Difunctional Initiator Based on 1,3-Diisopropenylbenzene. 6. Synthesis of Methyl Methacrylate−Butadiene−Methyl Methacrylate Triblock Copolymers

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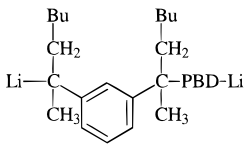
ABSTRACT: Synthesis of PMMA−PBD−PMMA (MBM) triblock copolymers with a 1,3-diisopropenylbenzene- (DIB-) based initiator is studied. Diethyl ether, *tert*-butyl methyl ether, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and THF were found to be efficient polar additives for obtaining PMMA−PBD−PMMA triblock copolymers, but these triblock copolymers displayed a high 1,2-microstructure of the PBD block. A combination of the initiator seeding technique and weakly polar additives has allowed MBM triblock copolymers with high 1,4-microstructure of PBD to be obtained. These copolymers exhibited a definitely higher upper service temperature than conventional thermoplastic elastomers, i.e. SBS or SIS Kratons. The influence of chain microstructure, copolymer composition and block length on the mechanical properties has been studied. Short polystyrene blocks of ca. M_n 2000 have been incorporated in between the PBD central block and the PMMA outer sequences. A higher tensile strength was observed for these MBM-like triblock coplymers. Contamination by a diblock structure expectedly had a very depressive effect on the bulk properties, and the stress−strain behavior mainly depended on the PMMA content and secondarily on molecular weight.

Introduction

Vinyl monomers such as diene and styrene can be now polymerized in a well-controlled anionic manner, with formation of chains of a predictable molecular weight and a narrow molecular weight distribution. Moreover, block copolymerization of diene and styrene can be initiated from either dienyl or styrenyl anionic species. In fact, a poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (SBS) can be synthesized by sequential polymerization of styrene, butadiene, and styrene, initiated by butyllithium, or by coupling of a living diblock (S−B) copolymer.[1−4] In recent years, special attention has been paid to the synthesis of diene−methacrylate block copolymers, since poly(methyl methacrylate) has a higher glass transition temperature than polystyrene,[1−12] which allows one to increase the upper service temperature of traditional thermoplastic elastomers. Until recently, however, the synthesis of well-defined poly(methyl methacrylate-*b*-butadiene-*b*-methyl methacrylate) copolymer (MBM) had not been reported in the scientific literature.[14] The key problem for the synthesis of triblock copolymers with MMA as outer blocks is the intrinsic problem of initiating BD polymerization from MMA anionic species.[4] The use of a difunctional initiator for BD polymerization is thus the only possible pathway to the desired MBM triblocks, which explains why a lot of patents and papers[17−29] have claimed or reported on the synthesis of various difunctional species and particularly nonpolar solvent soluble organolithium diinitiators that may give the highest percentage of the 1,4-microstructure of polydiene, leading to optimal elastomeric properties.[17] Hogen-Esch *et al.* claimed that they successfully prepared a MBM triblock copolymer by using a difunctional initiator formed by reaction of *sec*-butyllithium (*sec*-BuLi) and 1,3-diisopropenylbenzene (1,3-DIB).[14] We have revisited these experiments and found that the product accordingly formed was essentially a diblock rather than the expected triblock copolymer.[30] Actually, two problems have been identified for the reaction of *sec*-BuLi with 1,3-DIB and for the use of the reaction product as an anionic diinitiator. First, the addition reaction of stoichiometric amounts of *sec*-BuLi and 1,3-DIB in hydrocarbons forms a mixture of multiadduct, diadduct, and unreacted *sec*-BuLi rather than a pure diadduct.[31] Furthermore, the Li diadduct does not react as a difunctional anionic initiator in hydrocarbons but rather as a monofunctional compound. The polybutadienyl chains initiated by the Li diadduct in hydrocarbons is thought to have the following structure:



Li-DIB-PBD-Li (I)

The species directly associated with the DIB moiety of **I** is sterically hindered to the point where end-capping with diphenylethylene is prevented from occurring, thus leading to the very early termination of MMA polymerization.[30] It is worth recalling that such an end-capping with diphenylethylene is required to provide a sterically hindered and highly delocalized (diphenylalkyl)lithium anion, which is well-known to be an efficient initiator for the controlled polymerization of (alkyl)methacrylates.[32]

A well-defined difunctional initiator, i.e. 1,3-bis(1-lithio-1,3,3′-trimethylbutyl)benzene (DiLi), can be obtained by the reaction of *tert*-butyllithium (*t*-BuLi) and 1,3-DIB in the presence of 1 equiv of triethylamine (Et_3N) at −20 °C.[33] However, in the previous paper of this series,[34] dormant species have been observed on that diinitiator during the initiation process in a hydrocarbon solvent, and the use of a seeding technique and a weakly polar additive was strictly necessary to prevent residual initiator and promote equal activity of

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both ends. A high content of 1,4-units in SBS triblock copolymers can be obtained with that seeded initiator: these products have excellent mechanical properties comparable with those made with butyllithium.[34] In this paper, we now report the synthesis of MBM triblock copolymers and their characteristics. Once again, the combination of the seeding technique and the weakly polar additives is identified to yield an efficient difunctional initiator for synthesis of MBM triblock copolymers based on a high content of 1,4-units for the inner PBD block.

