Polymerization of Styrene–Butadiene Block Copolymers Using a Dicarbanion Initiator Made by the Reaction of Lithium with α-Methylstyrene

Henry Chi-Chen Hsieh,* H. C. Kao, and D. Otto Cheng

Taiwan Synthetic Rubber Corporation, Ta-she Petrochemical Industrial Park,
Kaohsiung, Taiwan, Republic of China

Raymond Chien-Chao Tsiang and Der-Chi Huang

Department of Chemical Engineering, National Chung Cheng University,
Chiayi, Taiwan, Republic of China

Received October 4, 1994; Revised Manuscript Received March 17, 1995[⊗]

ABSTRACT: Linear styrene–butadiene block copolymers of the polyA-*block*-polyB-*block*-polyA type (SBS) have been synthesized using a dicarbanion initiator formed by the reaction of metal lithium and α-methylstyrene. While being unable to initiate polymerization in cyclohexane and/or *n*-hexane, the diinitiator performed well in benzene. Various promoters such as tetrahydrofuran (THF), tetramethylethylenediamine, and hexamethylphosphoric triamide have been added during the making of diinitiators, resulting in initiators of different functionalities and activities. The presence of THF facilitated the formation of the diinitiator, and the resulting polymers made with this diinitiator have been analyzed and mechanically tested. The effect of process variables on the polymerization kinetics and molecular characteristics was also investigated.

Introduction

Styrene–butadiene block copolymers of the polyA-*block*-polyB-*block*-polyA type (SBS) have been traditionally made via either (1) a sequential method wherein the three blocks are formed sequentially using a monoanionic organolithium compound as the initiator or (2) a linking method wherein diblock precursors are linked by the linking agent, leading to the formation of the final polymer. However, neither of these two methods are suitable for synthesizing triblock copolymers with active functional groups at both chain ends, such as hydroxyl-terminated SBS and carboxyl-terminated SBS. Therefore, various attempts have been made to study the dicarbanion initiators (diinitiators).

Several ways of making diinitiators exist in literature. Bartz et al. formed an alkylene-bridged dihydroanthracene dimer as a diinitiator by a 2-fold deprotonation of 1,3-bis(9,9,10,10-tetrahydro-9,9-anthryl)propane.[1] Ohata et al. synthesized novel telechelic poly(methyl methacrylate) using a diinitiator made by the reaction of sodium naphthalene with 4-[2-(*tert*-butyldimethylsiloxy-)ethyl]-α-methylstyrene.[2] Wang et al. prepared block copolymers of *tert*-butyl methacrylate and ethylene oxide using potassium naphthalene as the diinitiator.[3] Nugay and Kucukyavuz, by reacting *sec*-BuLi with 1,5-diethenylnaphthalene, produced a new diinitiator which was effective in the synthesis of styrene–isoprene–styrene triblock copolymers.[4] Bandermann et al. tested the suitability of a dilithio initiator drived from 1,4-bis[4-(1-phenylvinyl)phenyl]butane for the anionic polymerization of dienes.[5] Warzelhan et al. studied the reaction rate when a dianion of α-methylstyrene was used as the diinitiator.[6,7] Morton and Fetters prepared the dimer of 1,1-diphenylethylene with a fine dispersion of lithium in a hydrocarbon solvent.[8] Journe and Widmaier made a similar dilithio initiator by lithiation of 1,1-diphenylethylene and described the mechanism as solvation of the active centers by diphenylethylene.[9] Levin et al. observed that it was easier to form diinitiators using naphthalene than anthracene and tetracene;[10] Jachimowicz et al. found that the smaller the atomic radius of the alkali metal was, the more difficult it was to form the diinitiators; the diinitiators were also found to form easier in diethyl ether or THF than dimethyl ether solvent.[11] Szwarc et al. also pointed out that the dicarbanion initiator was formed rapidly from a coupling of the styrene anions during the polymerization of styrene by sodium naphthalene.[12,13] Jachimowicz et al. found that phenyl-substituted vinylic species were capable of forming diinitiators.[14,15] Setzkorn et al.,[16] by reacting lithium or sodium dispersions with α-methylstyrene in toluene in the presence of methoxybenzene, synthesized an oligomer which was itself an initiator, but difunctionality was not demonstrated. Szwarc demonstrated that the diinitiators were readily made by reacting alkali metals with α-substituted vinyl monomers such as α-methylstyrene and 1,1-diphenylethylene.[17] Lutz et al.[18,19] and Foss et al.[20] studied the butyllithium diadduct of diisopropenylbenzene as a possible dicarbanion initiator soluble in nonpolar solvents. Sigwalt and Favier et al. employed the adducts of butyllithium onto α,ω-bis(isopropenylphenyl)alkanes as the diinitiators.[21–23] These initiators tend to associate, and a small amount of species of higher functionality exists in the system. Yamashita et al. made α,ω-difunctional polystyrene using a diinitiator formed by reacting sodium and α-methylstyrene.[24,25] Finaz et al.[26] and Berger et al.[27] also used sodium and α-methylstyrene to make a polystyrene containing α,ω-diacid chloride functional groups. Kamienski et al.[28] and Cameron et al.[29] discussed the difunctional lithium initiators made by reaction of *sec*-butyllithium or *n*-butyllithium with *m*-diisopropenylbenzene.

