

Using Heavy Ethers as Structure Modifiers in the Synthesis of SBS Block Copolymers in Cyclohexane

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ABSTRACT: Heavy ethers—diethoxyethane (DIOXO) and triethylorthoacetate (TEOA)—were evaluated and compared with monoethers such as tetrahydrofuran (THF) and diethylether (DEE) as structure modifiers during the synthesis of linear styrene–butadiene block copolymers of polyA-*block*-polyB-*block*-polyA type (SBS). A smaller amount of a heavy ether than a monoether was needed to achieve the same targeted content of the 1,2-polybutadiene (vinyl) microstructure. The vinyl content increased from 10 to 71% with increase in the amount of TEOA from 10 ppm to 1 wt %, while the *trans*-1,4 and *cis*-1,4 units decreased. Similarly, increasing the amount of DIOXO from 10 ppm to 1 wt % increased the vinyl content from 17 to 89%. TEOA, 300 ppm, or DIOXO, 50 ppm, were suggested for making an SBS copolymer with a targeted 40% vinyl content. The addition of heavy ethers as structure modifiers also increased the rates of polymerization for both styrene and butadiene. Among all ethers, DIOXO enhanced the rate of butadiene polymerization the most, whereas TEOA caused the highest rate of styrene polymerization. Heavy ethers accelerated the rates of polymerization more than did monoethers. Furthermore, for an SBS polymer synthesized via a sequential method, the addition of heavy ethers enhanced the crossover efficiency, resulting in a narrower molecular weight distribution with a lower polydispersity. For an SBS polymer made via a coupling method, the coupling efficiency decreased and varied with the type of the coupling agent used. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2543–2560, 1997

Key words: heavy ether; microstructure; modifier; polar; SBS; polymerization; block copolymer; kinetics; triethylorthoacetate; diethoxyethane

INTRODUCTION

Styrene–butadiene block copolymers (SBS) are an important class of thermoplastic elastomers. However, these copolymers do not have good long-term heat, weather, and UV stability due to the presence of a large amount of unsaturated aliphatic double bonds in the polybutadiene segment. Therefore, hydrogenation (saturation) has been practiced to improve the copolymer stability. To keep the hydrogenated SBS copolymer from

crystallizing and losing elastomeric properties, the microstructure of the polybutadiene segment needs to be modified prior to the hydrogenation, by raising the 1,2-polybutadiene (vinyl) content relative to the 1,4-polybutadiene.^{1–3} The use of polar species such as ethers and amines could result in an isomerization of the polybutadiene segment during the copolymer synthesis.^{4–7} Extensive studies have been reported on the use of various initiators in a variety of polar solvents.^{8–16} Issues such as the modifying powers for various organometallic initiators in polar solvents, the kinetics of polymerization, and the isomerization mechanism have also been reviewed by Morton,¹⁷ Young et al.,¹⁸ and Van Beylen et al.¹⁹

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Apart from these microstructure studies on homopolydienes synthesized in bulk polar ethers, Bywater and Worsfold^{11,13} studied the influence of tetrahydrofuran (THF) on the polymerization of styrene in benzene and found that the ratio of tetrahydrofuran to initiator significantly affected the polymerization rate. Morton¹⁷ found that tetrahydrofuran could alter the microstructure of polybutadiene from a high 1,4- to a high 1,2-content even in a nonpolar hydrocarbon solvent containing a very small amount of ether. Recently, renewed interest in tailor-made polymer architecture has prompted new microstructure studies. Van der Velden and Fetters²⁰ determined the microstructures of anionically prepared polybutadienes, either deuterated or nondeuterated, using ¹³C-NMR. Chang et al.²¹ studied the anionic polymerization of butadiene using tetramethylethylenediamine (TMEDA) as the modifier in hexane with a TMEDA-to-*n*-butyllithium (*n*-BuLi) molal ratio ranging from 0 to 3.5. Halasa et al.²² studied the solution polymerization of SBR random copolymers and found that each polybutadiene microstructure approached respective limiting values at around a TMEDA-to-*n*-BuLi ratio of 2. Hsu and Halasa²³ discovered that salts of tetrahydrofurfuryl alcohols could be used to modify anionic po-

lymerization of conjugated diene monomers. By selecting proper ratios of potassium 2-methyl-2-butoxide (*t*-AmOK) and THF to *n*-BuLi, Bu and Ying^{24,25} obtained styrene-butadiene copolymers with unique randomness. Hergenrother et al.²⁶ found that the 2,1-addition predominated when adding a small amount of a polar modifier during the random copolymerization of styrene and butadiene using trialkyltin lithium as the initiator.

In addition, the optimal usage of THF and diethylether (DEE) as structure modifiers and their effects on the rate of SBS copolymerization in cyclohexane were reported in our previous work.^{27,28} While being the commonly used polar ethers, monoethers such as THF and DEE are apt to contaminate the recovered solvent during the solvent distillation due to their low boiling temperatures and the large quantity required during the polymer synthesis. Therefore, it is conceivable that heavy ethers which have higher boiling temperatures and stronger polarity could afford a catalytic amount of usage and, in the meantime, would not be distilled off together with the recovered solvent. Thus, the purpose of this work was to study the effect of heavy ethers and, more particularly, the diether-diethoxyethane (DIOXO) and the triether-triethylorthoacetate (TEOA). Further-

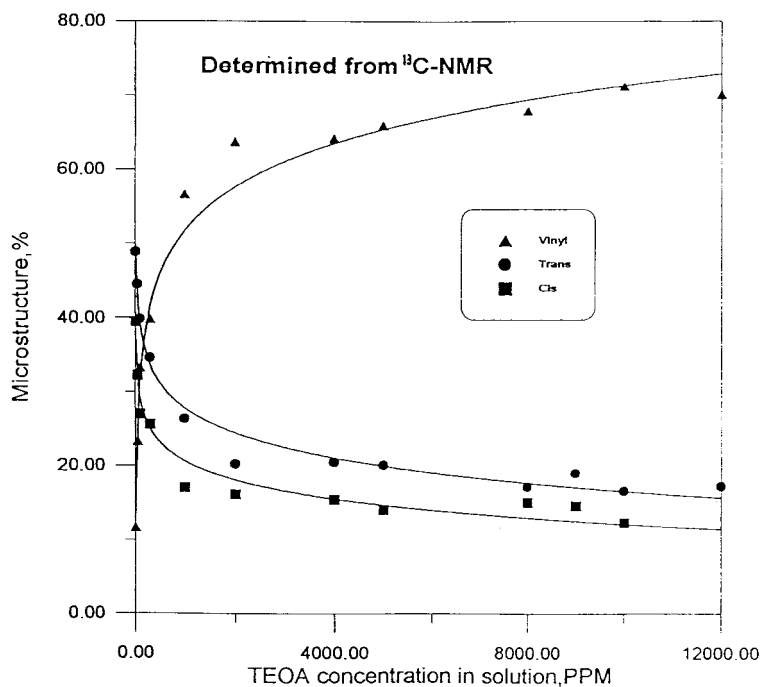


Figure 1 Microstructure of the SBS copolymer at varying TEOA concentrations.

more, since SBS can be synthesized via either a sequential method or a coupling method,^{17,29} the effects of heavy ethers on the crossover efficiency for the former and on the coupling efficiency for the latter were also studied.

EXPERIMENTAL

All materials used in this work were purified prior to their use. The styrene (from Taiwan Synthetic Rubber Corp., TSRC) was treated with activated alumina (from Alcoa Co.) to remove the inhibitor. The butadiene (from TSRC) was vaporized, recondensed, and treated with activated alumina to remove any impurities, moisture, and inhibitor. *n*-BuLi was purchased at a 15 wt % concentration from Merck. The cyclohexane solvent was obtained from TSRC, which was dried with activated alumina. 1,2-Dibromoethane (DBE) and methyl benzoate (MBZ) (Merck, > 99% purity) were used as coupling agents. Diethoxyethane and triethylorthoacetate were purchased from Merck and were treated with 4 Å molecular sieves and deoxygenated prior to their use.

In this work, the SBS copolymers were synthesized using a monoanionic organolithium initiator

such as *n*-BuLi in either of two different ways: (1) a coupling method wherein diblock precursors are linked by a coupling agent to form the final triblock copolymer and (2) a sequential method wherein the three blocks are formed sequentially. The experiments were conducted in a 1 L air-free glass autoclave (Taiatsu, Japan) using cyclohexane as the solvent.