Experimental Section

Materials. 1,3-Butadiene purchased from Air Liquid Co. was condensed after passing through a column containing freshly crushed calcium hydride, and then distilled over *n*-butyllithium just before use. Styrene (Janssen) was dried over CaH_2 for 2 days and then added to fluorenyllithium and distilled just before use. Methyl methacrylate (MMA) purchased from Aldrich was dried over calcium hydride for 2 days, then added with $AlEt_3$ until a persistent yellow-green color was formed and finally distilled before use.[35] 1,3-diisopropenylbenzene, purchased from Aldrich, was dried over calcium hydride for 1 day, distilled from fluorenyllithium, and then diluted with dry cyclohexane. A commercially available *tert*-butyllithium solution (Janssen) was analyzed by the double titration method with 1,2-dibromobutane.[36] Diphenylethylene, purchased from Aldrich, was dried over *n*-BuLi and diluted with dry cyclohexane. This solution was added to (diphenylmethyl)lithium and distilled before use. Lithium *tert*-butoxide was prepared by the reaction of *tert*-butyl alcohol and *sec*-BuLi in a 1:1 molar ratio in toluene at room temperature and kept overnight. Cyclohexane and toluene were refluxed over calcium hydride for several days. THF was purified by refluxing it over a Na−benzophenone complex. Anisole, diphenyl ether (Ph_2O), *tert*-butyl methyl ether (tBME), diethyl ether (Et_2O) and *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA) were dried over calcium hydride for 1 day and then distilled under reduced pressure. Cyclohexane, toluene, anisole, Ph_2O, tBME, Et_2O, and TMEDA were distilled from living polystyryllithium oligomers just before use.

Seeded Initiator. 1,3-bis(1-lithio-1,3,3′-trimethylbutyl-benzene (DiLi) was synthesized by the addition reaction of 2 equiv of *t*-BuLi to a stoichiometric amount of 1,3-DIB at −20 °C for 1 h in the presence of 1 equiv of Et_3N as described elsewhere.[33] As-prepared DiLi (without removal of NEt_3), *t*-BuOLi, anisole (when necessary), and BD were added sequentially into a glass reactor containing cyclohexane. Concentrations of DiLi, *t*-BuOLi, and butadiene were ca. 0.03, 0.06, and 1.2 M, respectively. When necessary, the amount of anisole used was 15 vol % cyclohexane. Independent of the presence or not of anisole, the molecular weight of PBD oligomers was ca. 2000 (± 100) as determined by SEC (see below) and was in perfect agreement with the value calculated from the BD-to-DiLi molar ratio.[34]

Polymerization Procedure. Polymerization was carried out under a prepurified nitrogen atmosphere in a round-bottomed flask equipped with a rubber septum. Solvents, initiator (or seeded oligomers in cyclohexane), polar additives (in relevant cases), and monomers were transferred via a stainless steel capillary and/or syringe into the reactor. The butadiene was added in condensed form into the glass reactor containing the dilithium initiator solution in cyclohexane at 0 °C. In that polymerization solution, the butadiene concentration was ca. 20−30 g/L and the initiator concentration ca. 5×10^{-4} mol/L, depending on the requested molecular weight. Butadiene polymerization was essentially carried out at 40 °C overnight. If a polar solvent was used, the polymerization temperature was set at room temperature. In the case of five-block copolymers, styrene was added by a stainless steel capillary into the reactor. Styrene polymerization was carried out at 40 °C for 4 h in cyclohexane or at room temperature for 4 h in the presence of a polar solvent. Dry THF in a 1:1 volume ratio to cyclohexane and diphenylethylene (DPE) in a 5-fold molar excess vs BuLi were added sequentially. One hour later, MMA was added and polymerized at −78 °C for 1 h. The polymer solution was then precipitated in a large amount of methanol and the white fibrous rubbery precipitate isolated by filtration followed by redissolution in THF containing 0.5% (w/w based on polymer) IRGANOX 1010. THF was removed by evaporation and polymers dried in a vacuum oven at 40 °C for 1 day.

Analysis. Size exclusion chromatography (SEC) measurements were performed with a Hewlett-Packard 1090 liquid chromatograph equipped with four columns (pore sizes: 10^5, 10^3, 500, and 100 Å) and an HP 1037-A refractive index detector. Polystyrene standards were used for calibration, and THF at 40 °C was used as the elution solvent. A conversion factor of 0.55 was found to be appropriate to calculate the PBD molecular weight. The SEC values reported for the copolymers were accurate with less than 2% deviation. Both PBD microstructure and MMA tacticity were analyzed by ^{1}H NMR with a Bruker AM 400 spectrometer. The chemical composition of block copolymers was also analyzed by the same technique and compared to the theoretical composition based on monomer charges. Tensile properties of the triblock copolymers were tested at 25 °C with a Adamel Lomargy tensile tester. Films were cast from a THF/toluene (60/40, v/v) mixed solvent, and cut into DIN 53448 specimens. The cross-head speed was 200 mm/min. The permanent set (%) was calculated as the ratio of the unrecoverable deformation for the sample elongated at 300% for 60 min to the initial length. Differential scanning calorimetry (DSC) analyses were performed with a Dupont 9000 DSC apparatus. The heating rate was 20 °C/min.

Results and Discussion

Synthesis of M−B−M Triblock Copolymers. The synthesis of MBM triblock copolymers is complex, especially when one desires to maintain a high content of 1,4-units for the major PBD block and thus a low Tg of the rubbery PBD phase. That complexity develops as a result of strong restrictions in the selection of the polymerization solvents. A high 1,4-microstructure (>80%) for PBD is attainable only when organolithium initiators are used in hydrocarbon solvents, such as cyclohexane or toluene, but methyl methacrylate generally does not undergo living polymerization in those hydrocarbons. PBD−PMMA diblock copolymers can be prepared by sequential addition of MMA monomer to the living PBD anion, together with polar solvents and DPE.[12] However, the MMA lithium enolate is not sufficiently basic to reinitiate a second addition of BD monomer. Thus, triblock structures can only be prepared by employing a difunctional initiator. A DIB-based difunctional initiator has recently been developed in our laboratory, and SBS triblock copolymers of high tensile strength have been obtained from it.[33,34] In this study, the synthesis of a well-defined MBM triblock copolymer is carried out by using that same DIB-based difunctional initiator.