Considering factors such as stability, ease of making, and the commercial availability of constituting raw materials, we have been concentrating our study effort on a diinitiator made from metal lithium and α-methylstyrene. To better understand the effect of process

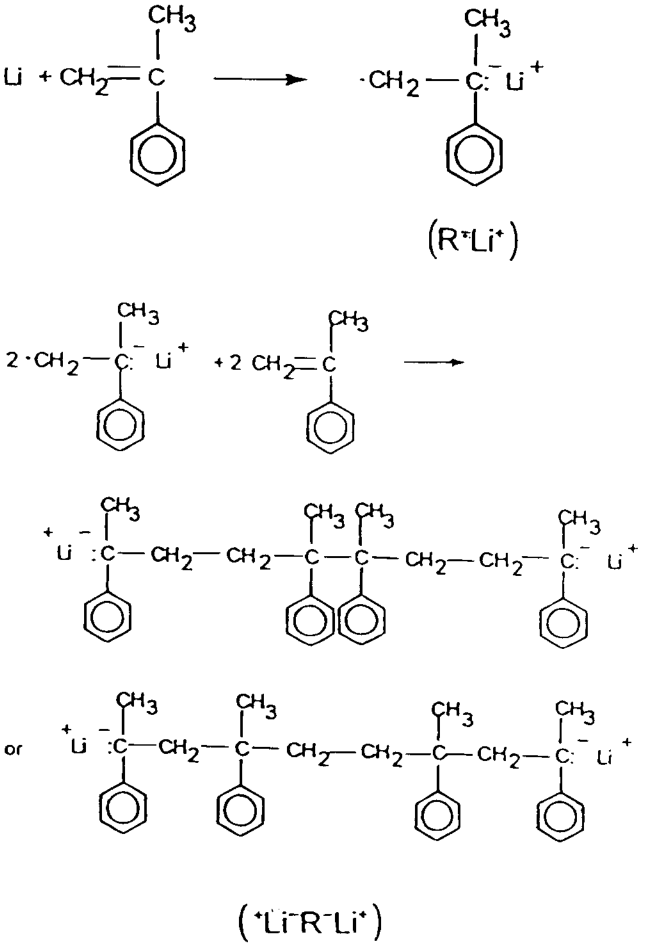
[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

variables on the making of such a diinitiator, this work is used first to make the diinitiator under various conditions and then to evaluate this diinitiator by using it to synthesize SBS linear block copolymers. The preparative method and the observed phenomena are discussed along with the evaluation results.

Experimental Section

(1) Materials. Butadiene and styrene used in this work were obtained from Taiwan Synthetic Rubber Corp. (TSRC) and had been pretreated with activated alumina (from Alcoa Co.). Benzene was also obtained from TSRC. α-Methylstyrene was obtained from Grand Pacific Co. and pretreated with activated alumina. Reagent-grade toluene and THF were purchased from Merck and pretreated with activated alumina. Both lithium ingots and 20% lithium powder dissolved in mineral oil were purchased from Lithco Co. Tetramethylethylenediamine (TMEDA) and hexamethylphosphoric triamide (HMPA) were purchased from Merck.

(2) Preparation of the Diinitiator. The dicarbanion initiator used for the polymer synthesis in this work was prepared by reacting lithium ingot or dissolved lithium powder with α-methylstyrene in benzene or toluene solvent. The experiments were conducted in an air-free environment such as a nitrogen bag. Lithium ingot, as used, would be floating; lithium powder, as used, would turn the solution into an opaque dark gray color. α-Methylstyrene was not reactive prior to the addition of THF, and the solution could be stored in a refrigerator for later use. When ready for making the diinitiator, the required amount of THF had to be added to stabilize the radical anion. The solution would turn red after shaking, indicating the formation of the diinitiator. The mechanism of the formation of the diinitiator is proposed as follows, similar to that proposed by Richard for Na:[30]



$(R^{\cdot -}Li^+)$

$(^+Li^-R^-Li^+)$

where $R^{\cdot -}$ was an aromatic radical anion formed by the transfer of an electron from the lithium metal to α-methylstyrene.

(3) Analysis of the Diinitiator. The diinitiator was analyzed using a Finnigan MAT GC/MS equipped with an ITD detector. This instrument has a DB-5 J&W capillary column of 30 m length and 0.25 mm diameter. The injection temperature was 280 °C. After being kept at 40 °C for 2 min, the column was heated at a rate of 6 °C/min to 285 °C and maintained at that temperature for another 30 min.

(4) SBS Synthesis Using the Diinitiator. In our polymerization experiments, appropriate amounts of benzene, THF, and butadiene were put into a 1-L pressure vessel. The vessel content was heated to 50 °C prior to the addition of the required weight of the diinitiator. Anionic propagation occurred at both anion ends of the diinitiator. Two to five minutes after the vessel temperature reached the maximum, the styrene monomer was charged into the vessel. The overall polymer synthesis reaction was as follows:

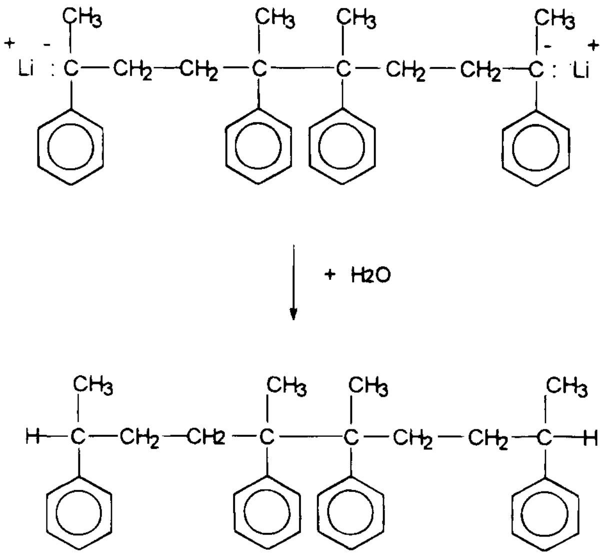
$$^+Li^-R^-Li^+ \xrightarrow{\text{butadiene}} {}^+Li^-bbRbb^-Li^+ \xrightarrow{\text{styrene}} {}^+Li^-sssbbRbbsss^-Li^+ \quad \text{(SBS)}$$

At the completion of the polymerization, the antioxidant was added and the polymer precipitated in methanol. The dried polymer was later analyzed for its molecular weight and tested for its mechanical properties.

(5) Analysis of Synthesized Polymer. The molecular weights and molecular weight distributions of synthesized polymers were determined by Waters gel permeation chromatography (GPC) equipped with Waters M-486 adsorbance (UV) and Waters 410 differential refractive index (RI) detectors. The GPC was operated using three Waters Ultrastyragel 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% in THF solvent. The refractive index of the synthesized polymer was measured using the Milton Roy refractometer. The microstructure was determined by the Schimadzu FTIR-8101M spectrometer using calibration samples of known microstructures as external standards.