To start a polymerization run, the cyclohexane was first put into the glass autoclave. This solvent was heated to 40°C prior to the addition of the heavy ether and *n*-BuLi. Then, the styrene was charged into the reactor. Anionic polymerization occurred and the living polystyryllithium chain ends formed, with the color of the solution turning red. Five minutes after the vessel temperature reached the maximum, the reaction content was cooled down to 40°C. Finally, the butadiene was charged into the vessel to continue the polymerization, forming the polystyrene-*block*-polybutadiene diblock polymer. The color of the solution changed from red into yellow, indicating the formation of the living polystyrylbutadienyl-lithium chain ends. Five minutes after the vessel temperature reached the maximum, the solution was cooled to and maintained at the desired temperature ready for the next step—a coupling or a sequential addition of styrene.

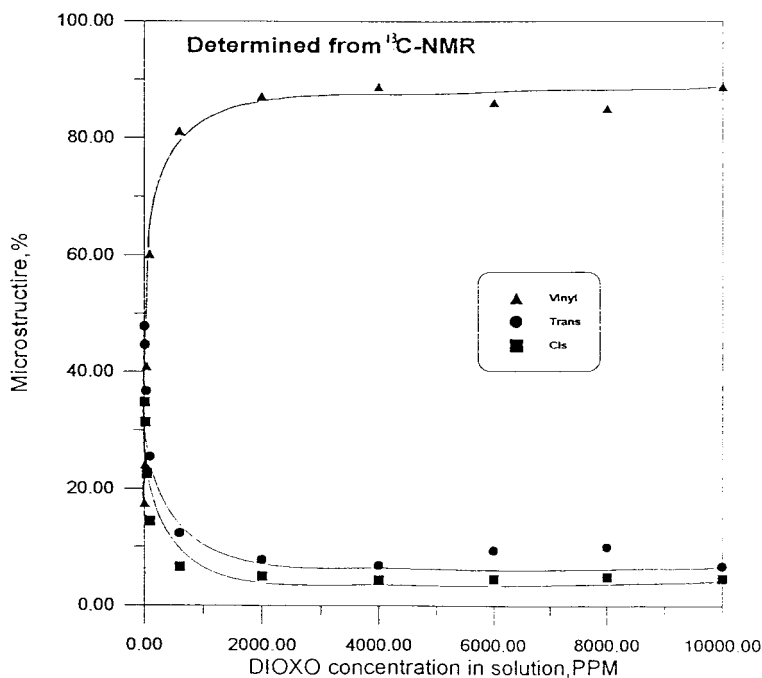


Figure 2 Microstructure of the SBS copolymer at varying DIOXO concentrations.

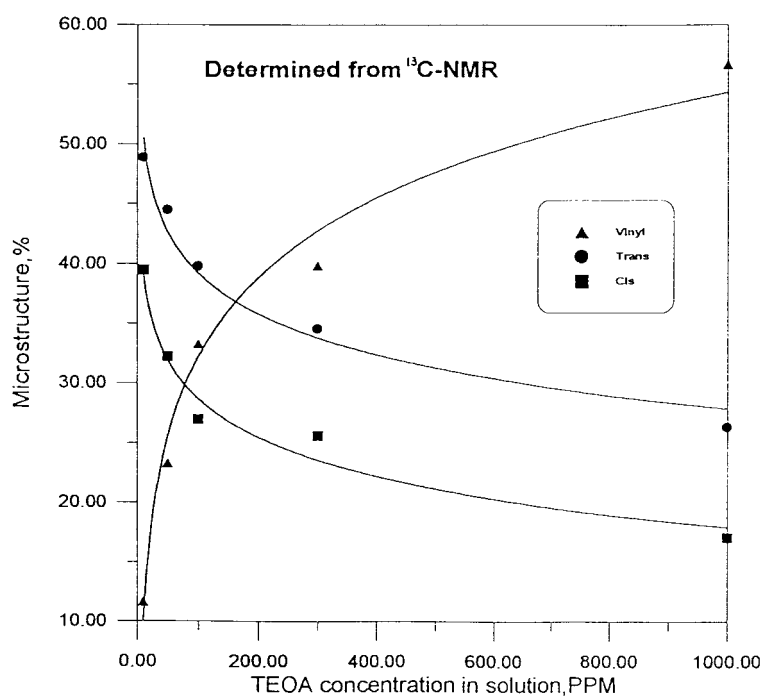


Figure 3 Microstructure of the SBS copolymer at TEOA concentrations ranging from 10 to 1000 ppm.

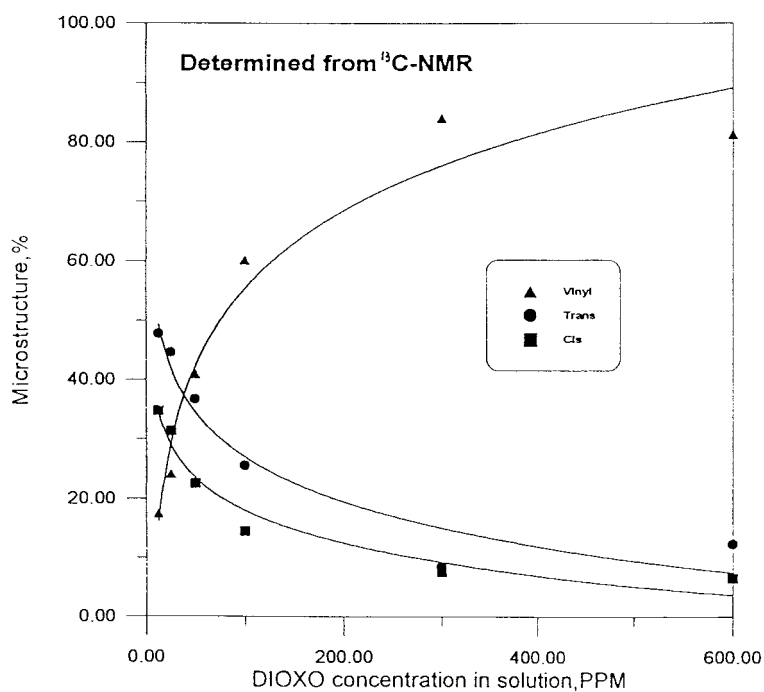
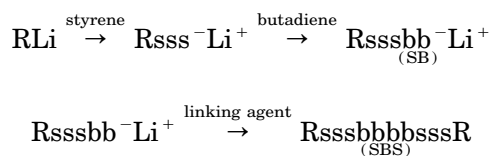


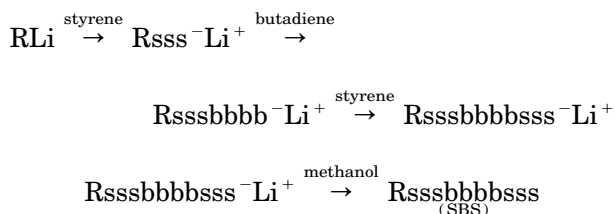
Figure 4 Microstructure of the SBS copolymer at DIOXO concentrations ranging from 10 to 600 ppm.

For synthesis by the coupling method, the coupling agent DBE or MBZ (with 25 mol % in excess of the stoichiometry) was charged to link the SB diblocks forming the final SBS copolymer. Thirty minutes coupling time was allocated to ensure the completion of the coupling reaction. The overall polymer synthesis reaction was as follows:



where $R = n$ -butyl. Afterward, an antioxidant, BHT, was added and the vessel content was poured into isopropanol and the SBS polymer precipitated. After drying in a vacuum oven, the polymer was analyzed for its molecular weight and microstructure.

For synthesis by the sequential method, the beginning n -BuLi charge had to be reduced by half. Furthermore, half of the beginning styrene charge had to be delayed until the butadiene polymerization was complete. No coupling agent was needed, but a small amount of methanol was added at the end to terminate the living styryllithium chains. The overall polymer synthesis reaction was as follows:



where $R = n$ -butyl.

The molecular weights and molecular weight distributions of synthesized polymers were measured by a Waters gel permeation chromatograph (GPC) equipped with Waters M-486 adsorbance (UV) and Waters 410 differential refractive index (RI) detectors. The GPC was operated using three Waters Ultrastyrigel columns (10^3 , 10^4 , and 10^5 Å) at a nominal flow rate of 1 mL/min with a sample concentration of 0.1 wt % in the THF solvent. The microstructure was determined using a Bruker AMX400 100.61 MHz ^{13}C -NMR.