Ladd and Hogen-Esch reported a simple way to prepare MBM triblock copolymers by using a *sec*-BuLi/1,3-DIB adduct as initiator.[14] However, our experimental results showed that the resulting copolymers prepared that way, i.e. as initiated by the *sec*-BuLi/1,3-DIB crude diadduct, were actually diblock instead of triblock in structure.[30] We have reexamined those conclusions by using a preformed pure diadduct, 1,3-bis(1-lithio-1,3,3′-trimethylbutyl)benzene (DiLi),[31] as initiator. A sequential polymerization of BD and MMA was initiated by DiLi. The dilithium solution had a deep red color. When butadiene was added to a cyclohexane solution of DiLi, the color switched rapidly to a faint orange, and the polymerization was carried out overnight at 40 °C. After completion, dry THF in a 1:1 volume ratio to

Table 1. Mechanical Properties of BD and MMA Block Copolymers Initiated by DiLi[a]

sample no.	1,2-PBD[b] (%)	PMMA (wt %)[c]		M_n ($\times 10^{-3}$)[d]		M_w/M_n		yield[e] (%)	tensile strength (MPa)	elongation at break (%)
		theor	NMR	theor	SEC/NMR	PBD	copo[f]			
1	8.9	33	29	90	93	1.05	1.10	98	1.5	300
2	9.0	34	30	121	128	1.05	1.10	97	1.8	300
3	8.8	40	37	100	110	1.05	1.10	97	2.6	250
4	8.9	40	36	133	137	1.05	1.10	97	2.4	250
5	9.0	50	46	120	123	1.05	1.10	97	3.5	150

[a] Butadiene polymerization was initiated in cyclohexane with DiLi. [b] From ^{1}H-NMR data. [c] Key: theor = theoretical value (BD/MMA in feed); NMR = from ^{1}H-NMR data. [d] Key: theor = theoretical value (monomers weight/mol of DiLi in feed); SEC/NMR = from SEC and ^{1}H-NMR data. [e] Yield = (polymer weight/monomers weight in feed) × 100. [f] Key: copo = copolymer.

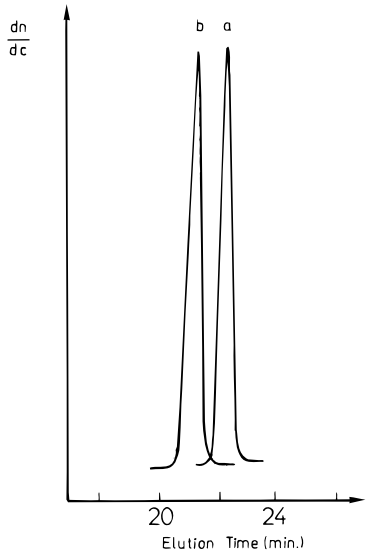


Figure 1. SEC traces of BD- and MMA-based block copolymer prepared in cyclohexane with DiLi: (a) PBD central block (M_n = 66 000; MWD = 1.05); (b) block copolymer (M_n = 93 000; MWD = 1.07).

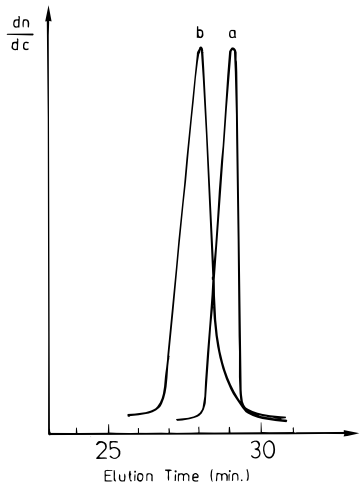


Figure 2. SEC trace of MB copolymer initiated in cyclohexane with a mixture of DiLi and AMS−Li: (a) PBD block (M_n = 5500; MWD = 1.06); (b) block copolymer (M_n = 10 500; MWD = 1.12).

cyclohexane and DPE in a 5-fold molar excess *vs* BuLi were added sequentially. A deep red color was observed, which disappeared upon MMA addition. The polymerization of MMA was carried out at −78 °C for 1 h and the viscosity of the solution increased, but no gelation occurred during that time. Characteristics of the resulting copolymers are shown in Table 1. Typical SEC traces of the PBD block and the final copolymer are shown in Figure 1: both have a monomodal and narrow molecular weight distribution (M_w/M_n < 1.1). Interestingly, the M_w/M_n ratio is much lower than that of copolymers initiated by *sec*-BuLi/1,3-DIB adduct under the same conditions,[14,30] and the molecular weight of PBD calculated from SEC data is just a little higher than the expected value (up ca. 5−10%). Conversely, the PMMA content of all samples was a little less than the expected value (ca. 3%). The yield in copolymer was not exactly quantitative (ca. 97%). The very poor mechanical properties of these samples (tensile strength below 4 MPa) indicate these copolymers to be diblock rather than triblock in structure.

Dormancy at both ends, in the minor part, and at one end, in the major part, of the DiLi species has been observed when DiLi was used to initiate butadiene polymerization in hydrocarbon solvents, resulting, after sequential polymerization of styrene, in a mixture of homopolystyrene and butadiene−styrene block copolymers, respectively.[34] A bimodal molecular weight distribution (MWD) was observed. A small peak on the low MW side (even lower than that of the first PBD block) was assigned as homopolystyrene, and a broad peak on the high MW side (higher than that of PBD) as butadiene−styrene block coplymer. However all of the samples in Table 1 display a monomodal MWD. It is worth mentioning that the product recovered from the filtrate after precipitation was actually found to be low MW PMMA (it has been observed that low MW homo-PMMA cannot be precipitated by pouring its THF solution into methanol), which provides a reasonable explanation for the above apparent contradiction; it also explains why the actual PMMA content was a little less than the expected value and the yield was not 100%.

A polymerization experiment has been made with a mixture of a monofunctional initiating species, i.e. (α-methylstyryl)lithium (AMS−Li) and the initiator DiLi. Polymerization was carried out under the same conditions as described above, the used amount of AMS−Li and DiLi were 2×10^{-4} and 4×10^{-4} mol, respectively, and the amount of butadiene was 3.0 g. The weight ratio of BD to MMA was 1:1. SEC traces shown in Figure 2 indicate that both PBD and the final copolymer still have narrow and monomodal MWD as if a single initiator were used (M_n of PBD = 5500). In other words, under the conditions used, DiLi does not contribute to the formation of triblock copolymers but to the formation of the same diblock copolymers as the monofunctional initiator.