Results and Discussion

In our experimental runs 1 and 2, lithium powder dissolved in mineral oil was used to react with α-methylstyrene in toluene with the presence of THF (amounts to 10% of toluene) at a lithium concentration of 2.35% by weight. The formation of the diinitiator was corroborated from GC/MS analysis of its hydrocarbon derivative after water termination:



(M.W. = 474)

Figure 1 shows the GC trace of this diadduct occurring in between 4200 and 4500 s. The three peaks located

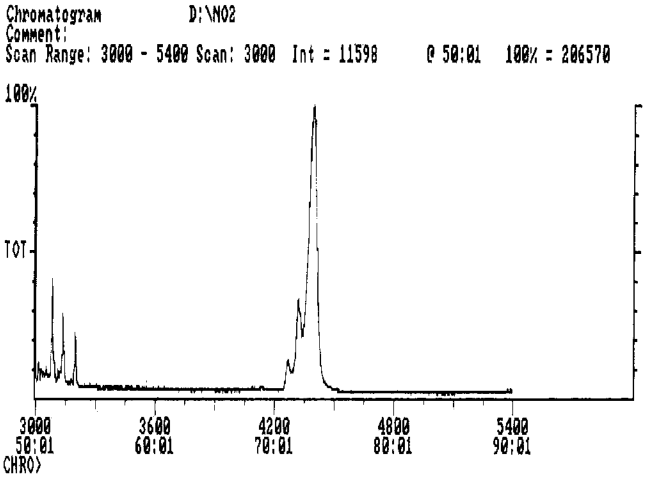


Figure 1. GC chromatogram of the diadduct.

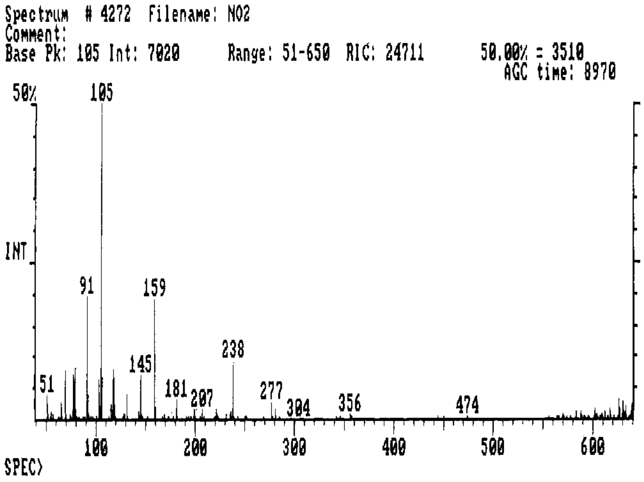


Figure 2. MS spectrum of the GC peak at 4272 s.

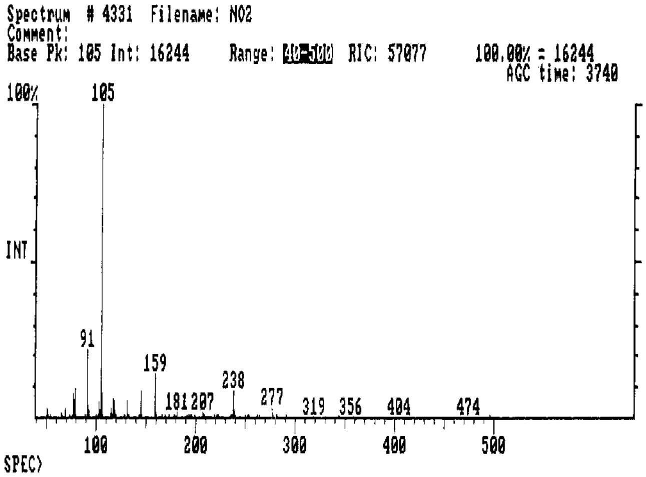


Figure 3. MS spectrum of the GC peak at 4331 s.

at 4272, 4331, and 4390 s pertain to three different isomers of the diadduct as corroborated by the corresponding MS spectra shown in Figures 2–4. These figures have verified that all three peaks are the diadduct having a parent ion of *m/e* 474. Other species shown at low *m/e* are the fragment ion of the parent ion. Thus, it was concluded that diinitiator, $^{+}Li^{-}R^{-}Li^{+}$, was the major species in our preparation of initiators.

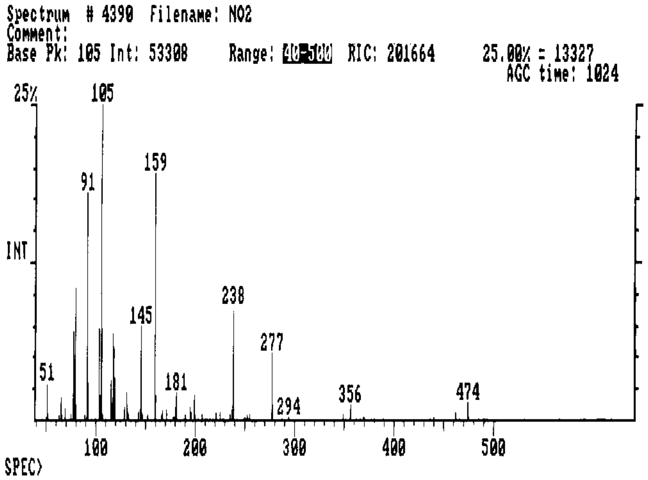


Figure 4. MS spectrum of the GC peak at 4390 s.

