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Syndiotactic Poly(methyl methacrylate) (sPMMA)−Polybutadiene (PBD)−sPMMA Triblock Copolymers: Synthesis, Morphology, and Mechanical Properties

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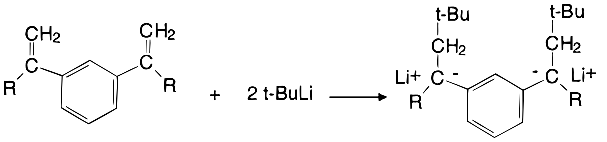
ABSTRACT: A series of syndiotactic poly(methyl methacrylate) (sPMMA)−polybutadiene (PBD)−sPMMA triblock copolymers, or MBM, have been successfully synthesized by using dilithium initiators (DLi's) based on the diadduct of *tert*-butyllithium (*t*-BuLi) to either 1,3-bis(1-phenylethenyl)benzene (PEB) or *m*-diisopropenylbenzene (*m*-DIB). The efficiency of these DLi's in building up MBM triblock copolymers has been compared under the same experimental conditions, i.e., in a cyclohexane/diethyl ether mixture for the butadiene polymerization at room temperature and in a cyclohexane/THF mixture for the MMA polymerization at −78 °C. Although all the synthesized copolymers show a monomodal, symmetric, and very narrow molecular weight distribution, the MBM copolymers synthesized with the *m*-DIB/*t*-BuLi diadduct are pure triblocks and show a high tensile strength, in contrast to copolymers initiated by the PEB/*t*-BuLi diadducts that are of a lower tensile strength and contaminated by MB diblock copolymers. Solvent cast films of MBM prepared with the *m*-DIB/*t*-BuLi diadduct are two-phase materials as confirmed by DSC and dynamic mechanical analysis (DMA). Transmission electron microscopy (TEM) shows a spherical morphology at a low sPMMA content, that changes into a cylindrical and finally lamellar morphology upon increasing the sPMMA content. Phase separation is observed for MBM with $\bar{M}_n$ of the sPMMA blocks as low as 6000. Dependence of tensile strength on copolymer structure and sample preparation has been studied. The smaller sPMMA molecular weight, $\bar{M}_n$(PMMA), required for high tensile strength depends on the PBD molecular weight, $\bar{M}_n$(PBD), e.g. 12 000 for M_n(PBD) = 36 000 and 6000 for M_n(PBD) = 80 000. The upper $\bar{M}_n$(PMMA) is ca. 20−25 000, whatever the M_n(PBD). The optimum tensile strength is observed for $\bar{M}_n$(PMMA) = 15 000, independently of M_n(PBD) in the studied range. As a rule, the tensile strength tends to level off and the elongation at break starts to decrease when the sPMMA content is increased beyond 35 wt %. At a constant sPMMA content, M_n(PBD) (>ca. 36 000) does not affect the ultimate tensile properties.

Introduction

Block copolymers of the ABA type exhibit a number of unique thermomechanical properties as a result of their phase morphology. The typical example is styrene−butadiene−styrene triblock copolymers (SBS). Microphase separation of the polystyrene blocks into glassy microdomains dispersed in the continuous rubbery polybutadiene (PBD) phase results in a physical network of flexible chains. The glassy microdomains primarily act as thermoreversible cross-links for the elastomeric matrix, although a role of reinforcing filler has also been proposed. The tensile strength of the thermoplastic elastomers depends upon the ability of the hard blocks to avoid a plastic deformation under stress. So, the strength decreases sharply as the glass transition temperature (T_g) of the hard block is approached. The upper service temperature of SBS is accordingly limited to ca. 70 °C. It would thus be worth substituting polystyrene (T_g = 100 °C) for a hard block of a higher service temperature. For this purpose,[1−5] poly(α-methylstyrene),[1,5] poly(ethylene sulfide),[2] and poly(*tert*-butyl methacrylate) (PtBMA)[4] have been considered as a substitute for polystyrene.

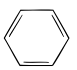
Methyl methacrylate (MMA) is a valuable candidate for the hard block, since syndiotactic PMMA (sPMMA) has a T_g higher than 120 °C depending on the molecular weight, and the additional advantage of forming a stereocomplex with isotactic PMMA (iPMMA). The melting temperature of the stereocomplex is close to 190 °C,[6] which is a very desirable upper service temperature.

Synthesis of sPMMA−PBD−sPMMA thermoplastic elastomers is, however, quite a problem. Indeed, living anionic polymerization of MMA is challenged by the difficult purification of MMA and by the side reactions that occur during propagation above −65 °C.[7−9] Furthermore, the higher thermodynamic stability of the MMA enolate compared to the dienyl anion requires starting the synthesis with PBD so that a difunctional initiator must be available which is soluble in hydrocarbons and forms rubbery *cis*-1,4-PBD. Finally, the polarity of the polymerization medium has to be increased before the addition of MMA, whose anionic polymerization is completely out of control in apolar solvents. Part of the living polybutadiene chains can be killed by impurities added on this occasion. Diadducts of alkyllithium on 1,3-bis(1-phenylethenyl)benzene (PEB) have been claimed as efficient difunctional initiators[10] for the synthesis of SBS with good mechanical properties. Compounds based on the metalation of *m*-diisopropenylbenzene (*m*-DIB) with *sec*- and *tert*-butyllithium have also been reported[11,12] as valuable difunctional initiators soluble in apolar solvents. These two types of difunctional initiators are schematized below:



PEB or m-DIB

I or II

PEB: R=  I=1,3-phenylenebis(3-dimethyl-1-phenylbutylidene)dilithium

m-DIB:R=CH$_3$ II=1,3-phenylenebis(3-dimethyl-pentylidene)dilithium

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Both *m*-DIB- and PEB-based difunctional initiators have been used in this work for the synthesis of a series of sPMMA−PBD−sPMMA thermoplastic elastomers. Indeed, the ultimate mechanical properties of thermoplastic elastomers strongly depend on the weight composition and the relative length of hard and soft blocks as supported by the fundamental structure−property relationships established for the SBS triblocks. In contrast, only very few data have been made available for the MBM copolymers until now. Although Hogen-Esch et al.[3] have used a *m*-DIB-based difunctional initiator for the synthesis of MBM triblock copolymers, they have not reported on the mechanical properties. It is why this paper aims at investigating the most reliable strategy for the synthesis of pure MBM triblocks, whose morphology and mechanical properties have been studied in a close relationship to the chemical composition and the relative block length.