RESULTS AND DISCUSSION

Effect of Heavy Ethers on the Microstructure of Polybutadiene Segment

NMR analysis was used to identify the various isomeric units of polybutadiene. Since it was difficult to quantify the overlapping *cis*-1,4 and *trans*-1,4 peaks in the ^1H -NMR spectra, ^{13}C -NMR was used. While it would be easy to determine the relative portions of *cis*-1,4, *trans*-1,4, and vinyl microstructures for homopolybutadiene, the analysis for a random copolymer of butadiene and styrene was much more complicated.^{30–36} However, for block-type copolymers such as SBS copolymers, the use of Inverse gated ^1H decoupling ^{13}C -NMR technique enabled us to determine the content of each isomeric unit based on the absorption peaks of vinyl, *cis*-1,4 and *trans*-1,4 along with the chemical shifts (γ -effect and β -effect) of *cis*-1,4 and *trans*-1,4 caused by the vinyl unit.^{37,38} The peak assignment, the typical ^{13}C -NMR spectrum, and the calculation method for each isomeric unit were described previously.^{27,28}

The effects of heavy ethers TEOA and DIOXO on the microstructure of the polybutadiene portion of the SBS copolymers are shown in Figures 1 and 2. The vinyl content increased from ~ 10 to $\sim 71\%$ with an increase in the amount of TEOA from 10 ppm to 1 wt %, while the *cis*-1,4 and *trans*-1,4 units decreased. By analogy, increasing the amount of DIOXO from 10 ppm to 1 wt % enhanced the vinyl content from ~ 17 to $\sim 89\%$ with a concomitant decrease in *cis*-1,4 and *trans*-1,4 units. To generate a 40% vinyl microstructure of the polybutadiene segment as required for the making of hydrogenated SBS copolymers, the optimal amounts of TEOA and DIOXO needed were 300 and 50 ppm, respectively, as determined from Figures 3 and 4 showing the enlarged portion of Figures 1 and 2.

Effect of Heavy Ethers on Polymerization Rates

It is well known that the living styryllithium or butadienyllithium chain ends tend to associate in nonpolar hydrocarbon solvents.¹⁷ This association phenomenon would alter the kinetic mechanism and slow down the polymerization rate. While the association does not occur in polar solvents due to their strong solvating power, the living chain end can exist in forms of the contact ion pair, loose ion pair, or free ions hav-

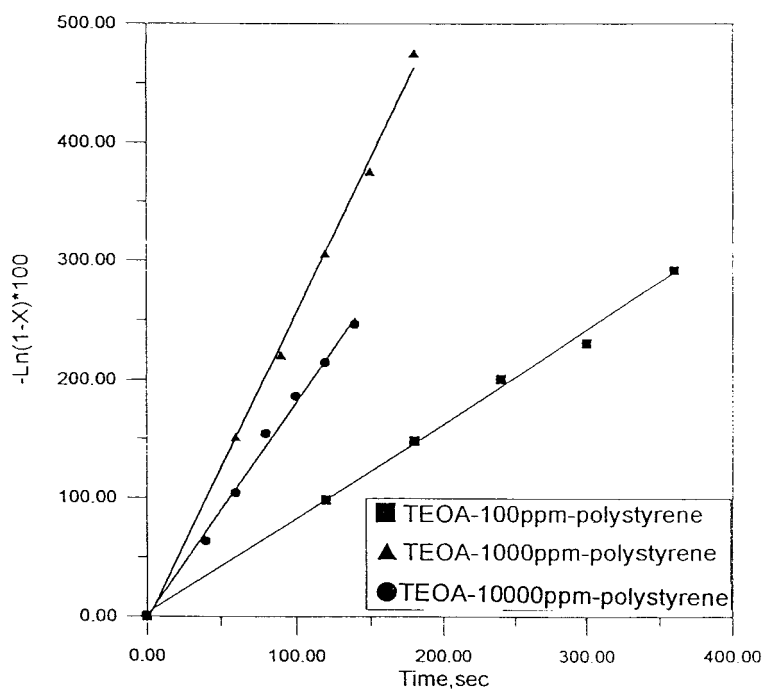


Figure 5 Conversion data for polymerization of styrene at 40°C with varying amount of TEOA.

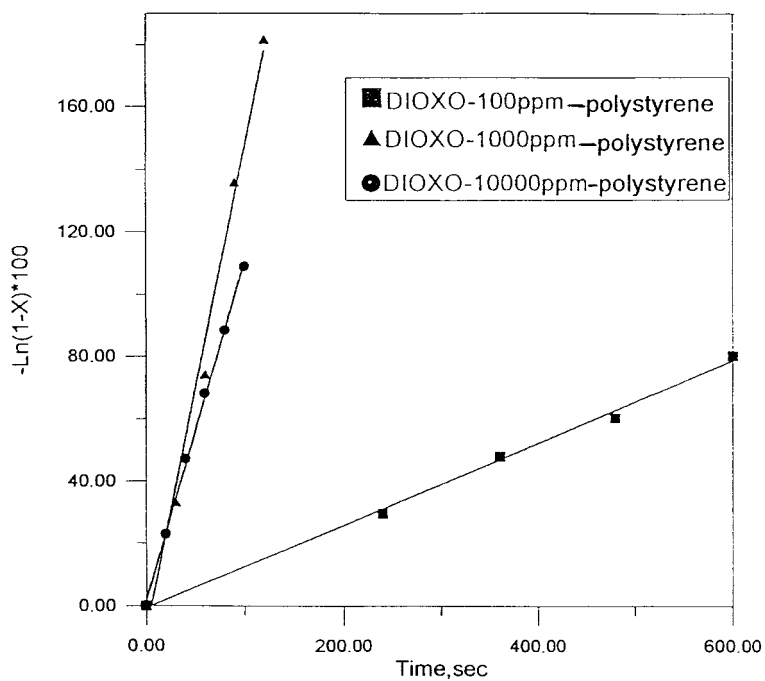


Figure 6 Conversion data for polymerization of styrene at 40°C with varying amount of DIOXO.

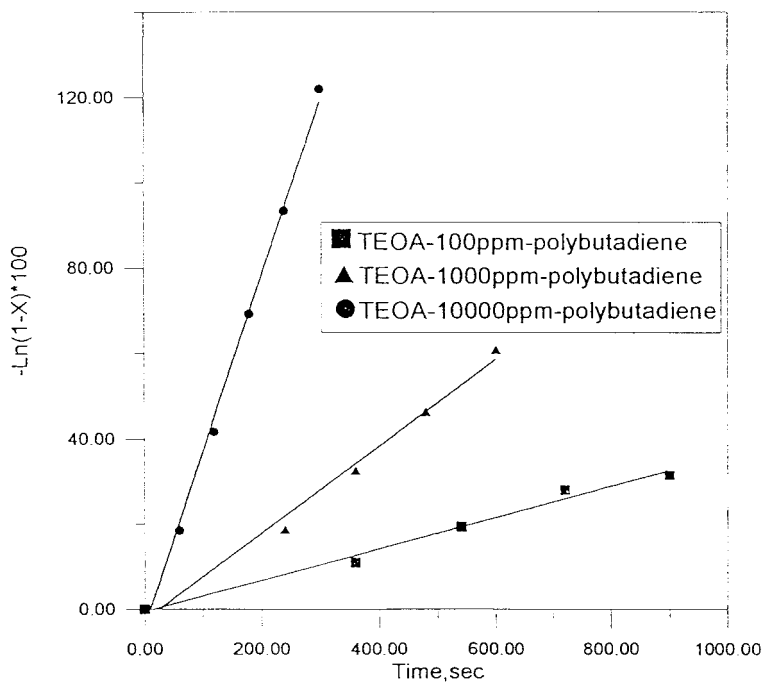


Figure 7 Conversion data for polymerization of butadiene at 40°C with varying amount of TEOA.

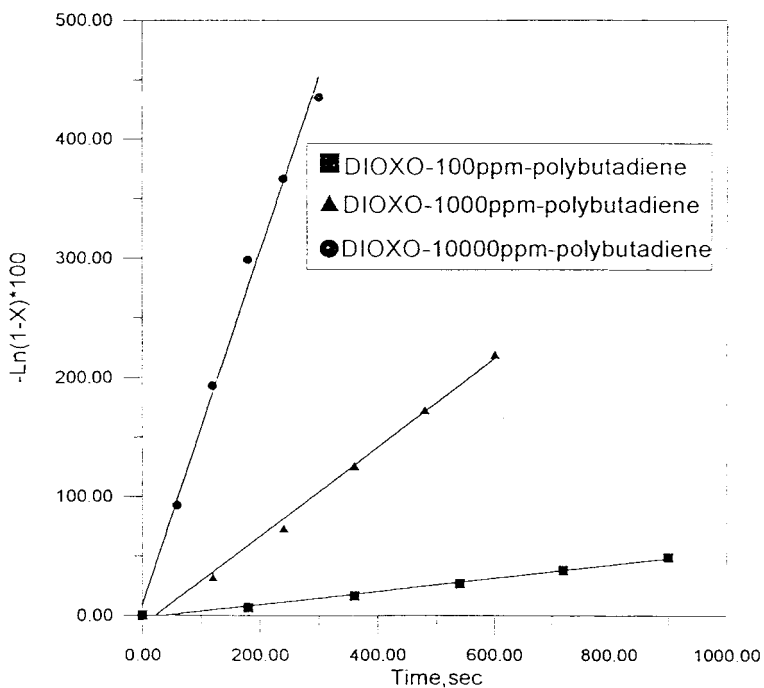


Figure 8 Conversion data for polymerization of butadiene at 40°C with varying amount of DIOXO.

