Attempted Synthesis of Multiblock Copolymers of Butadiene, Styrene, and α-Methylstyrene: Effect of Polar Additives on Copolymerizations

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SYNOPSIS

Owing to the low T_g of polystyrene, the mechanical properties of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) thermoplastic elastomers drop steeply above 60°C. To overcome this behavior, many research groups have considered the replacement of styrene (S) by α-methylstyrene (MS). We also attempted the synthesis of copolymers with a central polybutadiene (poly B) block and rigid blocks consisting of polystyrene (poly S) and poly(α-methylstyrene) (poly MS) blocks. Starting from a dilithium initiator, difunctional poly B's with low 1,2 content (10%) were prepared and toluene was added. After addition of a small amount of styrene, MS was added in the presence of a 15% (in vol) of THF at $T \leq -40$°C. The copolymers did not have the expected structure and poor mechanical properties resulted, which were, however, still measurable at 120°C. These results probably resulted from secondary reactions involving the MS carbanions. To identify these reactions and to control the polymer structure, the synthesis of multiblock copolymers was carried out with a monofunctional polybutadienyllithium to which were added successively S and MS (in a mixture of hexane and benzene as solvent). MS was added at low temperature in the presence of small amounts of THF or at room temperature after addition of TMEDA. These attempts were unsuccessful, the copolymer being always multimodal as a result of unwanted coupling reactions involving terminal double bonds. The synthesis of elastomers using a coupling reaction of poly MS–poly S–poly B was also considered but the yield in poly B was low since termination reactions involving the polar additive occurred.

INTRODUCTION

Mechanical properties of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) are known to be good at room temperature but are markedly affected by higher temperature, i.e., they drop steeply above 60°C. This phenomenom is directly linked to the glass transition temperature (T_g) of polystyrene. It is of interest to overcome this behavior by using glassy blocks with higher T_g. A good candidate is poly(α-methylstyrene) with a T_g around 170°C.

However, polymerization of α-methylstyrene (MS) presents several difficulties: first of all, the low ceiling temperature of the monomer. Consequently, temperatures much lower than room temperature have to be used unless polymerization is carried out in bulk. In hydrocarbon solvents, the rate of polymerization is very small. To accelerate the propagation, polar additives in substantial amounts or a large excess of monomer are required. Moreover, transfer or termination have been found to occur either in bulk or in solution.

In spite of all these difficulties, the synthesis of thermoplastic elastomers containing MS has been studied in many laboratories, either academic or industrial, as described later. We examined here only copolymers involving butadiene since we had prepared previously, using bifunctional organolithium

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Journal of Applied Polymer Science, Vol. 54, 1439–1447 (1994)
CCC 0021-8995/94/101439-09

initiators, SBS elastomers of a well-defined structure having, at room temperature, mechanical properties similar to those of a Kraton 1101 but a better heat resistance and a smaller permanent set.[1] This should permit elements of comparison.

Triblocks of the SBS type (and similar terpolymers) described in the literature have been prepared by three methods: a coupling reaction of diblocks, successive monomer additions, or polymerization of the monomers of the rigid blocks on a central bifunctional polybutadiene (poly B) (or polyisoprene).

The process involving a coupling reaction was described in several patents,[2-5] but the synthesis of the rigid block containing MS requires the addition of polar additives such as tetrahydrofuran (THF) or dimethoxyethane (DME) in amounts up to 15% in volume,[3] which should give a high content of the 1,2 structure for the poly B block. Gandini et al.[6] prepared the MS block in bulk at room temperature and then added a small amount of B. Thereafter, the mixture was diluted by cyclohexane, then B was added, and its polymerization was carried out. The coupling reaction was made at 95°C using diphenyldichlorosilane in the presence of THF. Lo and Tung also used a very similar procedure.[7] The end block [poly(S-*stat*-MS) copolymer] was first prepared in MS with *sec*-butyllithium as the initiator at 50°C, giving a tapered copolymer. Then, a small amount of B was added at this temperature. The remaining B was introduced after cooling at 5°C and the polymerization was then carried out at 50°C before addition of the coupling agent.

The second method corresponds to the successive formation of the rigid and elastomeric blocks by propagation on an organolithium, the first and third block being a poly MS (or its copolymer with styrene [S]) and the second block poly B.[2,8-11] A polar additive was generally necessary for the formation of the first block, which led to a high 1,2 content of the poly B units. The polymerization of the first poly MS block was also made in the absence of a polar reagent, and the mixture of B and S was added, giving a final rigid block rich in S.[10] The tensile strength at room temperature was similar to that of a SBS copolymer, but was better at 50 and 80°C.