It has been reported that polystyrene initiated by a mixture of DiLi and AMS−Li in THF had a bimodal MWD, indicating that DiLi had two active initiating ends in THF.[30,33] A MMA polymerization was initiated in THF with a mixture of DiLi and AMS−Li end-capped with DPE. The amounts of DiLi and AMS−Li used were 1.8×10^{-4} and 3.6×10^{-4} mol, respectively, for 1 g of MMA monomer. SEC trace of the resulting PMMA in Figure 3 shows that DiLi end-capped with DPE does not generate a PMMA with a MW two times larger than

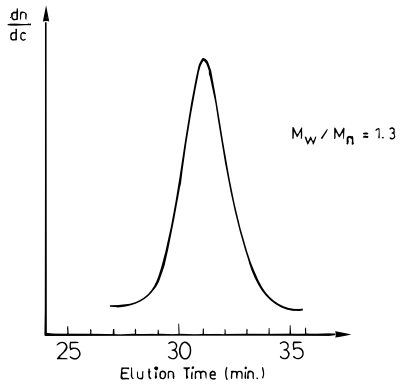


Figure 3. SEC trace of PMMA initiated in THF with a mixture of DiLi and AMS−Li end-capped with DPE (M_n = 2000; MWD = 1.30).

that of PMMA initiated by AMS−Li end-capped with DPE. That the M_n of PMMA is in good agreement with the molar ratio of MMA over DiLi plus AMS−Li (ca. 2000) provides another piece of evidence for the fact that initiator DiLi reacts only at one site with DPE, either in cyclohexane or in THF:[33] this may be attributed to steric hindrance rather than coordinative aggregation, which should normally be destroyed by THF. It is now clear that the polybutadienyl chains initiated by DiLi in hydrocarbon solvents have the Li−DIB−PBD−Li structure **I**.

The active site associated to the DIB moiety of **I** is sterically hindered to the point where end-capping with diphenylethylene is prevented from occurring, leading to a very early termination of MMA polymerization. The same conclusion has also been reached when benzene is used instead of cyclohexane for the synthesis of MBM by sequential polymerization initiated with the initiator DiLi.[37]

Effect of Polar Additives. Preparation of MBM triblock copolymers with DiLi in the presence of polar additives, such as triethylamine (Et_3N), anisole, diphenyl ether (Ph_2O), *tert*-butyl methyl ether (tBME), diethyl ether (Et_2O), lithium *tert*-butoxide (*t*-BuOLi), *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA), and THF have been studied, and the results are reported in Table 2. Sample 1 was prepared in the presence of 5 mol of Et_3N/mol of organolithium site. Although both PBD and the final block copolymer are of a very narrow MWD, it also has very poor mechanical properties. Sample 2 was prepared in the presence of *t*-BuOLi (*t*-BuOLi/Li = 1.0). MWD of the PBD block is broad with a shoulder on the low MW side, and that of the copolymer becomes narrower. Sample 2 has a higher tensile strength than sample 1, which is consistent with the presence of triblock structure. Samples 3, 4, 5, and 6 were prepared in the presence of 7.5 vol % of anisole, Ph_2O, tBME and Et_2O, respectively. The MWD of samples 3 and 4 are bimodal, and the mechanical properties are very poor. Both PBD and final copolymer in samples 5 and 6 have a narrow monomodal MWD, and these two samples exhibit both high tensile strength (35 MPa) and a large elongation at break (700%). Samples 7 and 8 were prepared in the presence of TMEDA (0.6 TMEDA/Li molar ratio) and THF (1.0 vol %). Although the MWD of both samples are narrow and monomodal, they each have a significantly smaller tensile strength than samples 5 and 6, which can be accounted for by the predominantly 1,2-PBD microstructure. It is worth noting that in contrast to experiments in pure cyclohexane, all of the samples in Table 2 have the expected PMMA content and are obtained in quantitative yield.

The above results suggest that the sequential polymerization of butadiene and MMA initiated with DiLi in cyclohexane in the presence of Et_3N, *t*-BuOLi, anisole, or diphenyl ether does not produce a MBM copolymer in a controlled manner. Such a well-defined MBM triblock structure can however be obtained by using DiLi in the presence of tBME, diethyl ether, TMEDA, or THF in cyclohexane, but it then displays a high 1,2-microstructure for the PBD block.

Seeded Initiator. The seeding technique has been reported as an effective method in narrowing the MWD of a polyisoprene obtained from a difunctional initiator and improving the properties of the corresponding SIS.[29] In that seeding technique, a small fraction of monomer to be polymerized is first reacted with the initiator, under controlled conditions, before the polymerization process is completed.

A seeded initiator has accordingly been prepared by reacting DiLi with a small amount of butadiene monomer in cyclohexane, the calculated M_n of the PBD oligomer being ca. 2000. The SEC trace of that sample taken after complete reaction shows that the PBD oligomer has a monomodal rather symmetric MWD with the expected MW. That seeded initiator was then used for the sequential polymerization of BD and MMA (THF and DPE being added before MMA polymerization). Both PBD and the final copolymer have monomodal and narrow MW distributions and M_n is close to the expected value. However, the poor mechanical properties (Table 3) suggest that these samples are essentially diblock rather than triblock copolymers.

It has been reported in the previous paper of this series[34] that when *t*-BuOLi is used together with anisole in the synthesis of the seeded initiator, the two lithium sites of the initiator may be of a comparable reactivity.