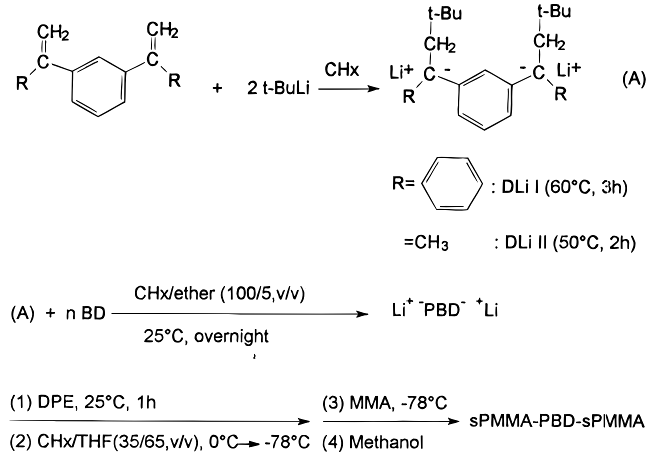
Experimental Section

Materials. Cyclohexane (CHx) and diethyl ether were dried over CaH_2 for 24 h. THF was purified by refluxing over the deep purple sodium−benzophenone complex. All the solvents were further distilled from poly(styryllithium) under reduced pressure just prior to use. *Tert*-Butyllithium (*t*-BuLi) (Aldrich, 1.3 M solution in cyclohexane) was diluted with cyclohexane (ca. 0.2 N) and titrated by the double titration method.[24] *m*-Diisopropenylbenzene (*m*-DIB, Aldrich) was first distilled over CaH_2 for 24 h and then from fluorenyllithium before use. 1,1-Diphenylethylene (PEB) was synthesized and purified according to a reported method.[13] 1,1-Diphenylethylene (DPE, Aldrich) was dried over *s*-BuLi and distilled from diphenylmethyllithium prior to use. Butadiene was dried over *n*-BuLi. Methyl methacrylate (MMA, Aldrich) was distilled from CaH_2 under reduced pressure and stored under nitrogen at −20 °C. Before polymerization, it was added with a 10 wt % $AlEt_3$ solution in hexane until a persistent yellowish green color was observed. It was then redistilled under reduced pressure just prior to use.

Initiator. Difunctional initiators (DLi's) were prepared in cyclohexane as reported in the scientific literature,[10b,11,12] by reaction of 2 equiv *t*-BuLi with PEB (DLi I) and *m*-DIB (DLi II), respectively. The reaction conditions were 3 h at 60 °C for DLi I[10b] and 2 h at 50 °C for DLi II.[11] The freshly prepared initiator solutions were homogeneous deep red color solutions (concentration of 0.05 N) free from any precipitate.

Block Copolymerization. Polymerization was carried out in a 2 L round-bottomed flask equipped with a magnetic stirrer under a dry-nitrogen atmosphere. Details of the experimental techniques were reported elsewhere.[3,12] Briefly, the synthesis consisted of the three steps shown in Scheme 1: (i) polymerization of butadiene initiated by I (or II) in a cyclohexane/diethyl ether mixture (100/5, v/v) at room temperature for one night; (ii) end-capping of the PBD dianions by diphenylethylene (DPE) at room temperature for 1 h, which is necessary to avoid side reactions during the initiation of MMA by PBD anions;[7] (iii) Addition of LiCl containing THF at 0 °C so that the cyclohexane/THF v/v ratio was 35/65 and the LiCl/Li molar ratio was 5. MMA was then added at −78 °C. In this polar reaction medium, the anionic polymerization of MMA was living and the content of syndiotactic PMMA triad was high, resulting in a higher T_g compared to that of PMMA prepared by radical polymerization. Copolymers were recovered by precipitation in methanol and dried at room temperature under vacuum for 2 or 3 days. Polymerization yields were quantitative.

Scheme 1. Synthesis of MBM Triblock Copolymers



Homo sPMMA. sPMMA of the same microstructure as the M block in the MBM triblocks was prepared by initiating the MMA polymerization by the adduct of 1,1-diphenylethylene (DPE) and *t*-BuLi.[8] Polymerization was carried out in THF in the presence of LiCl ([LiCl]/[Li] = 5) at −78 °C for 30 min. This polymerization time was arbitrarily fixed, although longer than the time required for the complete polymerization.

Sample Preparation. Films were prepared by casting a copolymer solution (8 wt %: 80 mL) containing a hindered phenol antioxidant (tetrakis[1-(methoxycarbonyl)-2-(3′,5′-di-*tert*-butyl-4′-hydroxylphenyl)ethyl]-methane, Irganox 1010, Ciba-Geigy Corp.; 1 wt %) in a 100 mm diameter Petri dish. The solvent was evaporated over 3−4 days at room temperature. Films were dried to a constant weight in a vacuum oven at 40 °C for ca. 2 days. The 0.6 mm thick films were colorless, transparent, and elastomeric with a smooth surface.