Table 1. Polymer Synthesis in Different Solvent Systems Using Diinitiator Formed by Reacting Lithium Powder with α-Methylstyrene

	run 1	run 2
solvent type	cyclohexane/*n*-hexane	benzene
solvent wt (g)	500	500
additional THF (phm)	0.84	0.83
diinitiator (g)	6.16	6.18
butadiene (g)	70	70
styrene (g)	30	30
starting temp (°C)	51	51
refractive index		1.5357
max temp (°C)		78.2
polymer	none	SBS
beginning styryllithium color	none	dark red
ending styryllithium color	none	yellow

Table 2. Polymer Synthesis Using Diinitiator of Various Amounts

	run 3	run 4	run 5
solvent type	benzene	benzene	benzene
solvent wt (g)	500	500	500
additional THF (phm)	0.875	0.875	0.875
diinitiator (g)	9.96	8.45	6.61
butadiene (g)	56	56	56
styrene (g)	24	24	24
starting temp (°C)	52.3	51.7	51.6
refractive index	1.5391	1.5377	1.5365
polymer	SBS	SBS	SBS
M_n	5.0×10^4	9.8×10^4	14.9×10^4
M_w	6.1×10^4	13.6×10^4	24.1×10^4
polydispersity	1.22	1.38	1.61

The readily formed diinitiator was then used to synthesize SBS linear triblock copolymers (with a 30:70 styrene/butadiene ratio) in two different solvent systems as shown in Table 1. It was found that the diinitiator tended to associate and form light gels during the storage. This gelling phenomenon disappeared when the diinitiator was injected into benzene, but the inhomogeneity remained if injected into a cyclohexane/*n*-hexane mixed solvent. This is because the aromatic solvent stabilizes the α-methylstyrene-based diinitiators better than the aliphatic solvent. As a result, the polymerization reaction proceeded well in benzene solution but not in the cyclohexane/*n*-hexane mixed solvent system. However, the dark red color, characteristic of living styryllithium chain ends, gradually faded away after the styrene polymerization reached the maximum temperature 78 °C, and a yellow color was observed. This clearly indicates a thermal deactivation of the dicarbanion styryllithium chain ends, and 78 °C is too high to maintain the livingness under our experimental conditions. A typical GPC trace of the synthesized

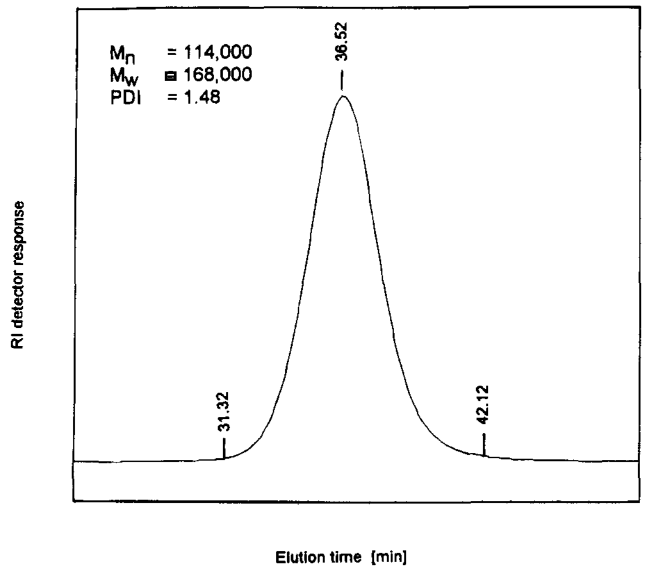


Figure 5. Typical GPC trace of the synthesized polymer.

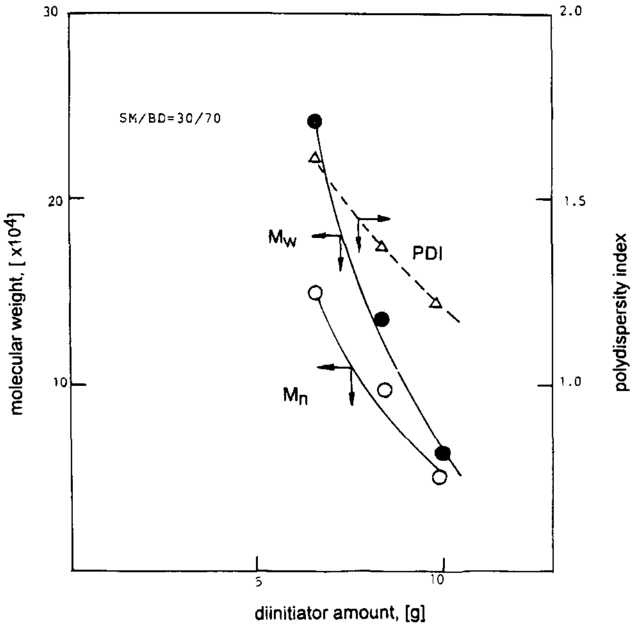


Figure 6. Effect of the amount of diinitiator on molecular weights and MWD of the synthesized polymer.

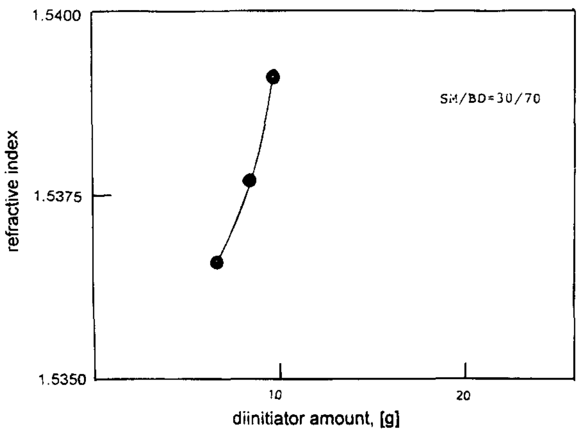


Figure 7. Effect of the amount of diinitiator on RI of the synthesized polymer.

polymer in Figure 5 shows that the diinitiator produces a low polydispersity polymer. While it is not unusual for a diinitiator system to give rise to a low polydispersity polymer,[18,29] the fact that our diinitiator is unable to produce a molecular weight distribution quite as narrow as does the conventional initiator like *n*-BuLi or *sec*-BuLi suggests the likely existence of a small amount of monoinitiator.