Table I Rate Constants of Polymerization of Styrene Using Varying Amounts of Ethers at 40°C

Nonpolar	Solvent		Polymerization Rate (K · 10 ³ , s ⁻¹)
	TEOA (ppm)	DIOXO (ppm)	
Cyclohexane	100		7.97
Cyclohexane	1000		26.70
Cyclohexane	10,000		18.08
Cyclohexane		100	1.32
Cyclohexane		1000	15.53
Cyclohexane		10,000	10.88

n-BuLi initiator $[I] = 3.89 \times 10^{-3}$ mol/L; $[M]_0 = 0.37$ mol/L.

ing different reaction rates. Therefore, in our reaction system using the nonpolar cyclohexane as the solvent in the presence 0.001–1 wt % of polar structure modifiers, the polymerization rate varied with the amount of modifiers. To study the polymerization rate, isothermal experiments were carried out to synthesize homopolystyrene and homopolybutadiene under various modifier concentrations. The polymerization can be treated as a pseudo-first-order reaction as follows:

$$-\frac{d[M]}{dt} = k_{\text{obs}}[M]$$

where $[M]$ is the monomer concentration, and k_{obs} , the apparent rate constant comprising the true rate constant and the concentration of living chain ends. At isothermal conditions, this equation can be integrated as

$$\ln \frac{[M]}{[M]_0} = -k_{\text{obs}}t$$

$$\ln(1 - X) = -k_{\text{obs}}t$$

where $[M]_0$ is the monomer concentration at $t = 0$, and X , the monomer conversion. The k_{obs} can be obtained from the plot of $-\ln(1 - X)$ vs. t .

The conversion, X , was calculated based on the progressive molecular weights measured from GPC in the following manner:

$$X = 1 - \frac{[M]}{[M]_0} = \frac{MW}{MW_f}$$

where MW is the molecular weight at time t , and MW_f , the molecular weight at the completion of polymerization.

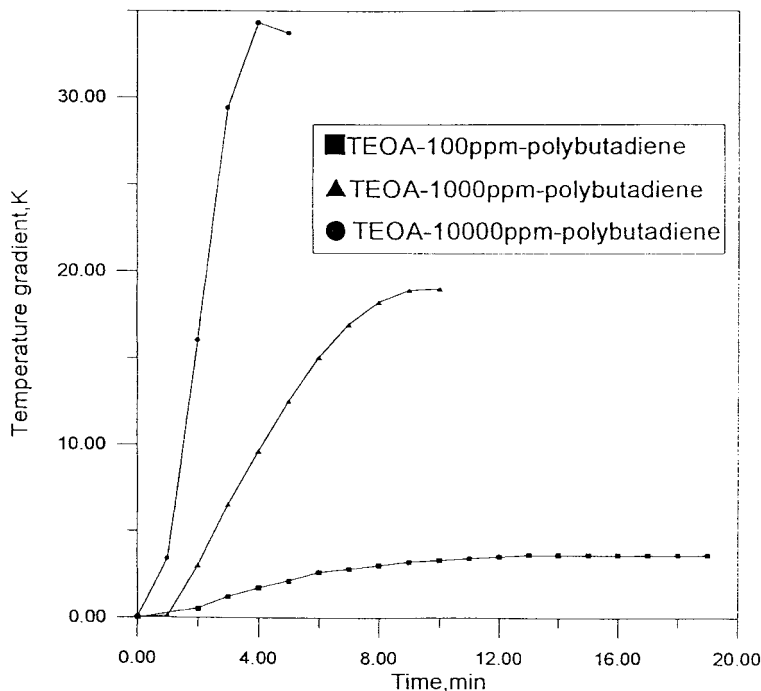


Figure 9 Temperature profiles for polymerization of butadiene starting at 40°C with varying amount of TEOA.

Table II Rate Constants of Polymerization of Butadiene Using Varying Amounts of Ethers at 40°C

Nonpolar	Solvent		Polymerization Rate (K · 10 ³ , s ⁻¹)
	TEOA (ppm)	DIOXO (ppm)	
Cyclohexane	100		0.37
Cyclohexane	1000		1.02
Cyclohexane	10,000		4.11
Cyclohexane		100	0.56
Cyclohexane		1000	3.74
Cyclohexane		10,000	14.78

n-BuLi initiator $[I] = 4.36 \times 10^{-3}$ mol/L; $[M]_0 = 1.85$ mol/L.

The experimental data of polymerization of styrene and butadiene at 40°C using various amounts of TEOA or DIOXO as the modifier are shown in Figures 5–8. The rate of polymerization for styrene at a TEOA concentration of 1000 ppm was significantly higher than that at a concentration of 100 ppm. Nevertheless, a 10,000 ppm TEOA concentration resulted in a slight rate de-

crease. A similar situation was observed for the case using DIOXO. The styrene polymerized much faster at 1000 ppm DIOXO concentration than at 100 ppm concentration, while a 10,000 ppm DIOXO concentration did not further accelerate the styrene polymerization. In another aspect, the polymerization rate of butadiene increased monotonically with an increase in either TEOA or DIOXO in the concentration range studied. The corresponding rate constants are tabulated in Tables I and II. Albeit the above analyses were done under 40°C isothermal conditions, the observed rate changes caused by the polar modifier was equally true even under a nonisothermal condition. As an example, the temperature profiles for nonisothermal polymerization of polybutadiene are shown in Figures 9 and 10 for the usage of TEOA and DIOXO, respectively. The effect of polar modifiers on the rate enhancement, reflected by the early rise of these temperature curves, was consistent with our previous observation under isothermal conditions. Thus, for making SBS copolymers, the addition of a heavy ether as a structure modifier could increase the polymerization rate of both styrene and butadiene. Moreover, there exists an optimal amount of mod-

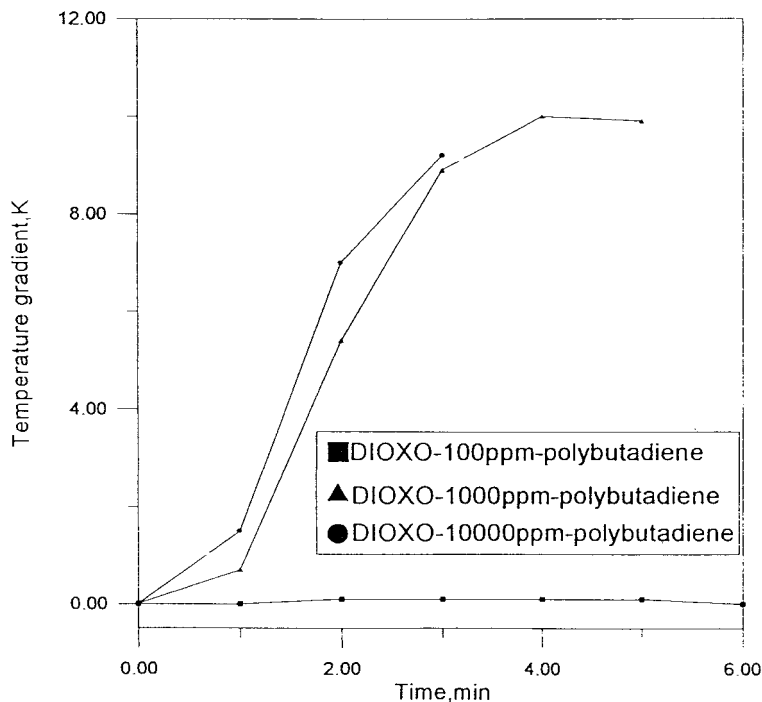


Figure 10 Temperature profiles for polymerization of butadiene starting at 40°C with varying amount of DIOXO.