Analysis. Molecular weight and molecular weight distribution were measured by size exclusion chromatography in THF with a Waters GPC 501 apparatus equipped with linear styragel columns. The molecular weights of PBD and sPMMA were calculated according to the universal calibration method[18] by using polystyrene standards and the appropriate viscosimetric relationships:

$$[\eta] = 4.57 \times 10^{-4} M^{0.693} \text{ (PBD in THF)}^{28}$$

$$[\eta] = 1.36 \times 10^{-4} M^{0.714} \text{ (PS in THF)}^{19}$$

$$[\eta] = 1.298 \times 10^{-4} M^{0.688} \text{ (PMMA in THF)}^{26}$$

^{1}H NMR spectra were recorded with a Bruker AN-400 spectrometer, by using $CDCl_3$ as a solvent at 25 °C. The 1,2 unit content of PBD was calculated from the relative intensity of the signals at 4.9 ppm (=CH2, 1,2 units) and 5.4 ppm (CH=, 1,2 units and −CH=CH−, 1,4 units), respectively. The copolymer composition was calculated from the relative intensity of the signals at 4.9 ppm (1,2 units) and 3.6 ppm (O−CH_3 of the MMA units), respectively. From copolymer composition and PBD molecular weight, the M_n of PMMA was easily derived.

Differential scanning calorimetry (DSC) was carried out with a DuPont 900 instrument, calibrated with indium. The heating rate was 20 °C/min, and the glass transition temperature was reported at the inflection point of the heat capacity jump. The width of the glass transition (ΔT_g) was the difference in the temperatures at the intersections of the tangent to the heat capacity curve at T_g with the extrapolated baselines.

Dynamic mechanical analysis (DMA) was carried out with a TA 983 dynamic mechanical analyzer. Samples (8 × 10 × 2 mm) were deformed at a constant frequency (1 Hz) and strain amplitude (0.4 mm).

A transmission electron microscope (Philips CM-12) was used at an accelerating voltage of 100 kV in order to observe ultramicrotomed sections (70 nm thick) previously exposed to a 1% aqueous solution of OsO_4 for 20 min.

Tensile properties were measured with a Adamel Lhomargy tensile tester. Testing samples (microdumbells) were cut from solution cast films and extended at 200 mm/min at room temperature. Each measurement was repeated three times.

Results and Discussion

Synthesis. The prerequisite for the establishment of the fundamental structure−property relationships for the MBM triblock copolymers is the capability to synthesize these copolymers with well-defined molecular architecture, chain microstructure, molecular weight, composition, and narrow molecular weight distribution, in a large range of chain lengths. As recalled in the Introduction, difunctional initiators (DLi I and II) have been reported in the scientific literature for the preparation of the SBS triblock copolymers. In order to compare the efficiency of these two initiators, two series of MBM triblock copolymers have been synthesized under the same experimental conditions. The first series has been synthesized with the PEB/*t*-BuLi adduct as initiator (DLi I) according to the modified pathway by Tung et al.[10] The second method recently reported by our laboratory[12] and based on the *m*-DIB/*t*-BuLi adduct (DLi II), has been used for the synthesis of the second series of triblocks. Detailed studies on the efficiency of the DLi II initiator in neat cyclohexane and the effect of polar additives have been reported.[11,12] It is worth noting that diethyl ether has been used to enhance the initiator efficiency instead of *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) used by Tung et al.[10]

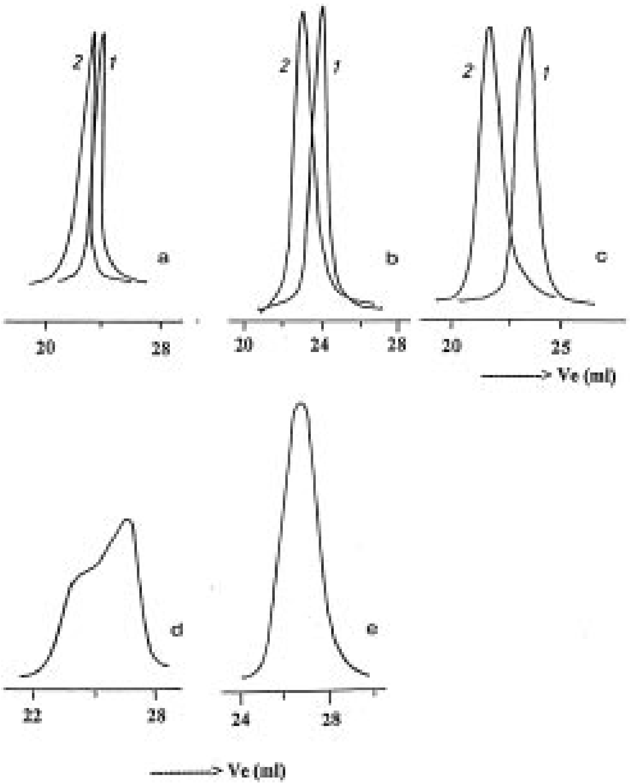


Figure 1. Typical SEC traces for the PBD precursor (trace 1) and the MBM triblock copolymer (trace 2) for samples A3 (a), B14 (b), and B6 (c). The same for the PMMA block released as result of the PBD degradation by OsO_4 for samples A3 (d) and B14 (e).

Table 1. Synthesis and Characterization of the sPMMA−PBD−sPMMA Triblock Copolymers

		PBD		PMMA (%)		MBM	
sample	DLi[a]	1,2 (%)[b]	$\bar{M}_n$cal[c]	content[d]	syndio[b]	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$
A1	I	54	45	41 (42)	78	16−46−16	1.10
A2	I	53	50	33 (45)	79	13−52−13	1.10
A3	I	51	65	38 (40)	78	20−66−20	1.20
B1	II	44	30	28 (30)	77	7−36−7	1.10
B2	II	44	30	32 (35)	78	9−36−9	1.10
B3	II	45	30	40 (42)	75	12−36−12	1.10
B4	II	44	30	53 (55)	77	20−36−20	1.05
B5	II	43	30	66 (67)	77	35−36−35	1.10
B6	II	43	30	72 (73)	77	46−36−46	1.10
B7	II	43	70	13 (15)	77	6−80−6	1.10
B8	II	46	70	20 (20)	78	10−80−10	1.10
B9	II	40	70	26 (25)	78	14−80−14	1.10
B10	II	40	70	33 (35)	77	20−80−20	1.10
B11	II	42	70	38 (40)	77	25−80−25	1.10
B12	II	46	70	56 (55)	78	50−80−50	1.10
B13	II	42	35	39 (38)	77	13−40−13	1.10
B14	II	43	50	35 (38)	77	16−60−16	1.10
B15	II	42	60	36 (38)	77	20−70−20	1.10
B16	II	43	100	38 (38)	77	40−130−40	1.10
B17	II	68	50	32 (33)	78	14−60−14	1.10

[a] Difunctional initiator, I = PEB/*t*-BuLi, II = *m*-DIB/*t*-BuLi. [b] ^{1}H NMR. [c] calculated as the ratio of the monomer weight over the initiator mole number. [d] ^{1}H NMR; values of the theoretical content are in parentheses.