The third method, involving a difunctional initiator, should be well suited to this type of synthesis since the poly B block can be obtained in the absence of polar additives and, as a consequence, has a low content of 1,2 structure. This method has been proposed, for instance, by the Polymer Corp.[2] using dilithium–diisoprene (?) as the initiator in mixtures of hexane and benzene or in pure benzene, followed by a sequential polymerization of MS in the presence of DME or THF at temperatures between 0 and −20°C, the poly B block being prepared at 50°C. Shimomura et al.[12] started from 1,4 dilithio-1,1,4,4 tetraphenylbutane dissolved in heptane containing the MS. The polymerization of B was carried out at 50°C until the appearance of the red color of MS carbanions. The solution was then cooled to room temperature and hexamethylphosphorotriamide was added for MS polymerization carried out at −78°C. More recently, Lo and Tung[7] used the dilithium adduct of *sec*-butyllithium on 1,3-bis(1-phenylethenyl)benzene or 1,3-di(1,4-methylphenylethenyl)benzene in cyclohexane. MS was added at the same time as B, then S was added. THF was used to facilitate the copolymerization of MS.

These copolymers are not structurally well defined. The presence of polar additives during B polymerization leads to high contents of 1,2 units. When they are used, the difunctional initiators (except for Ref. 7) are not clearly defined: The synthesis and structure of the "dilithium–diisoprene"[2] are unknown as well as the real functionality. The aim of these experiments, which was to reach significant tensile strength for thermoplastic elastomers above 100°C, has not been attained and mechanical properties were often rather poor. The best results were obtained by Lo and Tung,[7] with tensile strengths between 20 and 24 MPa (3000–3500 psi) at room temperature for copolymers of B (56–69%) with MS/S endblocks. These values are similar to those of the best SBS copolymers.

We had planned to synthesize block copolymers with a central poly B segment prepared using a dilithium initiator in an hydrocarbon solvent and containing less than 10% 1,2 units and to obtain block copolymers by successive polymerization of S and MS. This would permit us to obtain, e.g., a rigid phase with a T_g around 150°C by incorporation of about 60% MS.[13] The first step was to prepare α,ω-dilithio(polybutadiene) in hexane solution by using difunctional organolithium initiators,[14] which have been found to be quite efficient for the synthesis of SBS copolymers having good mechanical properties.[1] A first addition of S was made in order to have stable styryllithium end groups, and after that, MS and eventually again S, permitting control of the MS/S ratio. However, it was necessary to use toluene as the main solvent since the polymerization of MS has to be carried out at low temperature on account of its ceiling temperature. Moreover, polybutadienyllithium precipitates at low temperature in hexane. Polar additives such as ethers or amines were added in order to accelerate the propagation rate for MS (and also cross propagation). We shall describe some of these attempts that were not successful for the synthesis of block copolymers with well-defined structures. The aim of the research described here is mainly to examine what may be the reasons for these difficulties and what might be the possibilities to overcome them.

EXPERIMENTAL

Polymerizations and purification of the reagents were carried out using high-vacuum techniques (all-glass apparatus fitted with break seals).

Materials

Solvent and monomer purifications have been already described.[13,15] *N,N,N', N'*-tetramethylethylenediamine (TMEDA) (Aldrich) was twice fractionated on a spinning band column and dehydrated on H_2Ca and then on sodium mirrors.

The monofunctional initiator was *tert*-butyllithium purified as described previously.[15] The dilithium initiator was prepared by addition of *tert*-butyllithium in excess on 2,11-diphenyl-1,11 dodecadiene in hexane as described previously.[14] The dilithium adduct was recovered by filtration and washed with pure hexane to eliminate monofunctional species. It was then dissolved by addition of small amounts of B, giving soluble α,ω-dilithio(polybutadiene) seeds. These seeds were there after used as difunctional initiators, and in the present case, further polymerization of butadiene was carried out in toluene.

Analysis

Polymers were analyzed by size exclusion chromatography (SEC) with a 10^6, 10^5, 10^4, 10^3, 500, and 100 Å set of μ-Styragel columns. THF was used as eluent (flow rate 1 ml min^{-1}). Molar masses were also measured using osmometry ($\overline{M}_{nosm}$) in toluene solution (Mechrolab Model 501). ^{1}H-nuclear magnetic resonance (NMR) spectra, 200 MHz, were recorded at 25°C in $CDCl_3$ solutions (15% w/vol) with a Bruker spectrometer.

RESULTS AND DISCUSSION

Preparations Starting from Polybutadienyllithium

In the first study,[16] the synthesis of MS–B–MS block copolymers was attempted using as difunctional initiator the diadduct of *tert*-butyllithium with 2,11-diphenyl-1,11-dodecadiene.[14] The procedure was nearly similar to that we used successfully for the preparation of SBS.[1] However, toluene was used as solvent instead of hexane because of the precipitation of polybutadienyllithium at the low temperatures needed because of the low ceiling temperature of MS.