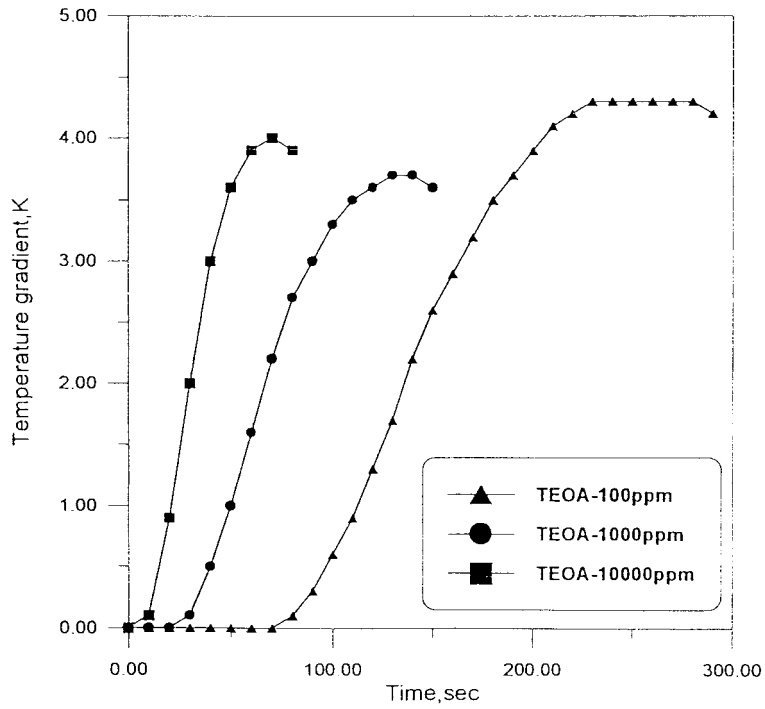


Figure 11 Temperature profile during the formation of the third block in a sequential synthesis of SBS copolymer at varying amount of TEOA.

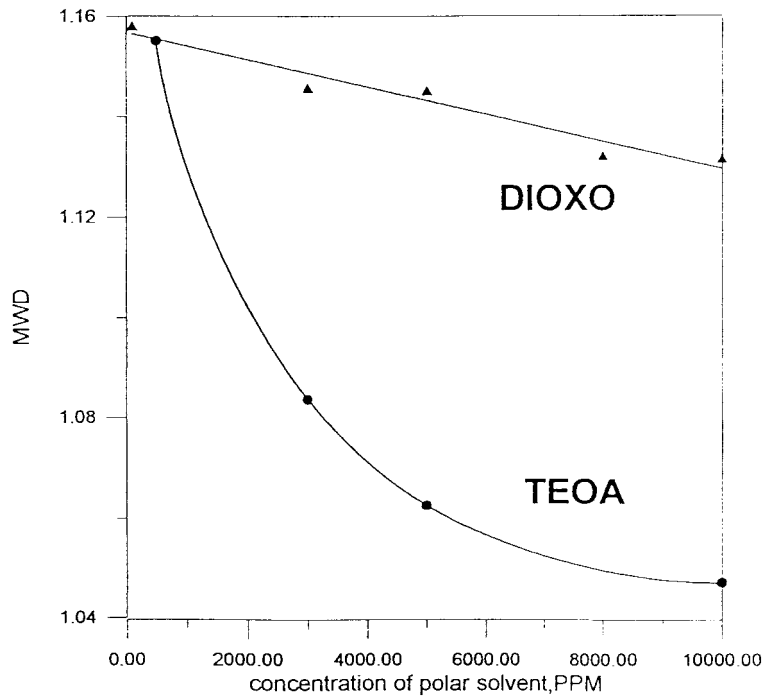


Figure 12 Effect of heavy ethers on the molecular weight distribution of SBS copolymer synthesized sequentially.

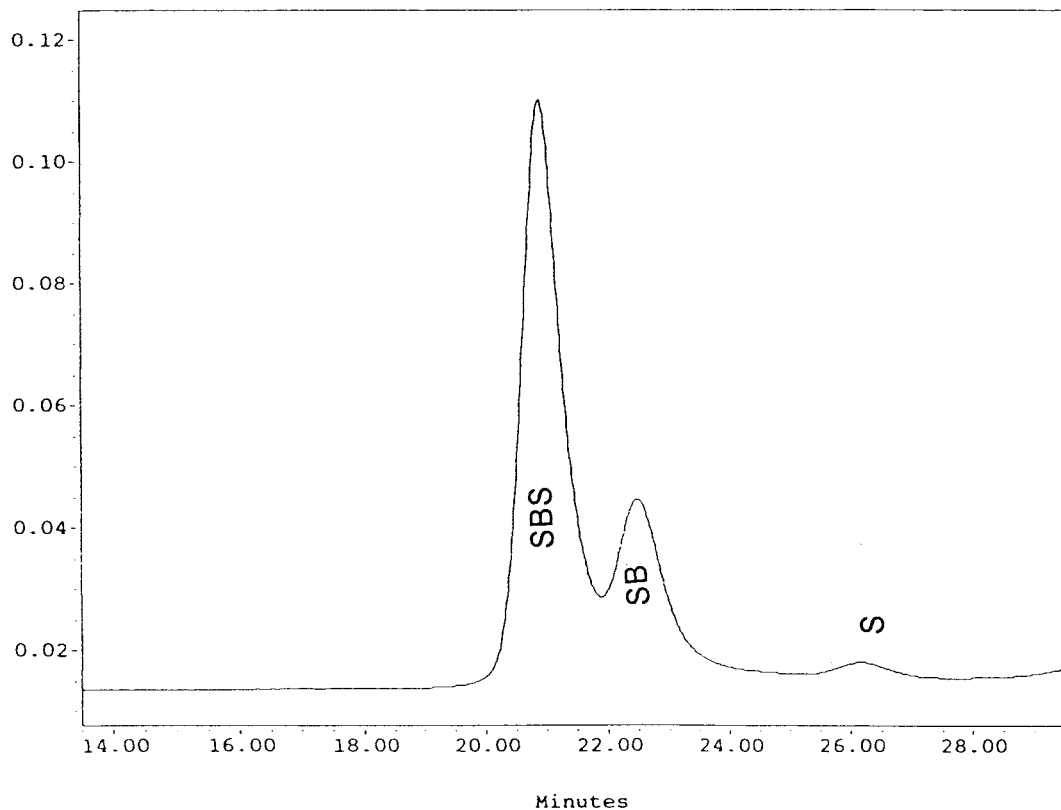


Figure 13 A typical GPC curve for SBS polymer made via coupling method.

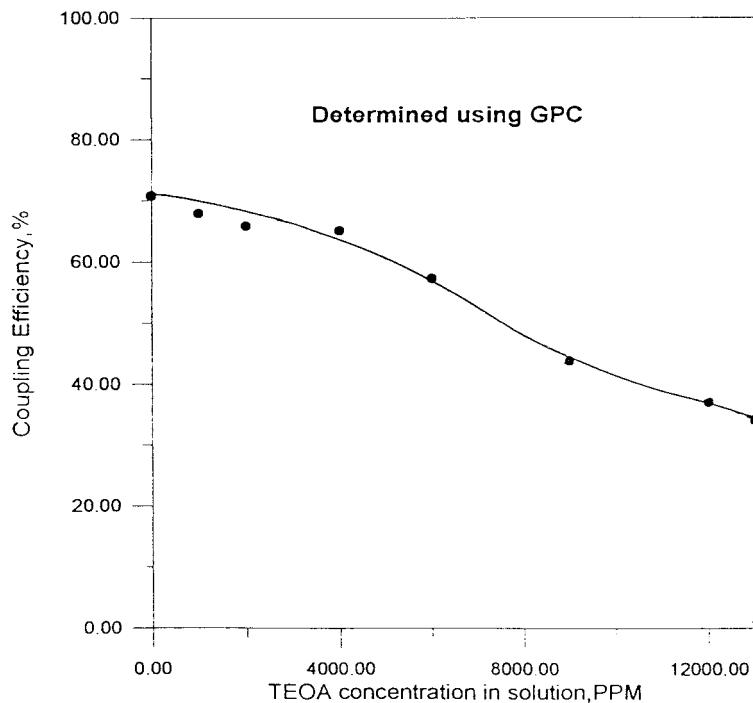


Figure 14 Effect of TEOA on the coupling efficiency using DBE as the coupling agent.