Molecular characteristics of the triblock copolymers are summarized in Table 1. Figure 1 compares the typical SEC traces of the PBD midblock and the final triblock initiated by DLi I (sample A3, Figure 1a) and DLi II (samples B14 and B6, Figure 1b,c), respectively. Molecular weight distributions are monomodal, symmetrical, and very narrow ($\bar{M}_w/\bar{M}_n \sim 1.10$). Furthermore, the molecular weight of the PBD midblock as estimated by SEC is in good agreement with the calculated value for DLi I and slightly higher than expected for DLi II (Table 1). Finally, the PMMA content is close to the predicted value in both cases. All these observations suggest that triblock copolymers are not contaminated by homopolymer or diblock copolymer, whatever the initiator used. In order to support this conclusion, the PBD midblock of these A3 and B14 copolymers has been degraded by oxidation with OsO_4, and the residual PMMA block which is stable under these conditions[11] has been analyzed by SEC, as shown in Figure 1. The molecular weight distribution of the residual PMMA in sample A3 is bimodal (Figure 1d) with a factor of ca. 2 between the molecular weight of the two populations of PMMA chains. From the relative area of the two elution peaks it appears that copolymer A3 is contaminated by ca. 40% diblock copolymer that contains a PMMA block ca. twice as long as the triblock copolymer. The presence of diblock copolymer is consistent with the lower tensile properties compared to pure triblock copolymers, as will be shown in the stress−strain section. In sharp contrast a monomodal distribution ($\bar{M}_w/\bar{M}_n = 1.20$) is observed for the residual

PMMA in sample B14 (Figure 1e). The average molecular weight of the PMMA block is in good agreement with the expected value for the pure triblock copolymer. The absence of significant contamination by diblocks is also supported by high mechanical performances, as discussed later. Although contamination of sample A3 by diblock copolymer cannot be predicted from the narrow molecular weight distribution observed for the crude copolymer, this contamination is reproducible and does not result from a fortuitous error in the experiments. A possible explanation might be a mixture of mono- and difunctional active species in DLi I leading to the simultaneous formation of di- and triblock copolymers. The difference in molecular weight of the sPMMA blocks in di- and triblock copolymers is unexpected and suggests a difference in reactivity for the mono- and difunctional species. A more detailed investigation is required to clear up this issue.

The addition of MMA to a DLi initiator results in gelation of the polymerization medium, even at a total copolymer concentration as low as 3 wt % in a cyclohexane/THF (50/50, v/v) mixture. In contrast, no gel is observed in the case of diblocks prepared under the same experimental conditions, at a higher copolymer concentration. It is essential to delay this gelation at least until MMA has been completely added to the reaction medium. For this purpose, the THF content of the solvent mixture has been increased (cyclohexane/THF 35/65) and LiCl has been added ([LiCl]/[Li] = 5), which is known to contribute to the living polymerization of MMA[7] while keeping the PMMA tacticity unchanged.[29] The gel becomes completely soluble upon termination of the copolymerization reaction by addition of small amounts of methanol. All these observations indicate that the living chain ends are in dipolar interactions as strong as the medium is apolar.

In a second step, DLi II has been systematically used to prepare a large series of MBM triblocks (Table 1). In reference to the SBS thermoplastic elastomers that contain a PBD block in the molecular weight range of 40 000−80 000 and polystyrene (PS) blocks of 10 000−20 000,[21] MBM samples have been synthesized with a PBD molecular weight in the range of 36 000−130 000 and PMMA in the range of 6000−50 000. The effect of composition and chain microstructure has also been studied by varying the PMMA content from 13 to 72% and the PBD microstructure from 40 to 68% 1,2 units. Actually, the 1,2 unit content has been varied in the 40−46% range by using diethyl ether as a polar modifier,[31] and it has been raised to 68% by traces of THF.[31] MBM containing PBD of smaller 1,2 unit content (<20%) will be reported in a forthcoming paper.[32] The cis-1,4/trans-1,4/1,2 units ratio is 20/37/43 for PBD prepared by anionic polymerization with ether as the polar additive.[30] All these samples have a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.10$). ^{1}H NMR analysis also shows that the PMMA tacticity is essentially constant in the whole series, with the syndiotactic content in the range 75−78%.

HomoPMMAs of molecular weight from 5000 to 77000 have also been synthesized for the sake of comparison in thermal studies (Table 2).

DSC Studies. Measurement of the glass transition temperature (T_g) is the most rapid although not the most sensitive way to detect the phase separation in block copolymers. Observation of as many glass transitions as immiscible constitutive blocks in the copolymer is predicted at temperatures that depend on the extent of phase separation. Figure 2 shows typical DSC traces for the MBM triblock copolymers, and particularly for the B1 to B6 series (Table 1) that contain a PBD block of the same molecular weight and PMMA blocks of increasing molecular weight (7000−46000). In all the cases, two T_g's are observed, which is a clear indication of phase separation, with the lowest T_g (T_{g_1}) characteristic of the PBD phase and the T_g at the higher temperature (T_{g_2}) assigned to the PMMA phase. For B1 and B2 samples of the lower molecular weight, T_{g_2} is diffuse due to the low content in PMMA. T_{g_1} is essentially independent of the copolymer composition, and thus of the PMMA molecular weight in this series (Table 3). This molecular parameter has thus no significant effect on the degree of phase separation in the studied range. T_{g_2} expectedly increases with the PMMA molecular weight in each series of triblocks containing the same central PBD block.