The difunctional seeds (prepared in hexane, see Experimental) were used for the polymerization of B in toluene at 40°C. The temperature was then lowered to −40 or −78°C, and a small amount of styrene and about 15% THF (in vol) were successively added. The polymerization of MS was then carried out for 48 h at −78°C and followed by that of a supplementary amount of S. The polymers had poor mechanical properties, which, however, remained significant up to 120°C.

The characteristics of some samples are given in Table I. It may be seen that the experimental molar mass was generally higher than the theoretical one but in the range of possible experimental errors.

Polymer samples were analyzed using the method of Cantow et al.[17] using a dual RI and UV detection for SEC made in THF solution. This method has been also used by others authors and particularly by Tung and associates.[18] Refractive index detection showed only minor irregularities, but UV detection gave multimodal curves, with a strong enhancement

Table I Synthesis of Terpolymers Starting from a Difunctional Polybutadienyllithium Initiator in Toluene in the Presence of 15% in Volume of THF

Terpolymer	1,2 Units in Poly B Block (%)	Weight Rigid Phase (%)	Weight MS/ [S + MS] (%)	$\overline{M}_{ntheo}$	$\overline{M}_{nosmo}$
1	11	32	35	125,000	160,000
2	9	22	50	125,000	123,000
3	11	21	47.5	142,000	175,000

in aromatic groups for the lower molecular weights (see Fig. 1 for terpolymer 1).

SEC chromatography diagrams of block copolymers not only show fractionation according to molecular weights, since for the same molecular weight the elution volume of poly S or poly MS is higher than that of poly B and still different from that of their copolymer, but this technique permits a deeper study of the composition of the terpolymers, particularly if a preliminary fractionation is made. We recovered samples eluted at fixed intervals (see Fig. 2) and obtained four fractions (I–IV) (see Table II) that have been examined by SEC and by proton NMR, which permits us to verify the percentage of MS/[MS +S](≅ 35%). The combination of the data for the separated fractions gives a molar mass equal to 130,000 in poly S equivalent, which is not far from the calculated or the experimental values.

This analysis confirms the enrichment of the low molecular weight polymer in the rigid phase. Moreover, the main fraction (I) has a molecular weight about double that of fractions II and III. This may be explained by the occurrence of coupling reactions leading to the formation of multiblock copolymers. This polymer had poor mechanical properties (e.g., 3.1 MPa at 25°C measured on cast films samples), which, however, remained measurable up to 120°C, thanks to the presence of poly MS blocks. Experiments 2 and 3 also gave similar results.

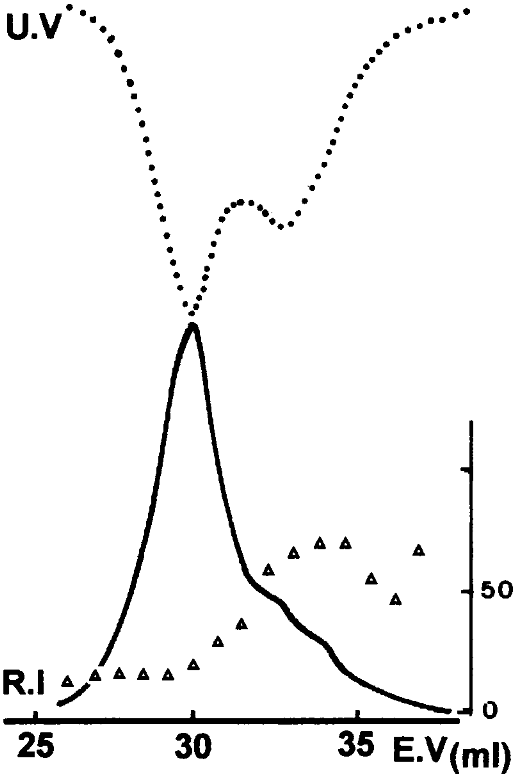


Figure 1 SEC chromatogram of terpolymer 1 with refractive index (RI) and UV detections. Synthesis starting from a difunctional initiator in toluene. (△△△) Calculated percentage of the rigid phase.