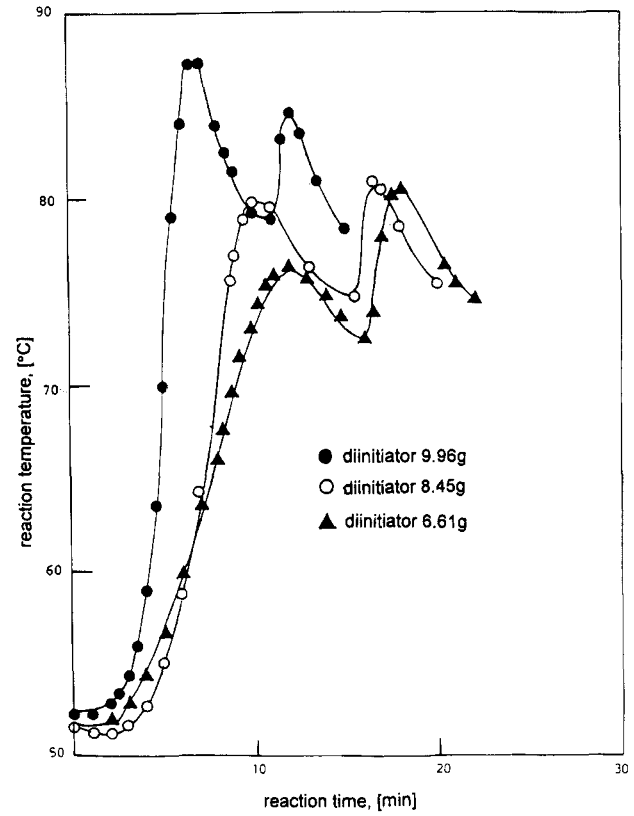


Figure 8. Effect of the amount of diinitiator on SBS polymerization kinetics.

Table 3. Polymer Synthesis Using Initiators Made with Different Polar Species

	run 6	run 7
Forming Initiators		
polar species used	TMEDA	HMPA
Synthesizing Polymers		
solvent type	benzene	benzene
solvent wt (g)	500	500
additional THF (phm)	0.875	0.875
diinitiator (g)	8.67	8.76
butadiene (g)	56	56
styrene (g)	24	24
starting temp (°C)	52	50
refractive index	1.5348	
polymer	SB	none
beginning styryllithium color	dark red	none
ending styryllithium color	red	none

Synthesis runs 3–5 were conducted using the same diinitiator solution as run 2. The process conditions and the analyses of the synthesized polymers are shown in Table 2 and Figures 6 and 7. The molecular weight of the resulting polymer increases with a decrease in the amount of diinitiator, as is typical of the anionic polymerization. However, contrary to the Poisson distribution for living polymerization, the polydispersity ranging from 1.22 to 1.61 increases with the molecular weight. The increase in polydispersity with the molecular weight is probably due to the deactivation of the dicarbanion styryllithium caused by the increasing viscosity. Aside from the above, the refractive index is lower with a decrease in the amount of diinitiator, indicating that the higher viscosity makes it difficult

Table 4. Polymer Synthesis with Additional THF of Various Amounts

	run 8	run 9	run 10	run 11	run 12
solvent type	benzene	benzene	benzene	benzene	benzene
solvent wt (g)	500	500	500	500	500
additional THF (phm)	0	0.438	0.875	2.175	6.52
diinitiator (g)	11.66	11.66	11.66	11.66	11.66
butadiene (g)	56	56	56	56	56
styrene (g)	24	24	24	24	24
starting temp (°C)	50.3	51.8	51.4	51.7	50.7
refractive index	1.5392	1.5386	1.5381	1.5376	1.5366
polymer	SBS	SBS	SBS	SBS	SBS
M_n	13.9×10^4	9.9×10^4	9.2×10^4	8.9×10^4	7.7×10^4
M_w	20.9×10^4	16.4×10^4	14.2×10^4	13.2×10^4	11.7×10^4
polydispersity	1.50	1.66	1.53	1.48	1.52
vinyl (%)	22.5	25.1	29.2	32.2	39.8

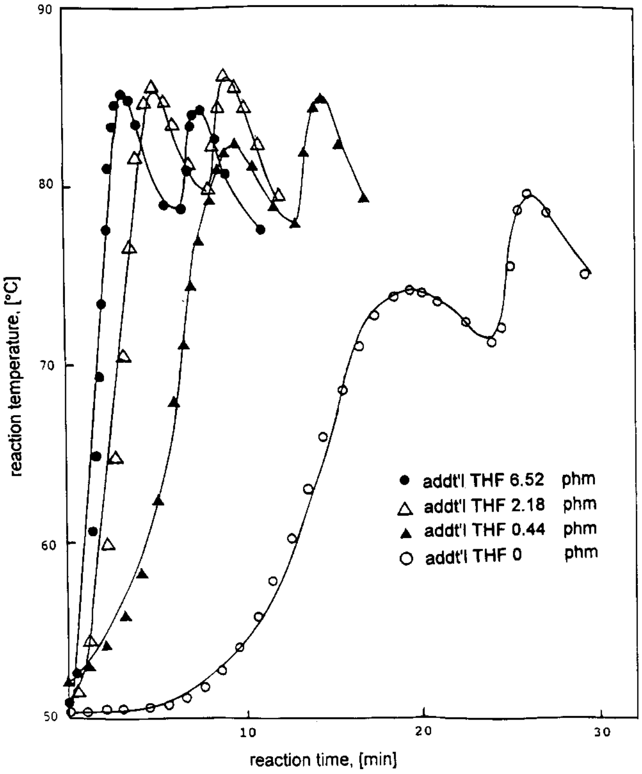


Figure 9. Effect of additional THF on SBS polymerization kinetics.

to extend the polymer chain with styrene monomer. The exotherms of the polymer synthesis are shown in Figure 8. For each set of reactions the first exotherm arises from the highly exothermic butadiene polymerization and the second exotherm is due to the polymerization of styrene charged 2–5 min after the first exotherm. The 2–5 min delay would ensure the completion of the butadiene polymerization. Utilizing more diinitiator has resulted in a faster kinetics and a higher peak temperature.

In runs 6 and 7, other polar species such as tetramethylethylenediamine (TMEDA) and hexamethylphosphoric triamide (HMPA) have been substituted for THF during the making of dicarbanion initiators. The effectiveness of these initiators in synthesizing SBS block copolymers is shown in Table 3. As THF was replaced by TMEDA, lithium ingot reacted with α-methylstyrene to form only a monofunctional initiator since the succeeding polymer synthesis has resulted in a diblock SB copolymer rather than the desired triblock SBS copolymer. This could be easily judged based on the mechanical strength of the synthesized polymer. The replacement of THF by HMPA has resulted in an initiator of a concentration too low (if it exists) to initiate any polymerization, as evidenced by the lack of styryllithium color. Either the monofunctionality or the zero reactivity could be caused by the extensive complexation of TMEDA or HMPA with diinitiators. In the absence of conclusive data, however, this argument must remain speculative.