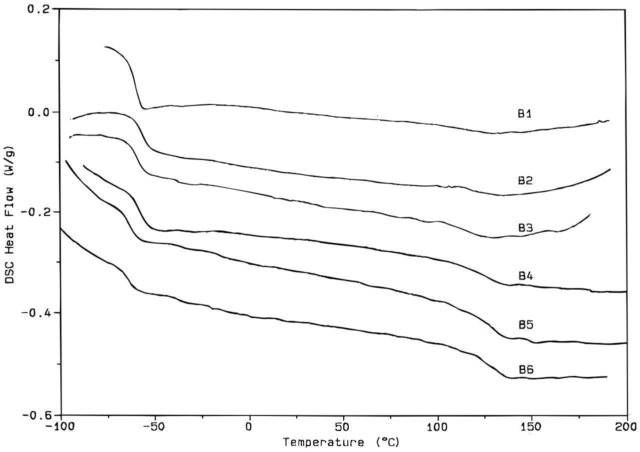


Figure 2. DSC traces for the B1 to B6 triblock copolymers (Table 1). Heating rate: 20 °C/min.

Table 2. Molecular Characteristics of HomoPMMA Initiated by the Adduct of 1,1-Diphenylethylene (DPE) and *t*-BuLi in THF at −78 °C

sample	$\bar{M}_n \times 10^{-3}$ [a]	$\bar{M}_w/\bar{M}_n$[a]	syndio (%)[b]
H1	5	1.20	77
H2	11	1.15	77
H3	19	1.10	77
H4	44	1.10	77
H5	77	1.10	77

[a] SEC with universal calibration (see text). [b] ^{1}H NMR.

The temperature and width of the glass transition are listed in Table 3 for triblock copolymers and homoPMMA's (H1 to H5). All samples have the same PMMA tacticity. In contrast to copolymer composition and molecular weight of each block, the microstructure of the PBD block has an effect on T_{g_1}, that increases from −60 to −38 °C when the 1,2 content of PBD is increased from 44% to 68%. This observation is in agreement with data reported in the scientific literature for PBD and SBS triblock copolymers.

Figure 3 and Table 3 show that the molecular weight dependence of T_g for PMMA is exactly the same for the homopolymer as for the outer block in the MBM triblocks. This observation contrasts with the T_g of PS, which is usually lower by ca. 20−30 deg compared to homopolystyrene (PS) of the same molecular weight ($\bar{M}_n$ < 121 000) in the SBS triblocks.[14] This difference in T_g for the outer blocks in MBM and SBS copolymers might be due to a better phase separation in MBM than in SBS as a result of a larger difference in the solubility parameter and polarity between the PBD and PMMA

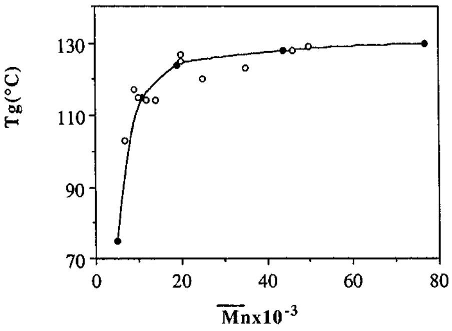


Figure 3. Molecular weight dependence of the glass transition temperature for PMMA: (●) homopolymers; (○) outer block in MBM triblocks.

Table 3. Glass Transition Temperature of PBD and PMMA Microphases in MBM Triblock Copolymers and for HomoPMMA

	DSC[a]			DMA[c]	
sample	T_g(PBD)	T_g(PMMA)	ΔT_g(PMMA)[b]	T_g(PBD)	T_g(PMMA)
A3	−60	120	20	nd	nd
B1	−59			−47	124
B2	−57	117	20	nd	nd
B3	−59	114	21	−43	125
B4	−60	127	20	−43	132
B5	−64	123	18	nd	nd
B6	−65	128	20	nd	nd
B7	−62			−46	128
B8	−62	115	20	nd	nd
B9	−63	114	21	nd	nd
B10	−65	125	20	nd	nd
B11	−64	120	20	−50	130
B12	−59	129	21	−44	136
B15	−62	120	19	−50	124
B17	−35	117	17	−22	134
H1		75	13		nd
H2		115	13		nd
H3		124	10		nd
H4		128	12		130
H5		130	10		nd

[a] heating rate 20 °C/min. [b] ΔT_g is the difference in temperature at the intersections of the tangent to the heat capcity curve at T_g with the extrapolated baselines. [c] heating rate: 5 °C/min. T_g was taken at the maximum of the G'' vs temperature curve (Figures 4 and 5).

blocks compared to the PBD/PS pair. The glass transition of PMMA in the MBM triblock copolymers is broader (17−20 °C) than that of homoPMMA's (10−13 °C) which might indicate the formation of a finite interphase between the PMMA and PBD microphases.

DMA Analysis. Figure 4 compares the temperature dependence of the dynamic shear storage (G') and loss (G'') moduli (from −100 to +180 °C) and the dynamic loss tangent (G''/G') for three triblock copolymers: B1 (Figure 4a), B3 (Figure 4b) and B4 (Figure 4c) and for the homoPMMA H4 (Figure 4d). All the triblock copolymers show two transitions in the vicinity of −45 and +130 °C, respectively (Table 3), which are assigned to the glass transition of the PBD and PMMA phases, respectively. In spite of the low molecular weight of PMMA in sample B1, the microphase separation is obvious (Figure 4a), since the two T_g's are clearly observed which was not the case by DSC (Figure 2). The storage modulus (G') increases with the PMMA content in the triblock copolymers. The rapid decrease in G', which is observed in the vicinity of T_g of PMMA, does not occur at a lower temperature in triblocks compared to homoPMMA (Figure 4), which indicates that the thermal resistance of PMMA is not adversely affected by the PBD phase.