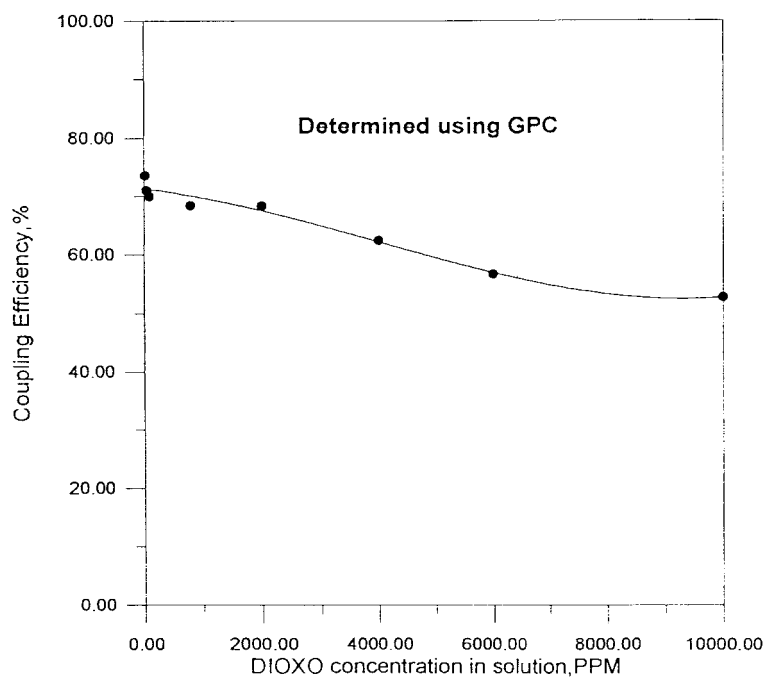


Figure 15 Effect of DIOXO on the coupling efficiency using DBE as the coupling agent.

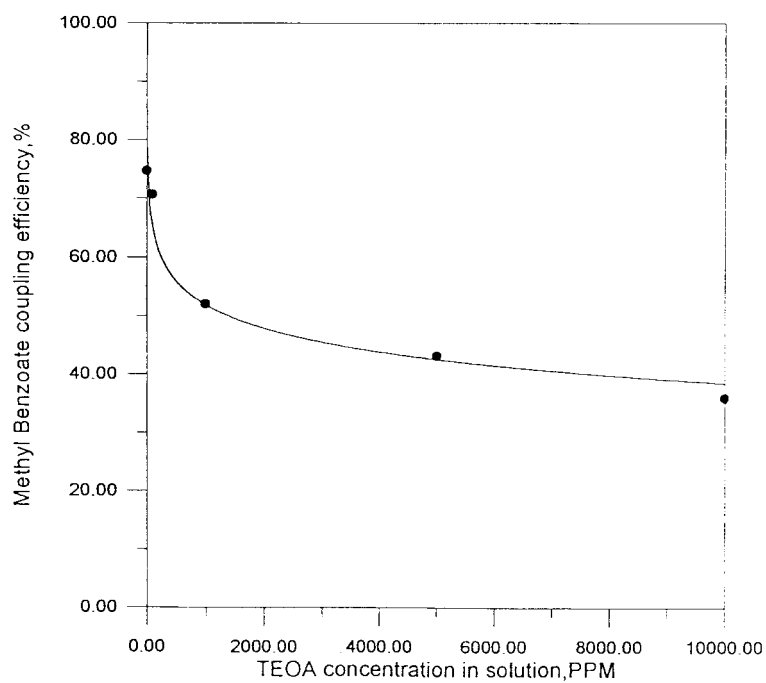


Figure 16 Effect of TEOA on the coupling efficiency using MBZ as the coupling agent.

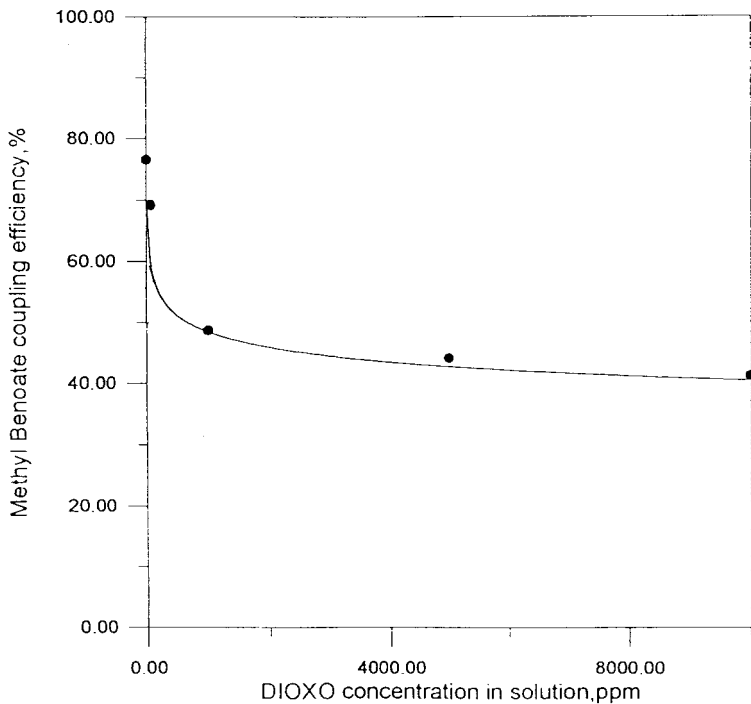


Figure 17 Effect of DIOXO on the coupling efficiency using MBZ as the coupling agent.

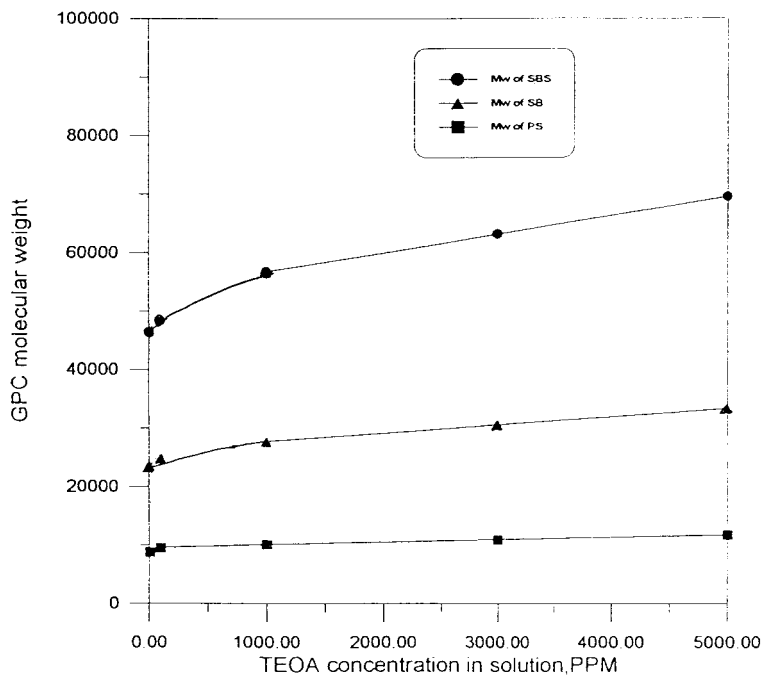


Figure 18 Effect of TEOA on the molecular weight of SBS copolymer coupled by MBZ.

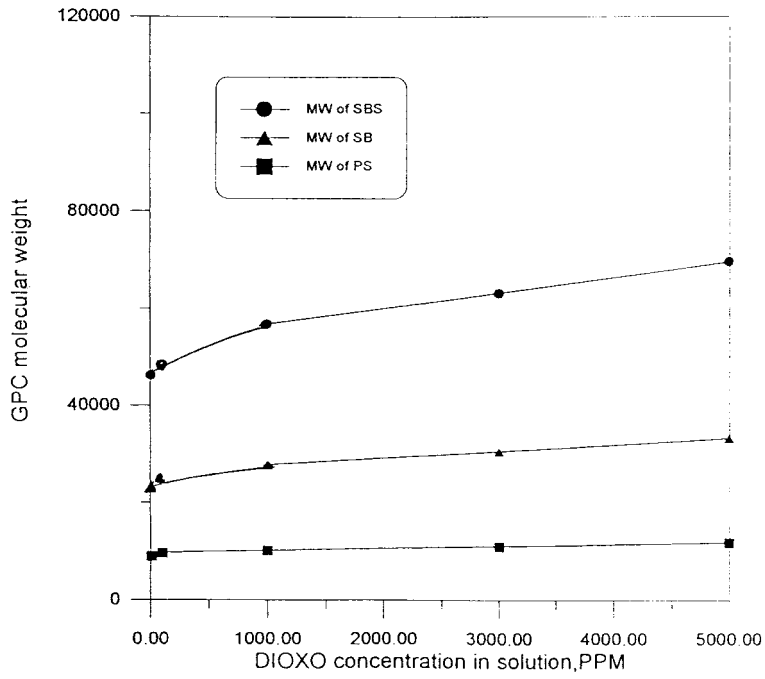


Figure 19 Effect of DIOXO on the molecular weight of SBS copolymer coupled by MBZ.