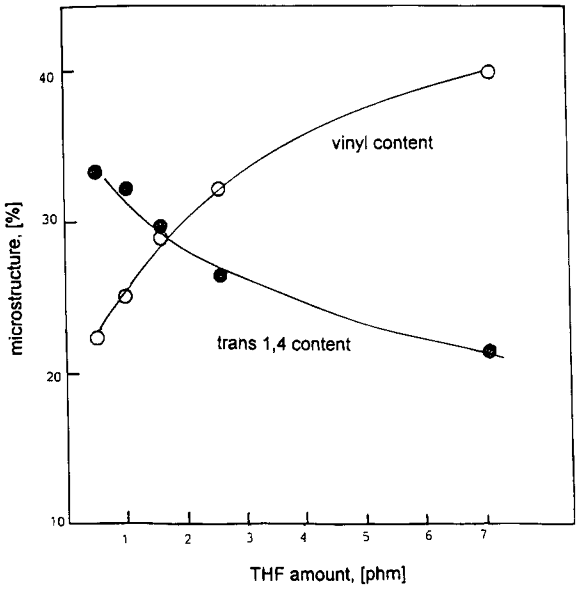


Figure 10. Effect of the total THF on the microstructure of the synthesized polymer using the diinitiator.

Although the THF carried into the polymerization by the diinitiator solution amounts to ~0.4 phm, additional THF was charged in runs 8–12 in order to study its effectiveness as a reaction promoter in breaking the chain end association (Table 4). Figure 9 indicates that polymerization rate increases with the amount of THF. Since THF also functions as a structure modifier for the diene polymer during the polymerization, an increase in THF would lead to an increase in the 1,2 addition of butadiene against the typical 1,4 addition as shown in Figure 10. This increased 1,2 addition also resulted in a smaller refractive index as shown in Figure 11. In addition, being a polar ether, THF will break the association of dicarbanion initiators (or living chain ends) and increase the effective initiator concentration. Thus higher THF content has led to a decrease in the molecular weight of polymers as shown in Figure 12. However, the polydispersity appears to be independent of the THF content.

The dicarbanion initiator has also been used to synthesize SBS triblock copolymers of varying styrene/butadiene compositions. It is shown in Figure 13 that higher butadiene content favors the first stage kinetics while higher styrene content accelerates the second

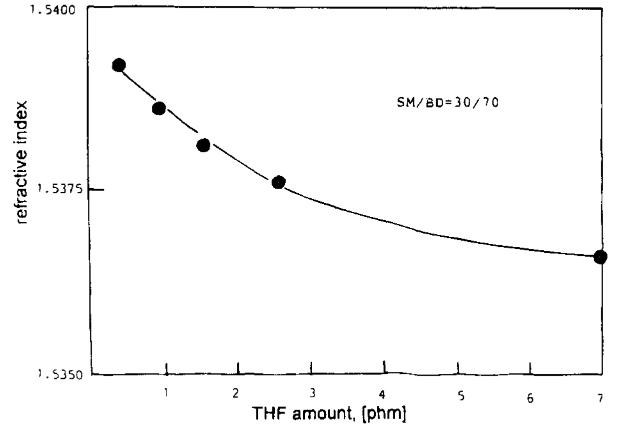


Figure 11. Effect of the total THF on RI of the synthesized polymer.

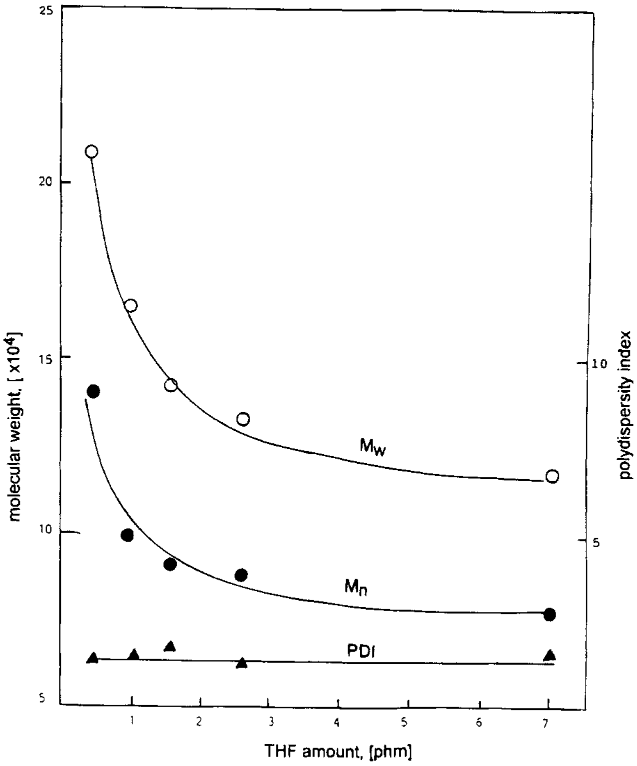


Figure 12. Effect of the total THF on molecular weights and MWD of the synthesized SBS polymer using the diinitiator.

stage kinetics. At constant total amount of monomers, a higher butadiene/styrene ratio would result in a higher maximum temperature due to the larger exothermic reaction heat of butadiene than styrene. The tensile testing results of the synthesized polymers are shown in Figure 14. Polymer with a higher styrene/butadiene ratio gives a higher tensile strength, a higher modulus at 300% elongation, and a lower elongation. These property characteristics are consistent with the SBS polymers made from monofunctional initiators.

Several SBS polymers having fixed composition (either a 40/60 or 30/70 styrene/butadiene ratio) but varying molecular weight have been synthesized and tested for mechanical properties. The results in Figures 15 and 16 clearly indicate that (1) at a 40/60 styrene/butadiene ratio and a M_w of 100 000–300 000, the tensile strength and modulus at 300% elongation are independent of the molecular weight of the polymer and (2) at a 30/70 styrene/butadiene ratio and a M_w of 50 000–250 000, the tensile strength increases with an increase in M_w. The modulus at 300% elongation remains constant except at the lower end where the modulus appears to drop with a decrease in the molecular weight.