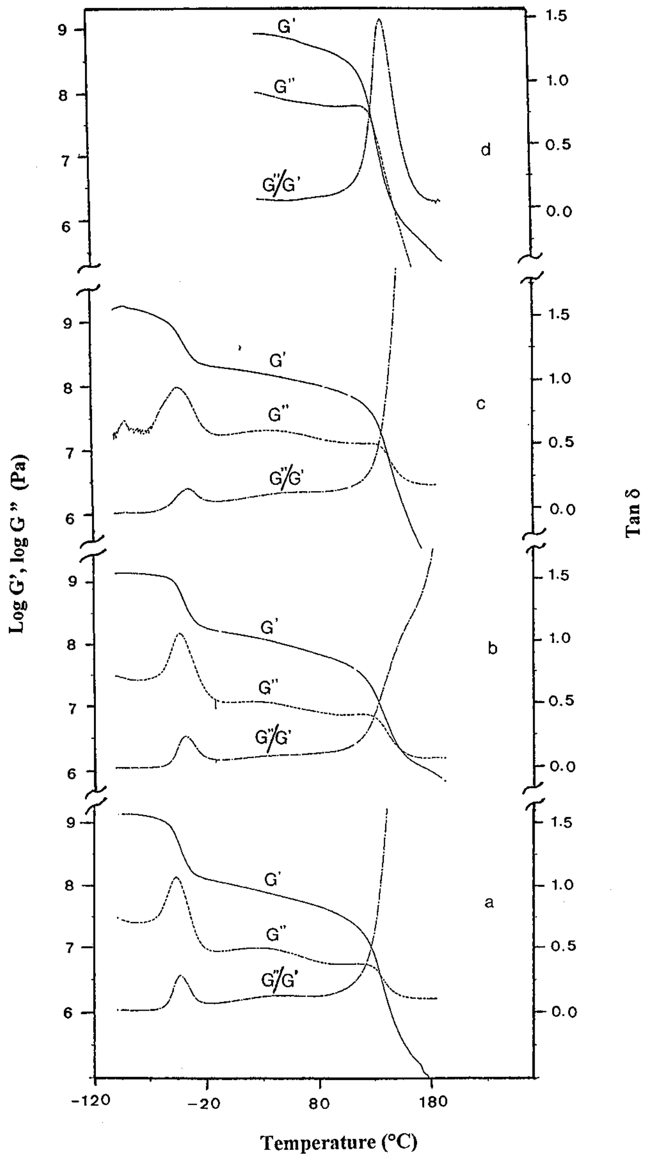


Figure 4. Shear storage (G') and loss (G'') modulus vs temperature at 1 Hz for samples B1 (a), B3 (b), B4 (c), and H4 (d). Heating rate: 5 °C/min.

Figure 5 compares the DMA curves for the B11 (Figure 5a) and B17 (Figure 5b) triblock copolymers which differ in the 1,2 content of the PBD block (42% for B11 and 68% for B17). Transition of the PBD phase is observed at a higher temperature (−22 °C) for the B17 sample, whereas the transition of the PMMA phase is quite comparable (Table 3).

Phase Morphology. It is well-known that the morphology of solvent cast films of SB and SBS copolymers strongly depends on the solvent used and the casting conditions, such as solvent evaporation rate and temperature.[16,17,23] It is why the solvent effect on the morphology of MBM copolymers has been investigated in this study. Figure 6 shows transmission electron micrographs for the B15 triblock copolymer cast from toluene (Figure 6a), cyclohexane/THF (20/80, v/v) (Figure 6b), and methyl ethyl ketone/THF (20/80, v/v) (Figure 6c), respectively. Toluene is a common solvent for PBD and PMMA; cyclohexane is a selective solvent for PBD, and methyl ethyl ketone (MEK) selectively dissolves PMMA. Since the MBM copolymer is insoluble in pure cyclohexane and pure MEK, a mixture of each of them with THF has been used for the film

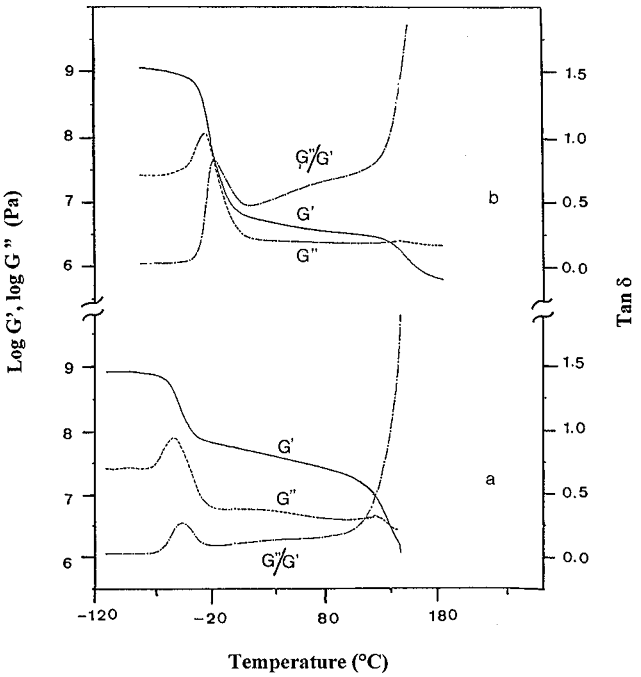


Figure 5. Shear storage (*G*′) and loss (*G*″) modulus vs temperature at 1 Hz for samples B11 (a) and B17 (b). Heating rate: 5 °C/min.

casting. Since PBD has been selectively stained by OsO_4, it is systematically observed as a dark phase. Figure 6a shows a highly regular cylindrical morphology with a hexagonal periodicity, which is characteristic of triblock copolymers of the ABA type with a content of 20–40% and cast from a common solvent for the two blocks.[17] When films are cast from a poor solvent for at least one of the two constitutive components, the microdomain morphology is perturbed, as illustrated by a poorly defined cylindrical morphology (Figure 6b compared to Figure 6a) when cyclohexane (in a mixture with THF) is used rather than toluene. When a selective solvent for PMMA is used (MEK/THF mixture: Figure 6c), a lamellar morphology is observed in spite of the relatively low PMMA content (36%). The selectivity of the solvent for the minor component explains that this component tends to form semicontinuous domains and why the PMMA layers are much thinner than the PBD ones.