Table 2. Mechanical Properties of MBM Triblock Copolymers Initiated by DiLi in the Presence of Polar Additives[a]

sample no.	additive[b]	1,2-PBD[c] (%)	PMMA (wt %)[d] theor	PMMA (wt %)[d] NMR	M_n ($\times 10^{-3}$)[e] theor	M_n ($\times 10^{-3}$)[e] SEC/NMR	M_w/M_n[f] PBD	M_w/M_n[f] copo[h]	yield[g] (%)	modulus (MPa)	tensile strength (MPa)	elongation at break (%)
1	Et_3N	12.5	34	34	90	96	1.05	1.10 (m)	100		3.5	400
2	*t*-BuOLi	15.0	34	33	90	92	1.20	1.15 (b)	100		8.2	600
3	anisole	28.5	34	33	90	100	1.65	1.45 (b)	100		6.5	500
4	Ph_2O	26.5	34	34	90	99	1.70	1.40 (b)	100		6.0	500
5	tBME	43.5	34	33	90	93	1.05	1.10 (m)	100	8.5	34.5	700
6	Et_2O	44.5	34	34	90	92	1.05	1.10 (m)	100	8.8	36.0	700
7	TMEDA	73.0	34	35	90	94	1.05	1.10 (m)	100	11.2	25.5	500
8	THF	84.5	34	33	90	95	1.05	1.15 (m)	100	13.2	20.5	400

[a] Butadiene polymerizatin was initiated in cyclohexane with polar additives. [b] Et_3N/Li = 5; *t*-BuOLi/Li = 1.0; anisole, Ph_2O, tBME and Et_2O were 7.5 vol % in cyclohexane; TMEDA/Li = 0.6; THF was 1 vol % in cyclohexane. [c] From ^{1}H-NMR data. [d] Key: theor = theoretical value (BD/MMA in feed); NMR = from ^{1}H-NMR data. [e] Key: theor = theoretical value (monomers weight/mol of II in feed); SEC/NMR = from SEC and ^{1}H-NMR data. [f] MWD: b for bimodal and m for monomodal. [g] Yield = (polymer weight/monomers weight in feed) × 100. [h] Key: copo = copolymer.

Table 3. Mechanical Properties of BD and MMA Block Copolymers Prepared by Using Seeded Initiator without Polar Additive[a]

sample no.	1,2-PBD[b] (%)	PMMA (wt %)[c] theor	PMMA (wt %)[c] NMR	M_n ($\times10^{-3}$)[d] theor	M_n ($\times10^{-3}$)[d] SEC/NMR	M_w/M_n PBD	M_w/M_n copo[f]	yield[e] (%)	modulus (MPa)	tensile strength (MPa)	elongation at break (%)
1	8.8	34	34	90	95	1.15	1.15	100	1.5	8.5	800
2	8.9	34	34	121	125	1.15	1.15	100	1.5	8.5	800
3	9.0	40	40	100	103	1.15	1.20	100	1.8	7.5	800
4	9.3	40	41	134	140	1.15	1.15	100	2.2	8.5	800
5	9.2	50	50	120	125	1.15	1.25	100	2.8	9.0	800

[a] Butadiene polymerization was carried out in cyclohexane with seeded initiator. Seeded initiator (PBD oligomer) was prepared in cyclohexane with DiLi; MW of the PBD oligomers was 2000. [b] From ^{1}H-NMR data. [c] Key: theor = theoretical value (BD/MMA in feed); NMR = from ^{1}H-NMR data. [d] Key: theor = theoretical value (monomers weight/mol of II in feed); SEC/NMR = from SEC and ^{1}H-NMR data. [e] Yield = (polymer weight/monomers weight in feed) × 100. [f] Key: copo = copolymer.

Table 4. Mechanical Properties of MBM Triblock Copolymers Prepared with Seeded Initiator Containing Polar Additives[a]

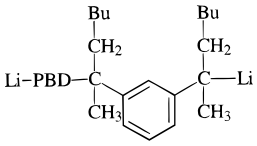
sample no.	1,2-PBD[b] (%)	PMMA[c] (wt %)	M_n[d] ($\times10^{-3}$)	M_w/M_n PBD	M_w/M_n copo[f]	yield[e] (%)	modulus (MPa)	tensile strength (MPa)	elongation at break (%)	permenent set (%)
1	17	33	74	1.05	1.10	100	2.8	16.5	1000	43
2	16	34	122	1.10	1.10	100	3.1	23.8	1000	17
3	16	40	132	1.10	1.30	100	5.3	22.0	900	18
4	17	44	144	1.10	1.10	100	8.2	26.2	700	17
5	16	37	176	1.10	1.20	100	4.2	21.8	1000	17
6	16	36	188	1.10	1.15	100	4.0	19.8	1000	18

[a] Butadiene polymerization was initiated in cyclohexane with seeded initiator. Seeded initiator (PBD oligomer) was prepared in cyclohexane with DiLi, *t*-BuOLi, and anisole; MW of the PBD oligomers was 2000. [b] From ^{1}H-NMR data. [c] From ^{1}H-NMR data. [d] From SEC and ^{1}H-NMR data. [e] Yield = (polymer weight/monomers weight in feed) × 100. [f] Key: copo = copolymer.

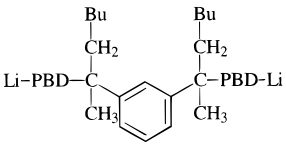
Although PBD and SBS prepared with this seeded initiator may occasionally have a bimodal MWD (the two peaks having a comparable area), these samples nevertheless have good tensile properties compared to those made with butyllithium in a commercial production: this suggests that both peaks should correspond to triblock structures.

After complete conversion of butadiene in cyclohexane, THF and DPE were added instead of styrene, followed by MMA polymerization at −78 °C. After MMA addition, the red color characteristic of DPE−Li disappears, and the viscosity of the solution increases rapidly; gelation finally occurs in all polymerization experiments. After the polymers were deactivated with methanol, the viscosity of the solution returned to a normal value. Clearly, physical cross-linking was responsible for the formation of a network structure. The mechanical properties of the resulting MBM triblock copolymers are shown in Table 4. Both PBD and the final copolymers of all these samples have a bimodal molecular weight distribution as shown in Figure 4. However, their tensile strength and elongation at break are definitely much higher than those in Table 3 wherein the samples have a narrow and monomodal MWD. Significantly, the tensile strength of the samples in Table 4 is still smaller than that of samples 5 and 6 in Table 2, indicating that the samples in Table 4 probably are contaminated with diblock copolymers.