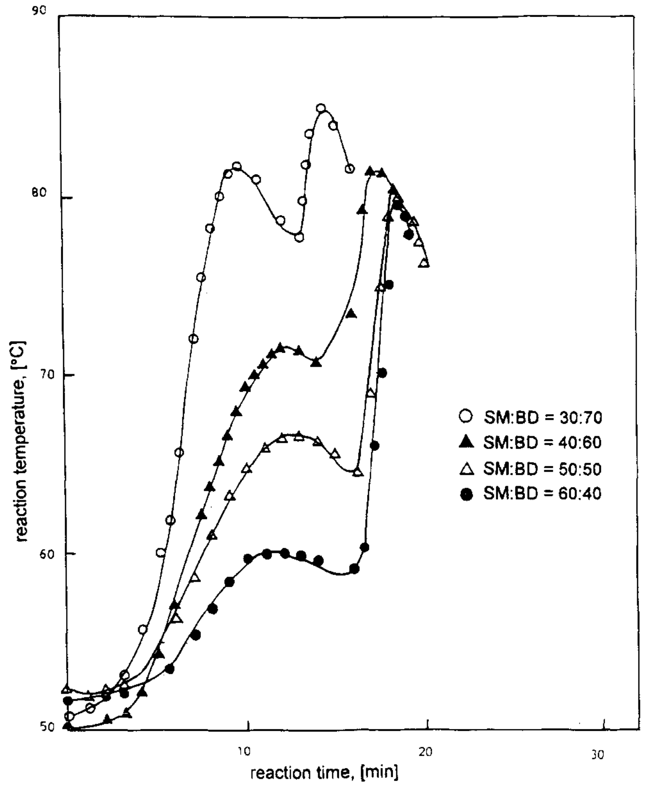


Figure 13. Effect of the styrene/butadiene ratio on SBS polymerization using the diinitiator.

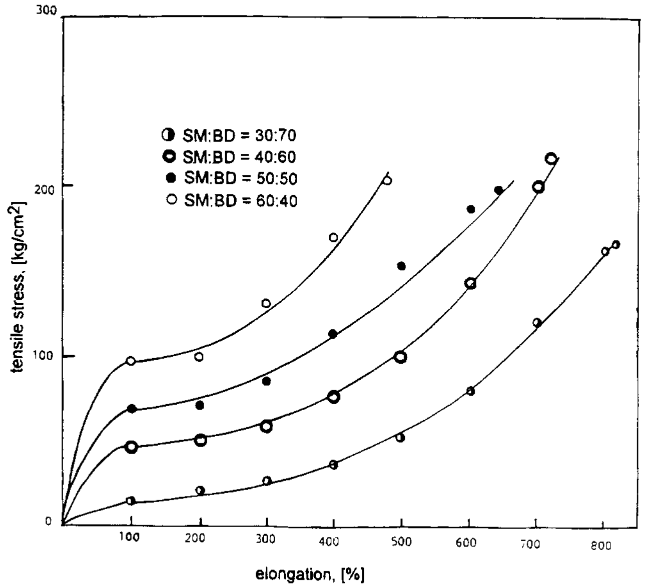


Figure 14. Effect of the SM/BD ratio on the mechanical properties of synthesized SBS polymer using the diinitiator.

In spite of a recent effort in the field of anionic living polymerization to develop difunctional organolithium initiators soluble in aliphatic hydrocarbons, our study results show that aliphatic hydrocarbons such as cyclohexane can not stabilize our diinitiator and keep it from associating (gelling) even in the presence of THF.

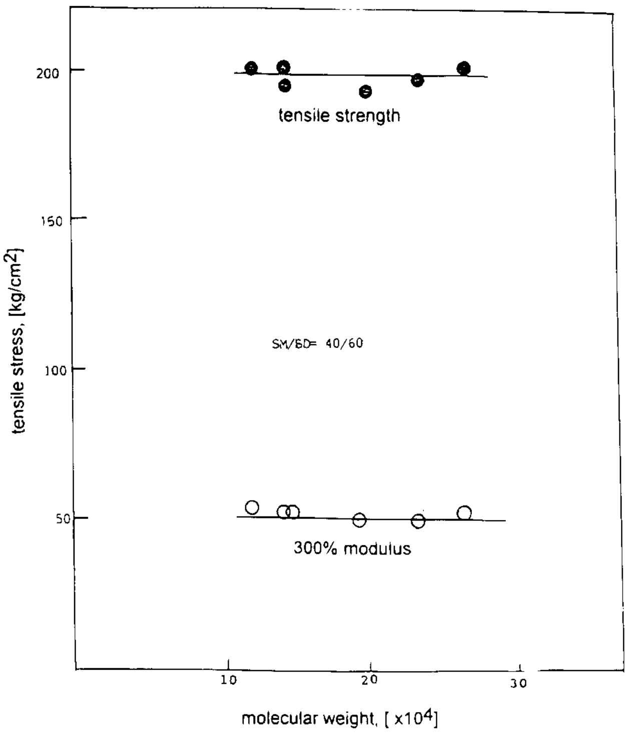


Figure 15. Effect of M_w on the mechanical properties of synthesized SBS polymer (for SM:BD = 40:60) using the diinitiator.

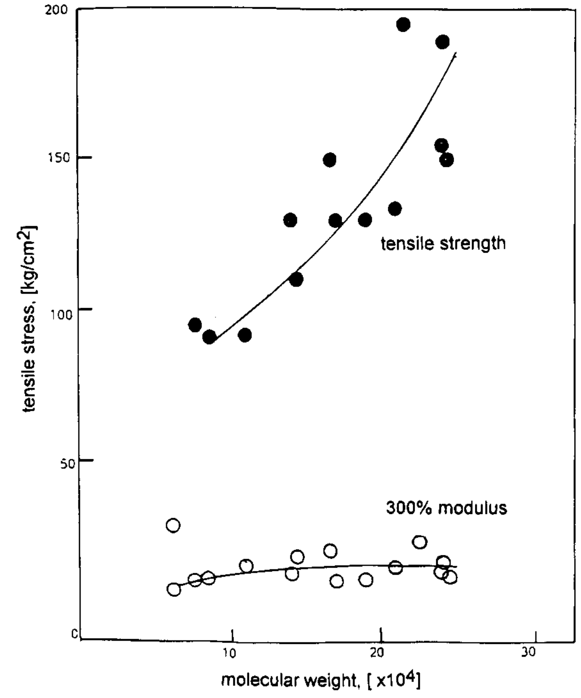


Figure 16. Effect of M_w on the mechanical properties of synthesized SBS polymer (for SM:BD = 30:70) using the diinitiator.