The phase morphology observed in Figure 6 for solvent cast films is generally out of the thermodynamic equilibrium, since the same copolymer shows two deeply different phase organizations. The equilibrium morphology is dictated by the copolymer composition, as reported for the SB and SBS triblock copolymers.[17,24,25] As a rule, a spherical morphology is observed for a PBD content in the range of 0–18 wt %. For a PBD content as high as 18–38 wt %, a cylindrical morphology is observed, whereas a lamellar morphology is reported for 36–60 wt % PBD.[25] For the sake of comparison of SBS and MBM block copolymers, a series of MBM copolymers covering a large PMMA content (12–76 wt %) has been analyzed by TEM. The samples have been annealed for 4 days at 140 °C under vacuum, thus at a temperature higher than the T_g of the hard PMMA blocks, in order to reach the phase equilibrium as closely as possible.

Figure 7 shows the three typical phase morphologies, i.e. spheres of PMMA (Figure 7a) for the B7 sample of a low PMMA content (13 wt %), PMMA cylinders

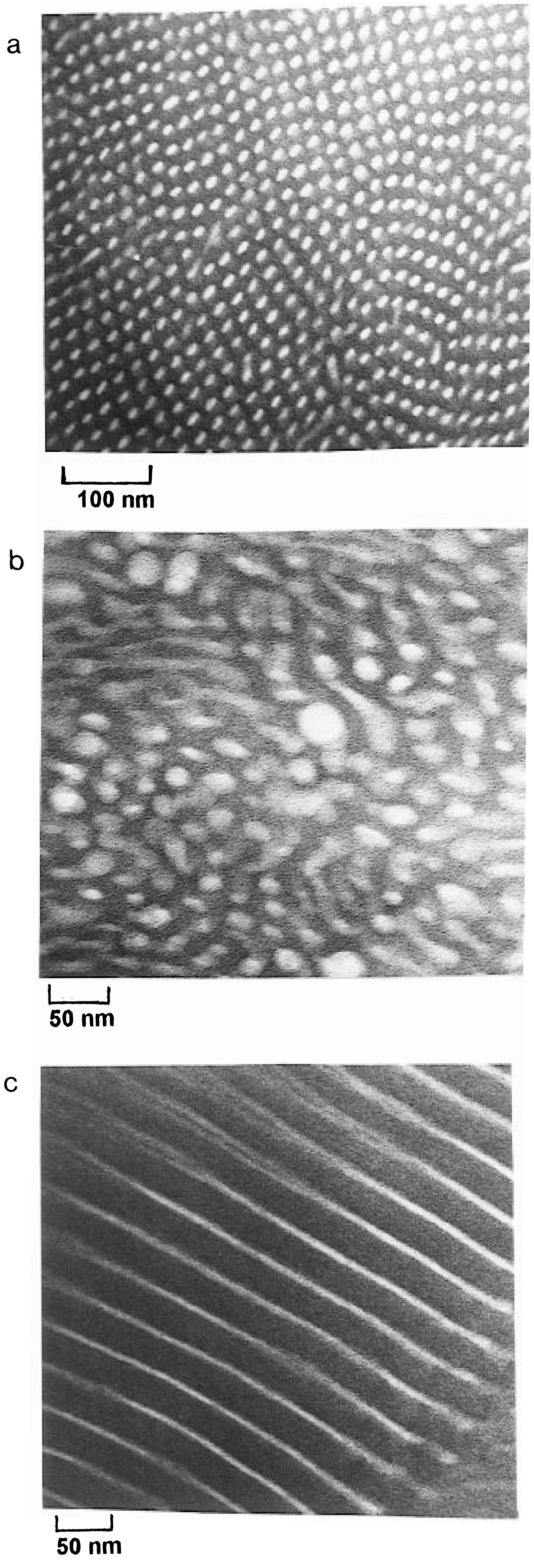


Figure 6. Transmission electron micrographs for the B15 sample cast from toluene(a), cyclohexane/THF (10/90, v/v) (b), and MEK/THF (10/90, v/v) (c). Selective staining of PBD by OsO_4.