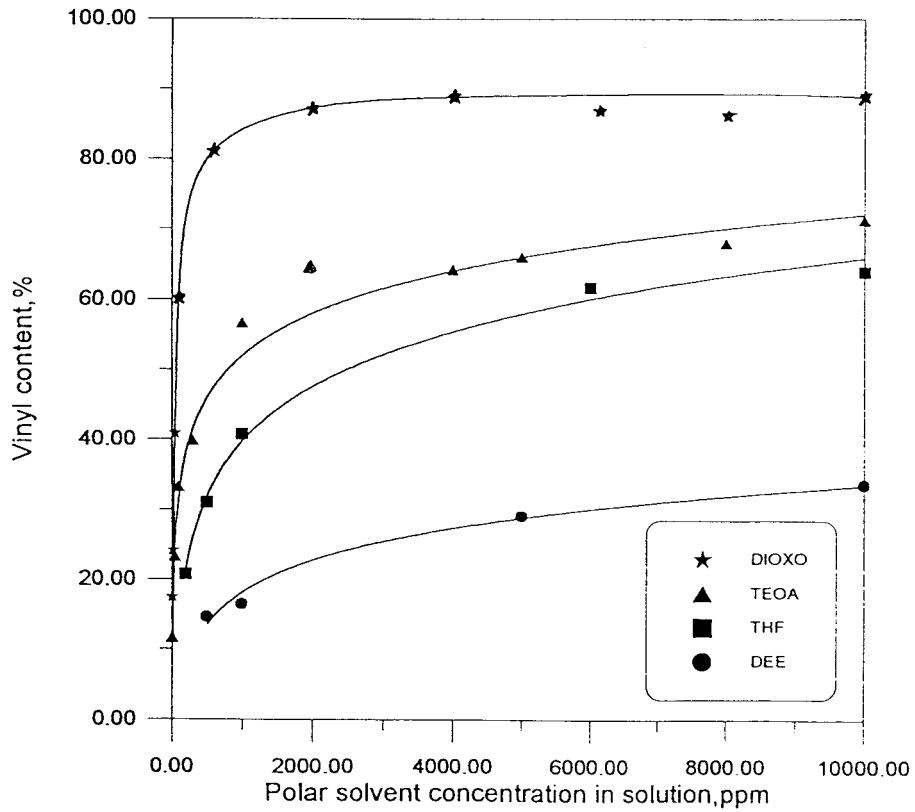


Figure 20 Effect of all ethers on the vinyl content of the polybutadiene segment of the SBS copolymer.

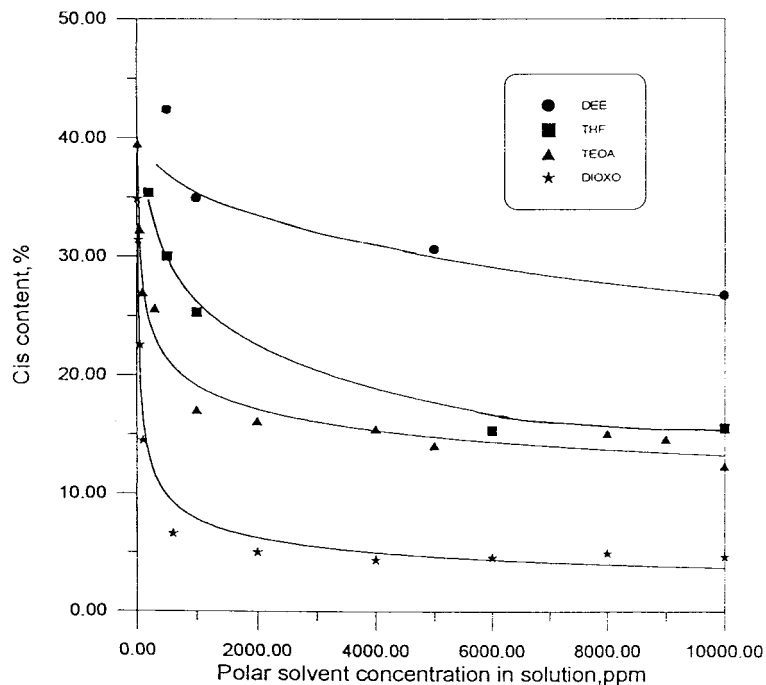


Figure 21 Effect of all ethers on the *cis*-1,4 content of the polybutadiene segment of the SBS copolymer.

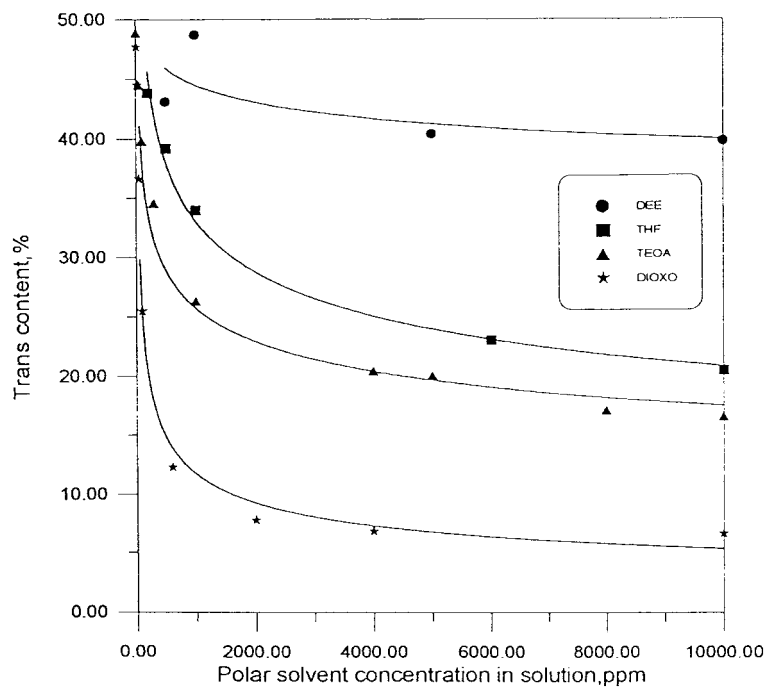


Figure 22 Effect of all ethers on the *trans*-1,4 content of the polybutadiene segment of the SBS copolymer.

Table III Comparison of the Polymerization Rate Constants in the Presence of Various Ethers at 1000 ppm Concentration at 40°C

Solvent	Modifier	Rate Constants (K · 10 ³ , s ⁻¹)	
		Styrene	Butadiene
Cyclohexane	TEOA	26.7	1.0
Cyclohexane	DIOXO	15.5	3.7
Cyclohexane	THF ^a	10.1	0.40
Cyclohexane	DEE ^a	3.0	0.16

^a Data reported in the previous work.^{27,28}

ifiers in regard to the rate of styrene polymerization.

Effect of Heavy Ethers on the Crossover Efficiency in the Sequential Polymerization of SBS

As the SBS copolymer was synthesized by the sequential method, the polystyrene block was made first, followed by the addition of butadiene to the living polystyryllithium chain end making the SB diblock copolymer. The synthesis of the SBS copolymer was finally completed by a further addition of a second charge of styrene, in an equal amount to the first styrene charge, to the living polystyrylbutadienyllithium chain end. However, the addition of styrene to the living polystyrylbutadienyllithium chain end in a nonpolar hydrocarbon solvent was slow compared to the styrene–styrene propagation reaction.³⁹ This low crossover rate could result in a skewed third block molecular weight distribution and a higher polydispersity.^{27,28} However, in our work, this crossover efficiency was enhanced by the heavy ethers added during the polymer synthesis. The ether increased the rate at which styrene adds to the living polystyrylbutadienyllithium chain end relative to the styrene–styrene addition. Such enhancement in the crossover rate can be best shown in the temperature profile of the reaction. As depicted in Figure 11, the amount of polar modifiers had a profound effect on the kickoff of the exotherm arising from the formation of the third polystyrene block. Since the rate of polymerization of styrene is lower at a 10,000 ppm TEOA concentration than at a 1000 ppm concentration as seen from Figure 5, the early kickoff of the exotherm at 10,000 ppm TEOA concentration must be caused by a faster crossover. The nar-

rower molecular weight distributions resulting from the addition of polar ethers are shown in Figure 12. A larger amount of modifiers enhanced the crossover efficiency, leading to a lower polydispersity.