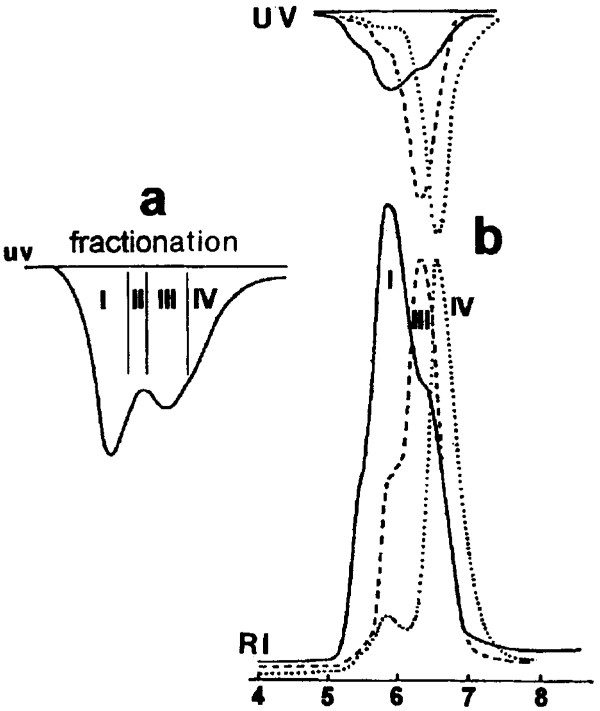


Figure 2 Fractionation of terpolymer 1 by SEC (see text): (a) UV trace of terpolymer 1 and scheme of fractionation into fractions I, II, III, and IV. (b) SEC chromatograms of the fractionated samples (RI and UV detection): (———) fraction I: (----) fraction III; (········) fraction IV.

We explain these results by the occurrence of side reactions involving the poly(α-methylstyryl-

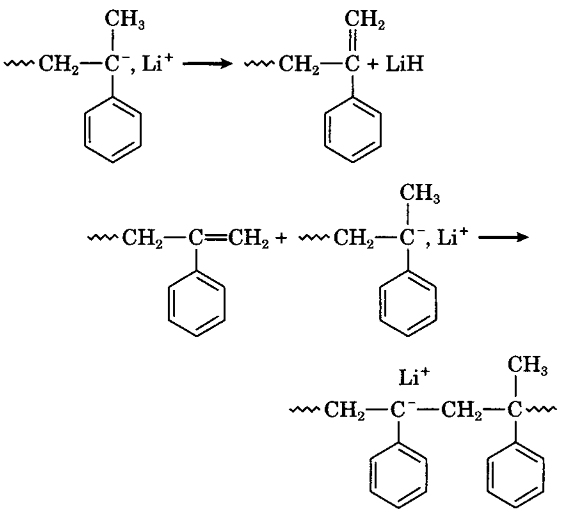
Table II Analysis of Fractions of Terpolymer I ($\bar{M}_{nosmo}$ = 160,000)

Fraction			
Sample	Weight (%)	$\bar{M}_n$ (Equivalent Poly S)	Rigid Phase[a] (wt %)
I	54	227,000[b]	22
II	11	127,000	28
III	25	91,000	50
IV	9	57,000	66

[a] Analysis by ^{1}H-NMR spectrometry.

[b] $\bar{M}_{nosmo}$ = 215,000.

lithium) carbanion, leading to a coupling reaction consecutive to HLi abstraction. Indeed, elimination of HLi from a poly (MS^-, Li^+) carbanion, as postulated by Ades et al.[19] in the case of the polymerization of MS in bulk, gives a terminal double bond that can react with a propagating chain acting as a coupling agent. Such a reaction can be described as follows:



(1)

To verify this explanation and to simplify the experiments, the synthesis of a triblock copolymer poly B-*block*-poly S-*block*-poly MS was attempted (Experiment 4, Table III). Poly B was polymerized at 20°C in toluene during 66 h at 25°C (initiation by *tert*-butyllithium) and S added at −70°C in the presence of 10% of THF. MS was then added and the copolymer recovered after 24 h. The MS content in the copolymer was very low ($\cong 1\%$), but the SEC chromatogram was monomodal and the polydispersity index was low ($I = 1.07$). The low yield in MS is rather surprising since at this temperature the concentration of MS at equilibrium should be very small. The reason for this behavior is probably the low rate of propagation at −70°C. Another explanation also may be considered: transfer to the MS monomer giving an inactive species.[20] Nevertheless, the unimodality of the copolymer and narrow molecular weight distribution is to be stressed. Chain transfer to toluene was observed at room temperature,[21] but it seems that the rate of this reaction is very low at −70°C.

To increase the propagation rate, we carried out experiments at a higher temperature, i.e., −40°C in the presence of 10–50% of THF in volume, but these attempts also failed (see Table III, Experiments 5 and 6). The copolymers had generally an experimental molar mass higher than the theoretical one and showed a trimodal distribution, with a population of low molecular weight polymer rich in styrenic compounds and, in the high molecular weights range, a molar mass at the peak that was approximately twice that of the main population as shown in Figure 3 for Experiment 5. We may explain this behavior by the presence of two types of side reactions. The low molecular weight fraction may result from transfer to toluene, giving benzyllithium and then polystyrenic compounds. High molecular weights may result from a coupling reaction of the block copolymer as shown in eq. (1).

Owing to these possible side reactions involving, in part, toluene, we ran Experiments 7–9 in benzene/hexane mixtures. This solvent was chosen in order to be able to carry out the reactions at low temperature, in the presence of THF. Other experiments were made at room temperature but with TMEDA (TMEDA/Li = r) as the additive.