The above results suggest that two types of the PBD central block might have been formed by using the seeded initiator containing *t*-BuOLi and anisole, i.e.:



Li-PBD-DIB-Li (I)



Li-PBD-DIB-PBD-Li (II)

When styrene is added along with THF to such PBD species, the two types of central block may both result in the formation of SBS triblock copolymers. Since the species directly associated to the DIB moiety of type **I** chains is sterically very hindered, end-capping with DPE might be prevented from occurring, which would be responsible for the very early termination of the MMA growing chain and formation of diblocks. If, prior to the MMA polymerization, PBD chains are end-capped with a few styrene units followed by DPE, a MBM-like triblock copolymer could be formed from initiation by PBD of type **I**.

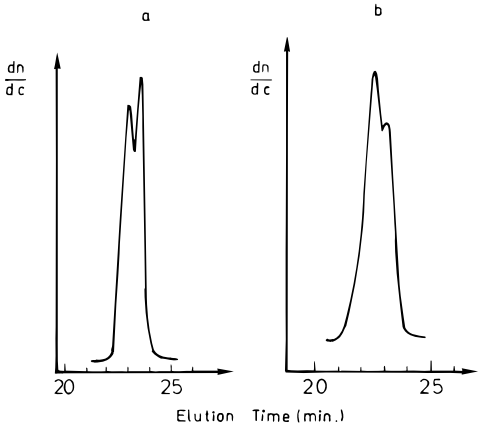


Figure 4. SEC traces of MBM triblock copolymer prepared in cyclohexane with seed initiator containing polar additive: (a) PBD central block (M_n = ca. 74 000 and 95 000 for right and left peaks, respectively; global MWD = 1.09); (b) block copolymer (apparent M_n = 84 000 and 108 000 for right and left peaks respectively; global MWD = 1.12).

Several MBM triblock copolymers have accordingly been prepared (Table 5) in toluene or in cyclohexane. When cyclohexane is used as a solvent, viscosity of the polymerization medium increases very rapidly upon MMA addition, gelation finally occurs, and mixing is stopped. This phenomenon might possibly be attributed to the high freezing point of cyclohexane (6.5 °C) and the poor solubility of PMMA in cyclohexane. However, gelation only occurs in the synthesis of MBM triblock copolymers, but never when a PBD−PMMA diblock

Table 5. Mechanical Properties of PMMA−PS−PBD−PS−PMMA Block Copolymers As Initiated in Cyclohexane with Seeded Initiator Containing Polar Additives[a]

sample no.	solvent[b]	1,2-PBD[c] (%)	M_n[d] PBD	PS	PMMA	M_w/M_n	modulus (MPa)	tensile strength (MPa)	elongation at break (%)	permanent set (%)
1	Tol/THF	21	60000	14000	2000	1.10	5.2	34.0	1000	18
2	Tol/THF	20	60000	12000	4000	1.10	4.8	30.5	1000	18
3	Tol/THF	20	60000	10000	6000	1.10	4.3	29.5	1000	17
4	Tol/THF	21	60000	8000	8000	1.10	3.5	26.5	1000	18
5	Tol/THF	20	60000	9000	2000	1.10	3.0	25.5	1000	20
6	Tol/THF	20	60000	4000	12000	1.10	2.8	15.5	800	45
7	Tol/THF	21	70000	0	18000	1.20		5.0	400	
8	CH/THF	17	60000	12000	5000	1.10	6.4	38.5	1000	17
9	CH/THF	15	60000	4000	12000	1.10	6.1	35.5	1000	18
10	CH/THF	16	60000	2000	14000	1.10	5.2	30.5	1000	18

[a] Seeded initiator (PBD oligomer) was prepared in cyclohexane with DiLi, *t*-BuOLi, and anisole; MW of the PBD oligomers was 2000. [b] Butadiene polymerization was carried out in hydrocarbon solvents (toluene or cyclohexane), THF and DPE were added before MMA polymerization. [c] From ^{1}H-NMR data. [d] From SEC and ^{1}H-NMR data, assuming a five-block structure.

copolymer is prepared with a monofunctional initiator under the same experimental conditions. In contrast the viscosity of the reaction medium decreases upon addition of styrene to PBD dianions instead of increasing. A stronger ionic aggregation of MMA−Li at each end of the polymer chain might thus be responsible for the tridimensional polymer network, since even a short MMA chain (M_n > 2000) is sufficient to lead to a physical gel. In toluene, which has a lower freezing point and a much better solvating power for PMMA, gelation never occurs.

It can be seen from Table 5 that tensile strength decreases together with PS chain length, particularly when toluene was used as solvent. Samples 1, 2, and 3 have good mechanical properties comparable with those of commercial SBS triblock copolymers. However, a MBM triblock copolymer (sample 7) prepared in toluene has very poor mechanical properties (a tensile strength of 5.0 MPa at 400% elongation) even though it has a MWD, composition, and microstructure similar to those samples prepared in cyclohexane. When both ends of PBD were end-capped by a PS block, mechanical properties of the resulting copolymers were improved. It is suspected that a chain transfer reaction from lithium species to toluene in the presence of a large amount of THF might occur in these experiments.

In comparison with the samples prepared in toluene, those obtained in cyclohexane have better mechanical properties, particularly at low PS content. A short PS block can apparently increase tensile strength compared to the tensile strength in MBM triblocks prepared with the same initiator under the same conditions: it remains to be determined if that is simply due to the better stability of styryl vs butadienyl anions (thus giving a higher purity of the symmetric block copolymer) or to the development of a more favorable interface morphology.

