained on the basis of the theory of Flory and Huggins.[3]

In the intermediate region, that is, in moderately concentrated solution, the polymer coils partially interpenetrate each other, so that the thermodynamic properties may be different from either dilute or concentrated solutions. The thermodynamic properties of moderately concentrated solutions have not extensively been studied in comparison with those of dilute and concentrated solutions. It is important to study the thermodynamic properties of moderately concentrated solutions not only because it is interesting to examine how the excluded volume is affected by coil overlapping but also because moderately

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