To obtain poly B-*block*-poly S-*block*-poly MS, we first prepared at room temperature a diblock poly B-*block*-poly S in a mixture of hexane and benzene

Table III Synthesis of Terpolymers Starting from Monofunctional Polybutadienyllithium

Exp.	Solvents	Additive	MS Temperature of Polymerization (°C)	Molecular Weight Distribution
4	Toluene	THF, 10%	−70	Unimodal
5	Toluene	THF, 17%	−40	Trimodal
6	Toluene	THF, 34%	−40	Unimodal
7	Hex/Bz	THF, 50%	−20	Bimodal
8	Hex/Bz	THF, 12%	−30	Bimodal
9	Hex/Bz	THF, 3%	−30	Bimodal
10	Hex/Bz	TMEDA, $r = 1$	30	Bimodal
11	Bz	TMEDA, $r = 2$	16	Unimodal

(1/1.5 in vol) (Experiment 7) and then added MS at room temperature and THF at −20°C (51% in vol). We observed a rapid discoloration of the solution. Analysis of the copolymer by SEC showed a bimodal distribution by refractometry and a trimodal one by UV detection (see Fig. 4). The experimental molar mass ($\overline{M}_{nosm}$ = 57,000) is higher than the theoretical one (39,000). We may again explain this result by the mechanism postulated in eq. (1) (HLi abstraction followed by a coupling reaction). The addition of MS is very small as shown by NMR (about 2%).

A similar procedure was used in another experiment (hexane/benzene = 5/1) but with only 12% of THF in volume added at −30°C (Experiment 8). The total yield was nearly complete (94%) in 19 h and 85% of MS was polymerized, giving for the concentration at equilibrium 0.07 molL^{-1} in these conditions. This shows that less termination took place than in the former experiment (with 51% of THF). But in the present case also, the experimental $\overline{M}_{nosm}$ (46,500) was higher than the theoretical one (31,900) and the distribution was at least bimodal as shown on Figure 5. The higher $\overline{M}_n$ may result again from the occurrence of coupling reactions.

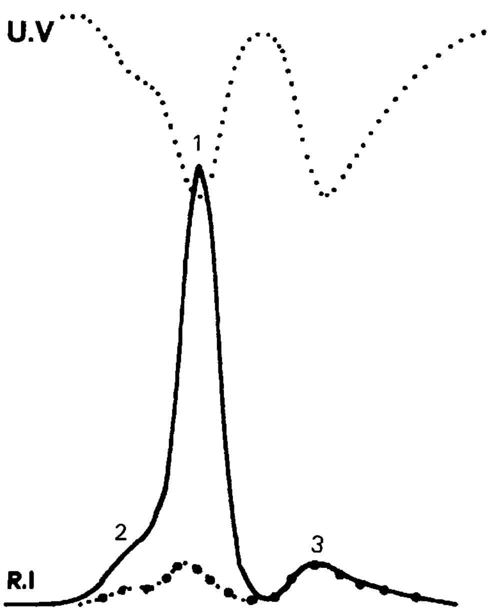


Figure 3 SEC chromatogram of terpolymer 5. Synthesis starting from a monofunctional polybutadienyllithium in toluene in the presence of 17% of THF. $\overline{M}_{nosmo}$ = 120,000. $\overline{M}_n$ in equivalent polystyrene at various elution volumes: (1) 243,000; (2) 600,000; (3) 52,000. (●●●) Relative amount of the rigid phase.

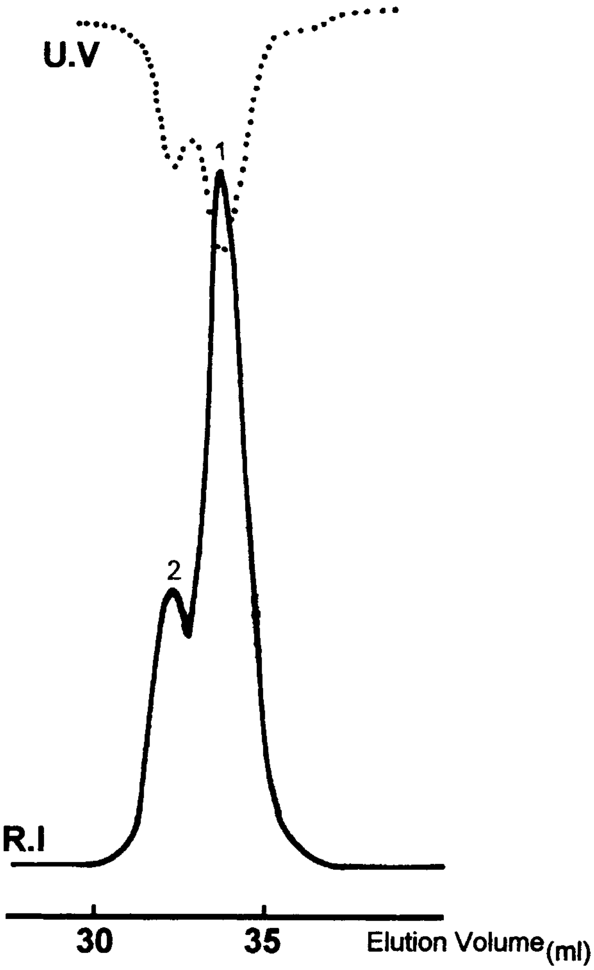


Figure 4 SEC chromatogram of terpolymer 7. Synthesis starting from a monofunctional polybutadienyllithium in a mixture of hexane and benzene in the presence of 50% THF. $\overline{M}_{nosmo}$ = 57,000. $\overline{M}_n$ in equivalent poly S: (1) 78,000; (2) 160,000.