Effect of Microstructure on Mechanical Properties. Solvents are known to exert a strong influence on the mode of diene polymerization.[38] In polar aprotic solvents, the organolithium compounds are more "ionic" and the diene monomer polymerizes preferentially in the 1,2-addition mode. As a result, the polydiene has more "short branching" and a higher glass transition temperature and in general poorer elastomeric properties. The microstructure of MBM triblock copolymers has been controlled by using solvents of varying polarity. Figure 5 shows stress−strain curves of those copolymers with various 1,2-contents in the PBD block (in sample D, PS chains were capped at both ends of the PBD chains). It clearly appears that the increase in 1,2-content decreases both the tensile strength and elongation at break, particularly in the case of predominating 1,2-content. Conversely, the Young's modulus of these samples increases with the 1,2-content.

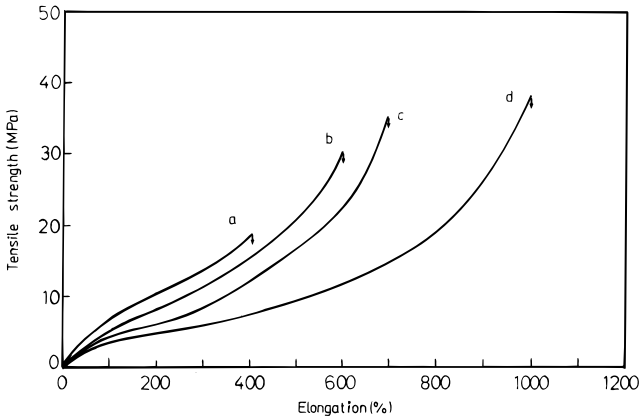


Figure 5. Effect of 1,2-content of the PBD block of MBM on the stress−strain curves: (a) 85% 1,2-units (MW = 95 000; PMMA content = 33 wt %; MWD = 1.15, prepared in cyclohexane with 1 vol % THF); (b) 66% 1,2-units (MW = 97 000; PMMA content = 33 wt %; MWD = 1.10, prepared in cyclohexane with TMEDA at a TMEDA/Li of 0.45); (c) 45% 1,2-units (MW = 92 000; PMMA content = 34 wt %; MWD = 1.10; prepared in cyclohexane with 7.5 vol % diethyl ether); (d) 17% 1,2-units (MW = 94 000; PMMA content = 11 wt %; PS content = 25 wt %; MWD = 1.10, prepared with the seeded initiator in cyclohexane).

Effect of Diblocks on Mechanical Properties. Morton et al. have reported[17] that, in SIS block polymers, the presence of as little as 2% by weight of SI diblock already causes a significant decrease in tensile strength, while 5% of SI polymer will cause a drop of as much as 23%. In order to study the effect of a PMMA−PBD diblock on the mechanical properties of MBM copolymers, a pure MB sample was prepared using *sec*-butyllithium as initiator. It was then mixed with the triblock at various weight ratios, the two polymers having similar total M_n, composition, and microstructure ($M_n = 1 \times 10^5$, 64 wt % PBD, and 45% 1,2-content). As shown in Figure 6, the tensile strength regularly decreases with the content in diblock. At ca. 35 wt %, the tensile strength drops to half of the starting value. However, the presence of that diblock has little effect on the elongation at break and at low amounts has no adverse effect on the permanent set at break. When the diblock content is higher than 35%, however, the permanent set significantly increases.

Effect of Composition and Block Length on Mechanical Properties. In Figure 7 are shown the

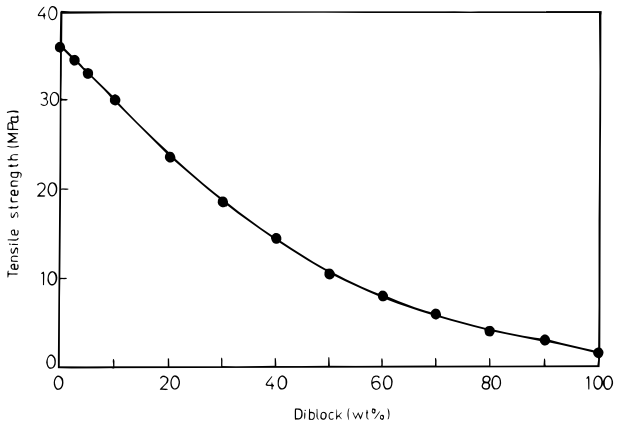


Figure 6. Effect of diblock on the tensile strength of MBM triblock (MBM:MW = 18000−65000−18000, 1,2-units = 45%, and MWD = 1.10; BM:MW = 63000−35000, 1,2-units = 45%, and MWD = 1.10; two polymers were prepared in cyclohexane with 7.5 vol % diethyl ether, using DiLi and *sec*-BuLi, respectively).

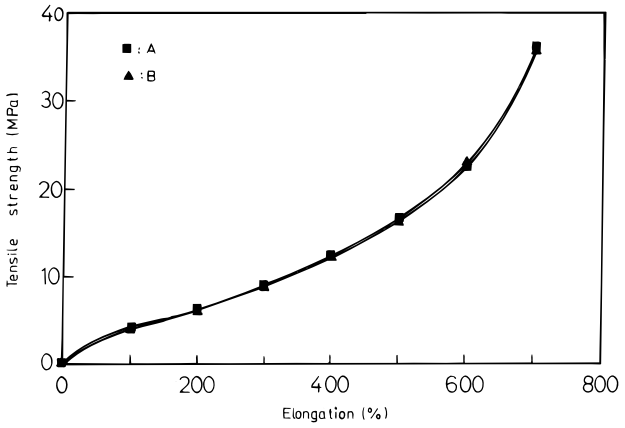


Figure 7. Effect of molecular weight on the stress−strain curve of MBM triblocks (PMMA content = 36 wt %; 1,2-units = 45%; MWD = 1.10): (A) M_n = 125 000; (B) M_n = 70 000. Both polymers were prepared in cyclohexane with 7.5 vol % diethyl ether.

stress−strain curves of two MBM copolymers. Both samples have the same PBD and PMMA contents (64 wt % PBD and 36 wt % PMMA), while samples A and B have M_n values of 125 000 and 70 000, respectively. The two curves are practically superimposable, which indicates that the molecular weight has a minimal effect on the mechanical properties of these materials, at least above a critical value linked to the entanglement length.