Effect of Heavy Ethers on Coupling Efficiency When SBS Is Made via the Coupling Method

The coupling efficiency for an SBS copolymer made via the coupling method can be determined from the GPC chromatogram (see Fig. 13). The coupling efficiency is defined as the ratio of the SBS peak area to the sum of the SBS and SB diblock peak areas:

Coupling efficiency

$$= \frac{\text{area of SBS peak}}{\text{area of SBS peak} + \text{area of SB peak}}$$

The addition of a heavy ether as a structure modifier adversely affected the coupling efficiency, and the impact is greater on the MBZ coupling process than on the DBE coupling process as illustrated in Figures 14–17. Although polar ethers enhanced the reactivity of the polymeric chain ends, too much of or too strong a polar ether led to an extensive chain end complexation, causing the drop of coupling efficiency. Furthermore, the steric hindrance arising from the increasing vinyl content could also hinder the coupling process. However, the results clearly indicated that adding a catalytic amount of heavy ether (300 ppm TEOA or 50 ppm DIOXO required for the structure modification as mentioned before) had minimal effect on the coupling efficiency.

The complexation of living chain ends with polar ethers can also be elucidated from the increase in the molecular weight of polymers synthesized. Figures 18 and 19 show that the molecular weights of both the intermediate SB diblock polymer and the final coupled SBS polymer increase with an increase in the concentration of polar ethers. Since the ethers were added into the system prior to the synthesis of the first block, the deactivation due to its contained impurities ought to have occurred during the synthesis of the first block and manifested itself by an increasing molecular weight of the first block with an increase in the concentration of ethers, as observed in the bottom curves in Figures 18 and 19. As a result, the increasing molecular weight of the SB diblock

and the final coupled SBS polymers with an increase in the concentration of ethers can no longer be ascribed to the impurities and must have arisen from the complexation of chain ends.

Comparison Between Heavy Ethers and Monoethers

The effectiveness of TEOA and DIOXO as structure modifiers were compared with that of monoethers such as THF and DEE reported previously.^{27,28} The vinyl content of the polybutadiene segment varied with the amount of various modifiers as shown in Figure 20. It clearly indicated that heavy ethers were more effective than were monoethers. As a result, a lesser amount was required of a heavy ether to achieve a targeted vinyl content. Also shown in Figures 21 and 22 are the effects of various ethers on *cis*-1,4 and *trans*-1,4 microstructures, correspondingly. The negative effects on *cis*-1,4 and *trans*-1,4 microstructures are concurrent to the positive effect on the vinyl content.

All ethers studied were also compared for their effects on the polymerization rate. Based on the available kinetic data collected in this work and reported previously,^{27,28} the rate constants are tabulated in Table III. As seen in Table III, the DIOXO enhanced the rate of butadiene polymerization the most, whereas TEOA caused the highest rate of styrene polymerization. Heavy ethers accelerated the rates of polymerization more than did monoethers. Among all the ethers, the effectiveness of DEE remained the lowest for enhancing polymerization rates.

CONCLUSION

Heavy ethers—DIOXO and TEOA—were used as structure modifiers during the synthesis of linear SBS block copolymers. The microstructures of synthesized polymers were analyzed, and the effect of these heavy ethers on polymerization kinetics was studied. For the SBS copolymer synthesized via a sequential method, the addition of a heavy ether as a structure modifier enhanced the crossover efficiency, resulting in a narrower molecular weight distribution with a lower polydispersity. For the SBS copolymer made via a coupling method, the coupling efficiency decreased and varied with the type of the coupling agent used. Compared with previously reported data for

monoethers like THF and DEE, a smaller amount of heavy ether was needed to achieve the same targeted vinyl content (40%). Optimal amounts of heavy ethers were found at 300 and 50 ppm by weight for TEOA and DIOXO, respectively. Among all ethers, DIOXO enhanced the rate of butadiene polymerization the most, whereas TEOA caused the highest rate of styrene polymerization. Heavy ethers accelerated the rates of polymerization more than did monoethers. Nevertheless, the effectiveness of DEE remained the lowest for both polymerization rates.

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REFERENCES

1. M. M. Ward and M. G. Quam, U.S. Pat. 3,700,633 (1972).
2. S. Davison and W. P. Gergen, U.S. Pat. 4,041,103 (1977).
3. Y. Kishimoto and H. Morita, U.S. Pat. 4,501,857 (1985).
4. E. R. Santee, L. O. Malotky, Jr., and M. Morton, *Rubb. Chem. Technol.*, **46**, 1156 (1973).
5. S. Bywater, *Adv. Polym. Sci.*, **4**, 66 (1965).
6. V. Colet-Marti, S. Dumas, J. Sledz, and F. Schue, *Macromolecules*, **15**, 251 (1982).
7. S. Bywater, Y. Firat, and P. Blank, *J. Polym. Sci.*, **22**, 669 (1984).
8. F. W. Stavely, *Ind. Eng. Chem.*, **48**, 778 (1956).
9. A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.*, **40**, 73 (1971).
10. M. Morton and L. J. Fetters, *Rubb. Chem. Technol.*, **48**, 359 (1975).
11. S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1565 (1962).
12. F. Schue, D. J. Worsfold, and S. Bywater, *Macromolecules*, **3**, 509 (1970).
13. D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **42**, 2884 (1964).
14. E. R. Santee, R. Chang, Jr., and M. Morton, *J. Polym. Sci. Polym. Lett.*, **11**, 449 (1973).
15. M. Morton, R. D. Standerson, and R. Sakata, *J. Polym. Sci. Part B*, **9**, 61 (1971).
16. M. Morton, R. D. Standerson, and R. Sakata, *Macromolecules*, **6**, 181 (1973).
17. M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, New York, 1983.
18. R. N. Young, R. P. Quirk, and L. J. Fetters, *Anionic Polymerization, Advances in Polymer Science*, Vol. 56, Springer-Verlag, New York, 1984, p. 1.

19. M. Van Beylen, S. Bywater, G. Smets, M. Szwarc, and D. J. Worsfold, *Advances in Polymer Science*, Springer-Verlag, New York, 1988, Vol. 86, p. 87.
20. G. P. M. van der Velden and L. J. Fetters, *Macromolecules*, **23**, 2470 (1990).
21. C. C. Chang, J. W. Miller, Jr., and G. R. Schorr, *J. Appl. Polym. Sci.*, **39**, 2395 (1990).
22. A. F. Halasa, C. C. Chang, J. W. Miller, Jr., and W. L. Hsu, *Polym. Int.*, **33**, 151 (1994).
23. W. L. Hsu and A. F. Halasa, U.S. Pat. 5,300,599 (1994).
24. L. Bu and S. Ying, *J. Appl. Polym. Sci.*, **44**, 1499 (1992).
25. L. Bu and S. Ying, *J. Appl. Polym. Sci.*, **44**, 1507 (1992).
26. W. L. Hergenrother, J. M. Doshak, D. R. Brumbaugh, T. W. Bethea, and J. Oziomek, *J. Polym. Sci. Part A Polym. Chem.*, **33**, 143 (1995).
27. D. C. Huang and R. C. Tsiang, *J. Polym. Res.*, **2**(2), 91 (1995).
28. D. C. Huang and R. C. Tsiang, *J. Appl. Polym. Sci.*, **61**, 333 (1996).
29. P. Rempp, P. Lutz, and E. Franta, *J. Macro. Sci. Pure Appl. Chem.*, **31**, 891 (1994).
30. V. D. Mochol, *Rubb. Chem. Technol.*, **54**, 685 (1967).
31. F. Conti, M. Delfini, and A. L. Serge, *Polymer (GB)*, **18**, 310 (1977).
32. Y. Tanaka, H. Sato, and K. Miyashita, *Rubb. Chem. Technol.*, **54**, 685 (1981).
33. A. L. Segre, M. Delfini, F. Conti, and A. Boicelli, *Polymer*, **16**, 338 (1975).
34. F. Conti, M. Delfini, and A. L. Segre, *Polymer*, **15**, 539 (1974).
35. D. Werstler, *Rubb. Chem. Technol.*, **53**, 1191 (1980).
36. J. C. Randall, *J. Polym. Sci. Polym. Phys.*, **15**, 1451 (1977).
37. R. Petiaud and H. Waton, *Proton & Carbon NMR Spectron of Polymers*, Quang Tho Pham., CNRS-SERVICE Central d'Analyse-Lyon France & Marie-France Llauro-Durricades CNRS-SERVICE des Materiaux Organiques-Lyon, France, 1991.
38. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 5th ed., Wiley, New York, 1991.
39. M. Morton and F. R. Ells, *J. Polym. Sci.*, **61**, 25 (1962).