With a smaller content in THF (3% in volume), a similar behavior was observed, the experimental molar mass being about twice the calculated one. The distribution was bimodal but "narrower" and the higher molar mass was about twice that of the lower one (see Fig. 6).

Since the results obtained with THF as the additive were not satisfactory, other experiments were carried out in the presence of TMEDA. As for the previous experiments, polymers were prepared in a mixture of hexane and benzene or in pure benzene. In Experiment 10, styrene was added at room temperature to poly B and the yield was quantitative. After polymerization of S, TMEDA (r = [TMEDA]/[Li] = 1) and MS were added successively at −78°C. The yield in MS was only 3%, for an unknown reason (slow rate of polymerization or termination?). The SEC chromatogram is shown in Figure 7.

A similar experiment was carried out in pure benzene. TMEDA ($r = 2$) was added after initiation of MS, which was in large excess (1.22 molL^{-1}). The polymerization was conducted at 16°C for 50 h. The yield in poly(styrene) was quantitative but only 2% of the MS was polymerized. So, TMEDA was not efficient enough to polymerize MS at this temperature even after a long time. (see Fig. 8).

Preparation Starting from the Hard Segment

A possible way to obtain an ABA triblock copolymer is to couple AB diblocks by a difunctional coupling agent. As the first step, we synthesized a poly(MS)-*block*-poly S-*block*-poly B copolymer with the aim to couple it later. We first polymerized MS at −40°C in toluene in the presence of 34% in volume of THF for 22 h, then added S at the same temperature. The solvent mixture was thereafter completely distilled off and the living block copolymer was redissolved in pure toluene before B was added in order to obtain poly B with a 1,4 unit content as high as possible.

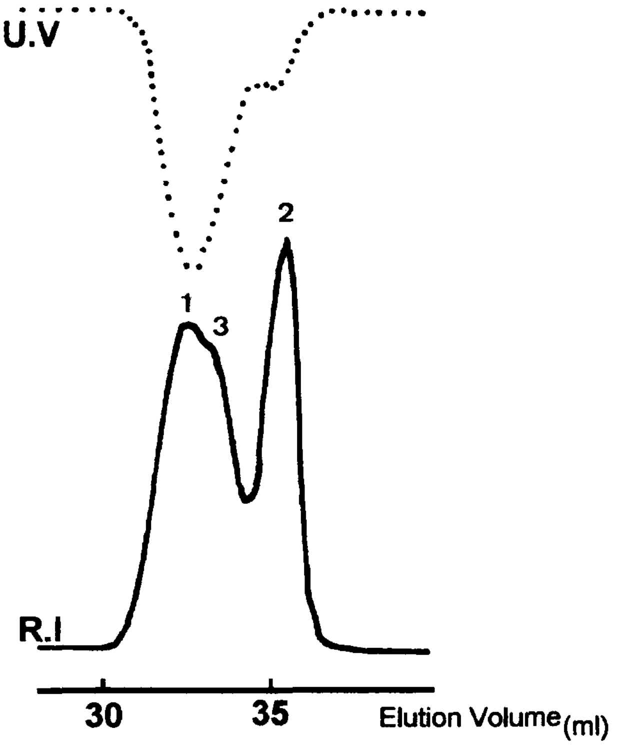


Figure 5 SEC chromatogram of terpolymer 8. Synthesis starting from a monofunctional polybutadienyllithium in a mixture of hexane and benzene in the presence of 12% THF. $\overline{M}_{n\mathrm{osmo}} = 46{,}500$. $\overline{M}_n$ in equivalent poly S: (1) 150,000; (2) 44,000; (3) 99,000.