Figure 8 displays two other stress−strain curves of samples having the same molecular weight (M_n = 100 000), but different PMMA contents, i.e. 42% and 28% for samples A and B, respectively. Increasing the MMA content thus promotes an increase in tensile strength and modulus, as expected at the expense of elongation.

DSC Analysis. Thermoplastic elastomers comprised of glassy−rubbery−glassy architectures are very useful materials under intensive investigation in both academic and industrial laboratories. The upper use-temperature of these triblocks is set by their thermal properties, i.e., the Tg of the glassy segment and the heat distortion temperature of the material (HDT). Since the Tg of polystyrene is below 100 °C, a dramatic decrease in SBS mechanical properties has been observed at temperatures higher than 70 °C.[39,40] PMMA has been known to have a higher Tg than PS, particularly when its syndiotactic content reaches 80%, i.e. a Tg around 130 °C.[32] From ^{1}H-NMR analysis it has been found that the PMMA block of all samples prepared under the present conditions (1:1 mixture of THF/cyclohexane and −78 °C) has ca. 78% syndiotacticity. Typical DSC thermograms are shown in Figure 9. A second order transition at low temperature is observed for the PBD phase from −90 °C to −8 °C, depending on the 1,2-units content. Another glass transition is seen at 125 °C for all samples, in good agreement with the value reported for homo-PMMA, confirming that the presence of a PBD block attached to the sPMMA chain does not influence the Tg of sPMMA domains and that phase separation of soft and hard components is complete.

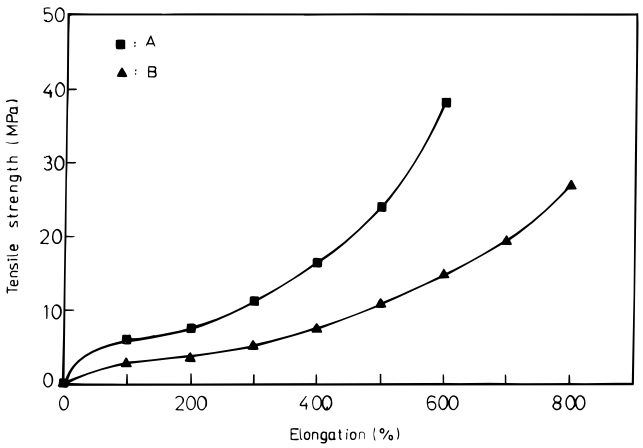


Figure 8. Effect of composition on the stress−strain curve of MBM triblocks (M_n = 100 000; 1,2-units = 42 wt %; MWD = 1.10): (A) PMMA content = 42 wt %; (B) PMMA content = 28 wt %. Both polymers were prepared in cyclohexane with 7.5 vol % diethyl ether.

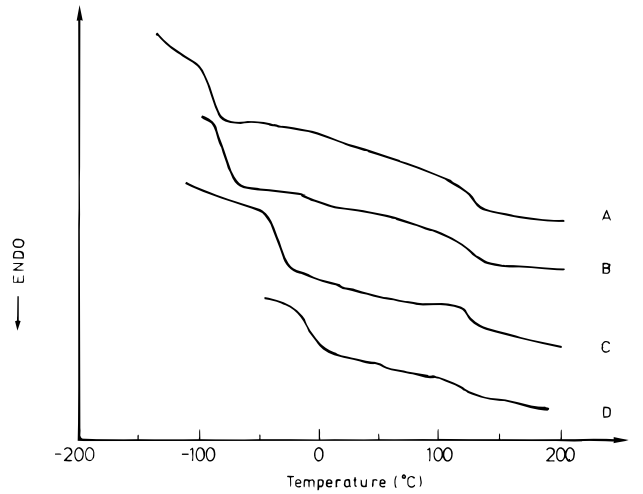


Figure 9. DSC curves of MBM triblock copolymers containing PBD moieties of various microstructures: (A) 17% 1,2-units (MW = 98 000; 33 wt % PMMA; MWD = 1.10); (B) 45% 1,2-units (MW = 92 000, 34 wt % PMMA; MWD = 1.10); (C) 66% 1,2-units (MW = 97 000, 33 wt % PMMA; MWD = 1.10); (D) 85% 1,2-units (MW = 95000; 33 wt % PMMA; MWD = 1.15).

Conclusion

Butadiene polymerization initiated with the difunctional initiator DiLi in hydrocarbon solvents produces a Li−DIB−PBD−Li chain rather than a Li−PBD−DIB−PBD−Li one. The species directly associated with the DIB moiety is sterically hindered to the point where the end-capping with diphenylethylene is prevented

from occurring, leading to the very early termination of the MMA polymerization. Thus, a direct synthesis of MBM triblock copolymer with high PBD 1,4-content by using DiLi is impossible. Triethylamine, anisole, and diphenyl ether are too weakly polar additives for promoting two active ends on the initiator. tBME, diethyl ether, TMEDA, and THF are efficient polar additives generating approximately two active species per DIB molecule, but also a high 1,2-content in the PBD central block. Although the seeded initiator prepared in the presence of *t*-BuOLi and anisole is efficient for the synthesis of a SBS triblock copolymer, the MBM copolymers prepared with it are contaminated with a variable amount of diblock. When PBD dianionic chains are capped with a very short styrene segment, a MBM-like triblock copolymer with a high 1,4-microstructure content was finally obtained. The polystyrene-modified MBM triblock copolymers were found to have better mechanical properties and higher service temperatures than conventional SBS thermoplastic elastomers. The microstructure, diblock content, and composition have an important effect on the bulk properties of those MBM triblock copolymers. An increase in 1,2-content decreases the tensile strength and elongation at break but increases the modulus. Tensile strength is also decreased when triblock copolymers are contaminated with diblock copolymers. Increasing the MMA content increases tensile strength and modulus at the expense of elongation.

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