Nevertheless, our diinitiator, made from the reaction of lithium with α-methylstyrene, is easy to prepare and polymerizes well in benzene due to its aromatic nature from α-methylstyrene. The polymer synthesized by this diinitiator has a MWD wth 1.2–1.6 polydispersity which is broader than that by conventional monoinitiators such as *n*-BuLi or *sec*-BuLi. Albeit this, the diinitiator has allowed us to have successfully synthesized SBS copolymers of molecular weights up to 300 000. On the other hand, the presence of THF required for the polymer synthesis inevitably leads to a high vinyl (1,2-butadiene) content in the product polymer. The vinyl content of the polymer synthesized in this work varies from 22.5% to 39.8% depending upon the amount of THF used. Since the vinyl content in commercial styrenic block copolymers ranges from 10% for SBS rubbers up to 40% for hydrogenated SEBS rubbers, the properties of our synthesized polymer would resemble those of the two polymers without losing any desirable elastomeric features.

Conclusion

A linear styrene–butadiene block copolymer of polyA-*block*-polyB-*block*-polyA type (SBS) has been synthesized using a dicarbanion initiator formed by the reaction of metal lithium and α-methylstyrene. While being unable to initiate polymerization in cyclohexane and/or *n*-hexane, the diinitiator performed well in benzene. The dicarbanion initiators are susceptible to thermal deactivation at elevated temperatures. Promoters, such as TMEDA and HMPA, if substituted for THF during the making of initiators, would result in monofunctional and inactive initiators, respectively. The presence of THF would facilitate the formation of dicarbanion initiator, break its association, and increase its effective concentration. Higher THF content led to a decrease in the molecular weight of the polymer, while the polydispersity was unaffected. Higher THF content also resulted in an increase in the 1,2 addition of butadiene. Based on a mechanical testing for synthesized polymers of molecular weights ranging from 100 000 to 300 000, the importance of molecular weight to the tensile properties diminishes as the polystyrene content of the polymer increases.

References and Notes

(1) Bartz, Th.; Klapper, M.; Muellen, K. *Acta Polym.* **1994**, *45*, 248.
(2) Ohata, M.; Ikeda, S.; Akatani, S.; Isono, Y. *Macromolecules* **1993**, *26*, 5539.
(3) Wang, J.; Varshney, S. K.; Jerome, R.; Teyssie, Ph. *J. Polym. Sci., Part A: Polym Chem.* **1992**, *30*, 2251.
(4) Nugay, T.; Kucukyavuz, S. *Polym. Int.* **1992**, *29*, 195.
(5) Bandermann, F.; Speikamp, H. D.; Weigel, L. *Makromol. Chem.* **1985**, *186*, 2017.
(6) Warzelhan, V.; Hoecker, H.; Schulz, G. V. *Makromol. Chem.* **1980**, *181*, 149.
(7) Warzelhan, V.; Schulz, G. V. *Makromol. Chem.* **1976**, *177*, 2185.
(8) Morton, M.; Fetters, L. J.; Inomata, J.; Rubio, D. C.; Young, R. N. *Rubber Chem. Technol.* **1976**, *49*, 303.
(9) Journe, J.; Widmaier, J. M. *Eur. Polym. J.* **1977**, *13*, 379.
(10) Levin, G.; Holloway, B. E.; Szwarc, M. *J. Am. Chem. Soc.* **1976**, *98*, 5706.
(11) Jachimowicz, F.; Wang, H. C.; Levin, G.; Szwarc, M. *J. Phys. Chem.* **1978**, *82*, 137.
(12) Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.
(13) Szwarc, M. *Nature* **1956**, *178*, 1168.
(14) Jachimowicz, F.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1977**, *99*, 5977.
(15) Jachimowicz, F.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1978**, *100*, 5426.
(16) Setzkorn, G.; Heldt, R.; Gehrke, K. F. *Wiss. Z. Tech. Hochsch. "Carl Schorlemmer" Leuna-Merseburg* **1977**, *19*, 589 (also in *Chem. Abstr.* **1978**, *88*, 153097d).
(17) Szwarc, M. *Carbanions, Living Polymers, Electron Transfer Processes*; Wiley: New York, 1968.
(18) Lutz, P; Beinert, G.; Franta, E.; Rempp, P. *Macromol. Chem.* **1978**, *179*, 551.
(19) Lutz, P.; Beinert, G.; Franta, E.; Rempp, P. *Polymer* **1982**, *23*, 1953.
(20) Foss, R. P.; Jacobson, H. W.; Sharkey, W. H. *Macromolecules* **1977**, *10*, 287.
(21) Sigwalt, P.; Favier, J. C.; et al. *Polymer* **1981**, *22*, 1724.

(22) Sigwalt, P.; Favier, J. C.; et al. *Polymer* **1982**, *23*, 73.
(23) El Madani, A.; Favier, J. C.; Hemery, P.; Sigwalt, P. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 329.
(24) Yamashita, Y.; Hane, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 425.
(25) Yamashita, Y.; Nakamura, Y.; Kojima, S. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 823.
(26) Finaz, G.; Gallot, Y.; Parrod, J.; Rempp, P. *J. Polym. Sci.* **1962**, *58*, 1363.
(27) Berger, M. N.; Boulton, J. J. K.; Brooks, B. W. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 1339.
(28) Kamienski, C. W.; Morrison, R. C.; Rathman, T. L. *Lithium: Current Applications in Science, Medicine, and Technology*; John Wiley & Sons, Inc.: New York, 1985.
(29) Cameron, G. G.; Buchan, G. M. *Polymer* **1979**, *20*, 1129.
(30) Richard, D. H. *Polymer* **1978**, *19*, 109.

MA946222X