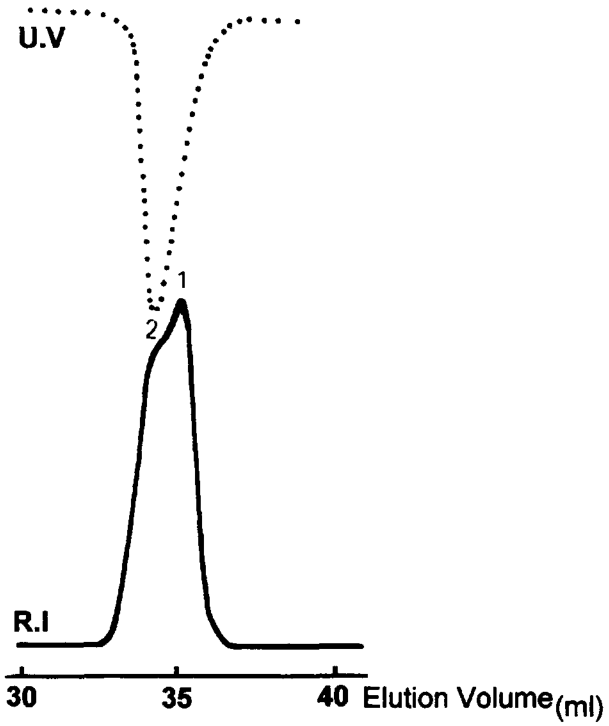


Figure 6 SEC chromatogram of terpolymer 9. Synthesis starting from a monofunctional polybutadienyllithium in a mixture of hexane and benzene in the presence of 3% THF. $\overline{M}_{n\mathrm{osmo}} = 45{,}000$. $\overline{M}_n$ in poly S equivalent: (1) 49,000; (2) 80,000.

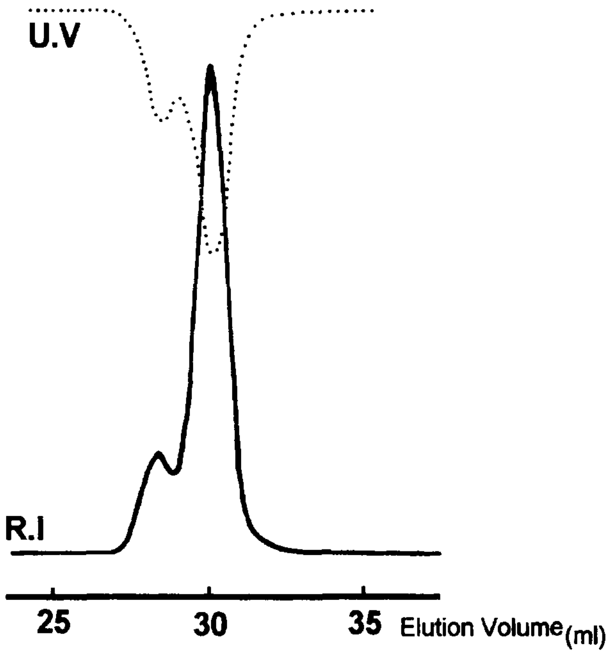


Figure 7 SEC chromatogram of terpolymer 10. Synthesis starting from a monofunctional polybutadienyllithium in a mixture of hexane and benzene in the presence of TMEDA (TMEDA/Li = 1).

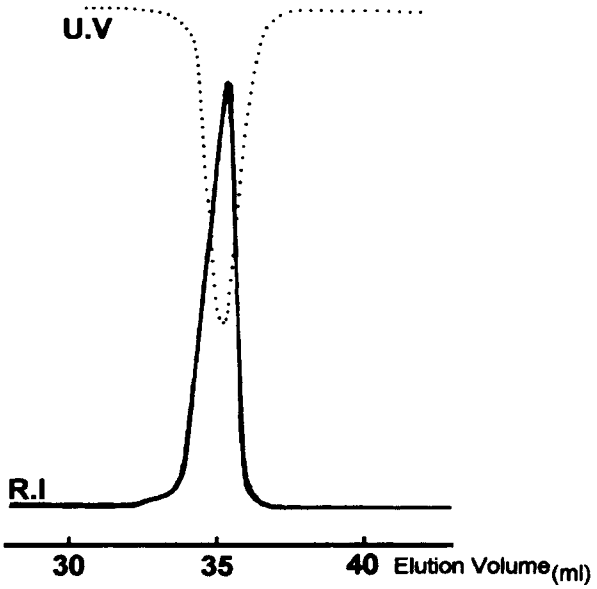


Figure 8 SEC chromatogram of terpolymer 11. Synthesis starting from a monofunctional polybutadienyllithium in a mixture of hexane and benzene in the presence of TMEDA (TMEDA/Li = 2).

Polymerization was then carried out for 6 h at 25°C. The yield in terpolymer was low (53%) either because the rate of polymerization of B is small at this temperature or, most probably, as a result of termination of active centers, due to the presence of the remaining THF solvating the lithium counterion (1,2 units content = 80%). Nevertheless, the polymer exhibited a unimodal distribution with I:1.1. Moreover, the analysis of the MS content by NMR permitted us to estimate the concentration of MS at equilibrium in the system at −40°C. It was about 0.01 $\mathrm{molL^{-1}}$ which value is lower than that in pure THF (0.06 $\mathrm{molL^{-1}}$).[22] This result is in agreement with Leonard's hypothesis.[23] According to Leonard, for a given monomer, the monomer concentration at equilibrium is determined essentially by the interaction parameter between monomer and solvent. It is probable that this parameter is very different in toluene (with small amounts of THF) and in pure THF.

DISCUSSION AND CONCLUSION

The methods considered present difficulties of different types: Starting from the block containing MS, a polar additive has to be used to prepare it but this leads to a poly B block with high content in 1,2 units. The attempts to remove completely the polar reagent were unsuccessful and termination reactions occurred. The best method would be, in principle, to use bifunctional organolithium initiators in nonpolar solvents to prepare poly B with a low content of 1,2 units. But, on account of the low ceiling temperature of MS and its low reactivity, further polymerization of MS has to be carried out at low temperature and for a long time. The model studies using monofunctional polybutadienyllithium clearly showed that the polymerization of MS does not occur in the absence of polar additives, and even in their presence, the rate of polymerization and yields were very low at −70°C.

By working at an intermediate temperature (e.g., −40°C) with various concentrations of THF, copolymers with polymodal molecular weight distributions were obtained, even when an intermediate block of poly S was inserted before MS addition in order to transform the unstable polybutadienyllithium (in the presence of polar additives) into polystyryllithium. This polymodality resulted from secondary reactions in the polymerization of MS: termination and coupling of polymer chains. The results were not better when the solvent mixture benzene–hexane was used instead of toluene, and the use as additive of a low concentration of TMEDA (instead of THF) was also unsuccessful. When the temperature is too high, secondary reactions occur, and when it is too low, the polymerization rate of MS is too low.

In conclusion, the preparation of block copolymers of dienes with MS is not possible at very low temperature (−70°C) in the absence of polar additives. Even when they are added, the polymerization rate is still low and higher temperatures have to be used, but this leads to secondary reactions and to formation of block copolymers with multimodal distribution through the occurrence of termination and coupling reactions.

REFERENCES

1. P. Guyot, J.-C. Favier, M. Fontanille, and P. Sigwalt, *Polymer*, **23**, 73 (1982).
2. Polymer Corp. Ltd (Polysar), Br. Fr. 1,573,989 (1969).
3. F. E. Neuman, Ger. Offen. 2,015,250 (1970) (to Shell).
4. F. E. Neuman, Ger. Offen. 2,015,249 (1970) (to Shell).
5. H. A. J. Schepers, Ger. Offen. 2,444,849 (1975) (to Stamicarbon).
6. A. Gandini, G. Perego, A. Roggero, R. Vitali, and A. Zazzeta, *Polym. Bull.*, **12**, 71 (1984).
7. G. Y. Lo, and L. H. Tung, *Am. Chem. Soc. Polym. Prep.*, **26**, 16 (1985).

8. M. M. Wald, and M. G. Quam, U.S. Pat. 3,076,817 (1972) (to Shell).
9. R. E. Cunningham, *J. Appl. Polym. Sci.,* **22,** 2387 (1970).
10. V. P. Shatalov, L. A. Grigor'eva, A. E. Kistereva, and V. D. Alekhin, USSR Pat. 401,155 (1974).
11. V. P. Shatalov, L. A. Grigor'eva, and A. E. Kistereva, USSR Pat. 254,773 (1968).
12. T. Shimomura, H. Nagata, and Y. Murakani, Ger. Offen. 2,224,616 (1972) (to Sumitomo Chemical Co.).
13. P. Phalip, J.-C. Favier, and P. Sigwalt, *Polym. Bull.,* **12,** 231 (1984).
14. P. Guyot, J.-C. Favier, H. Uytterhoeven, M. Fontanille, and P. Sigwalt, *Polymer,* **22,** 1724 (1981).
15. I. Obriot, J.-C. Favier, and P. Sigwalt, *Polymer,* **28,** 2093 (1987).
16. P. Phalip, These de 3° Cycle, Paris VI, 1984.
17. H. J. Cantow, J. P. Probst, and Ch. Stojanov, *Kaut. Gummi Kunst,* **13,** 2359 (1969).
18. J. R. Runyon, D. E. Barnes, J. F. Rudd, and L. H. Tung, *J. Appl. Polym. Sci.,* **13,** 2359 (1969).
19. D. Ades, M. Fontanille, and J. Leonard, *Can. J. Chem.,* **60,** 564 (1982).
20. Yu. Ye. Eizner and I. L. Ushalova, *Acta Polym.,* **42,** 295 (1991).
21. L. S. Wang, J.-C. Favier, and P. Sigwalt, *Polym. Commun.,* **30,** 248 (1989).
22. S. Bywater and D. J. Worsfold, *J. Polym. Sci.,* **26,** 299 (1967).
23. J. Leonard, *Macromolecules,* **2,** 661 (1969).

Received March 15, 1994
Accepted March 25, 1994