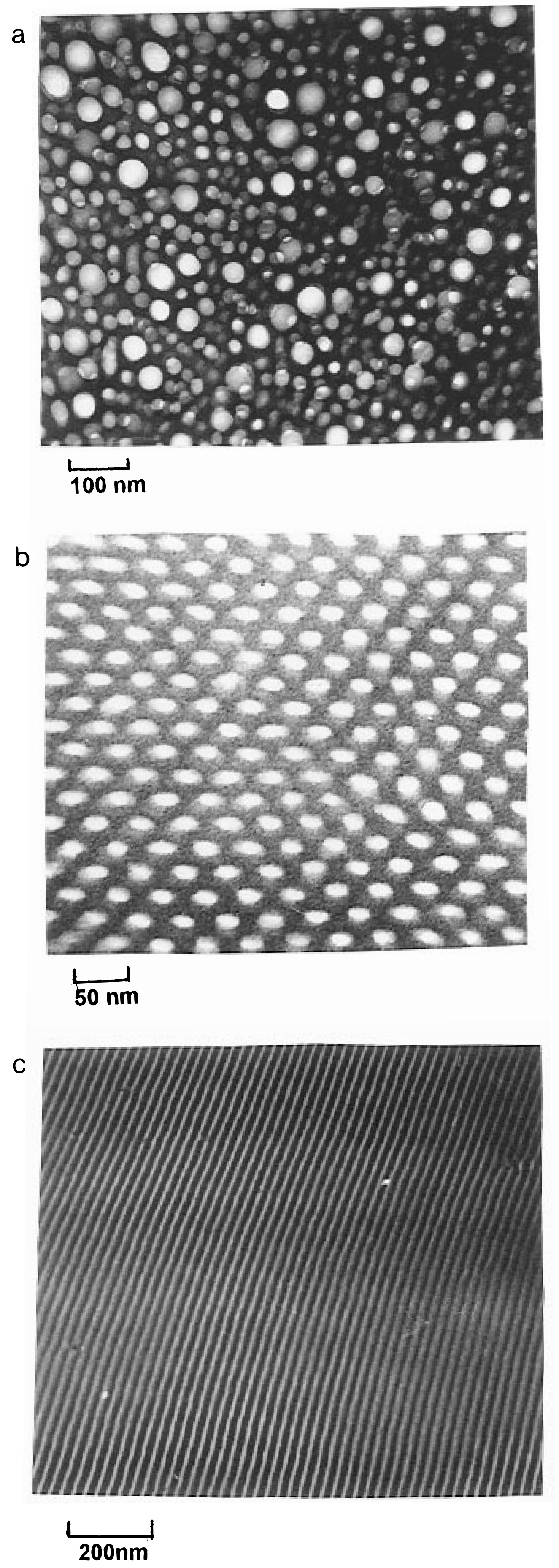


Figure 7. Transmission electron micrographs for samples B7 (a), B15 (b), and B6 (c). Annealing at 140 °C for 4 days.

Table 4. Composition Dependence of MBM Phase Morphology and Domain Size

samples	PMMA (%)	domain	R (nm)(TEM)[a]	R_{calc} (nm)[b]	R (nm) (SAXS)
B7	13	spheres	12.0	8.7 (1.5)	11.7
B8	20	cylinders	8.0	8.5 (1.5)	
B9	26	cylinders	8.2	9.7 (1.5)	9.1
B15	36	cylinders	10.3	12.0 (1.5)	11.5
B17	35	cylinders	11.2	10.0 (1.5)	
B4	53	lamellae	4.0	11.2 (1.0)	3.4
B5	66	lamellae	5.1	15.0 (1.0)	

[a] R stands for the radius of spheres and cylinders and the half-thickness of lamellae depending on the geometry of the PMMA microphases. [b] Calculated R as explained in the text. The value of α is shown in parantheses and is selected for the best fit with the experimental data.

(Figure 7b) for the B15 sample of an intermediate PMMA content (36 wt %), and alternate PBD and PMMA lamellae (Figure 7c) for the B6 sample of a high PMMA content (72 wt %). The copolymer composition–phase morphology relationship that emerges from the analyzed samples is shown in Table 4. At low PMMA contents (13 wt %), the spherical morphology is observed. When the PMMA content is increased to 20 wt %, a hexagonal cylindrical morphology is visible and is changed to a lamellar morphology when the PMMA content is higher than 40 wt %. It is worth noting that B7 shows a well-defined spherical morphology, although $\bar{M}_n$(PMMA) is very low (6000), and no phase separation occurs in the SBS copolymer containing such a short PS block.[24]

Table 4 also compares the domain size measured by transmission electron microscopy and by small angle X-ray scattering (SAXS), as will be discussed in a forthcoming paper. The domain size has also been calculated from the molecular weight of the individual blocks according to the following equations:[20]

$$\text{sphere} \quad R = 1.33\alpha K M^{1/2} \tag{1a}$$

$$\text{cylinder} \quad R = 1.0\alpha K M^{1/2} \tag{1b}$$

$$\text{lamellae} \quad R = 1.4\alpha K M^{1/2} \tag{1c}$$

where K is the ratio between the unperturbed root-mean-square end-to-end distance and the square root of the molecular weight for PMMA (56.5×10^{-3})[19] and R is the radius (nm) of spheres and cylinders, or the half-thickness of lamellae depending on the phase morphology observed. α is the perturbation which varies from 1.0 to 1.5 for most cases of interest. The agreement between experimental and calculated R values for spheres and cylinders is good, in contrast to what happens in the case of lamellar morphology, where the calculated values are 2 or 3 times higher than observed.

Stress–Strain Behavior. Tensile properties of triblocks prepared with the DLi I (samples A1 to A3) and the DLi II (samples B1 to B19) initiators are reported in Table 5. The initial modulus of the copolymers is essentially independent of the initiator used. The situation changes when tensile strength and permanent set at break are concerned. The ultimate tensile strength (σ_b) of block copolymers synthesized with DLi I is generally much lower compared to copolymers initiated by DLi II (Table 5). As shown by SEC analysis, samples synthesized with DLi I are contaminated by diblocks which are known to have a depressive effect on the tensile properties in the case of SBS triblock

Table 5. Mechanical Properties of MBM Triblock Copolymers

sample[a]	yield stress (MPa)	initial modulus (MPa)	ultimate tensile strength (MPa)	elongation at break (%)	permanent set at break (%)[d]
A1		7	10	500	27
A2		5	15	800	22
A3		5	20	740	20
B1		3	2	320	60
B2		12	11	800	42
B3	3	30	30	850	26
B4	11	106	33	700	64
B5	19	130	34	400	97
B6	42	700	35	140	124
B7		1	15	1300	26
B8		3	22	1100	29
B9		5	28	1000	31
B10		10	33	850	37
B11	5	80	34	800	57
B12	14	220	34	600	180
B12*	16	250	31	500	200
B13		9	34	850	37
B14		3	34	900	36
B15		5	34	890	31
B16		4	34	850	40
B17		7	26	700	37
B18[b]		3	27	700	57
B19[c]	6	46	27	600	100

[a] all samples were cast from toluene, except for B18 and B19. [b] sample B15 cast from cyclohexane/THF (90/10, v/v). [c] sample B15 cast from MEK/THF (90/10, v/v). [d] ratio of the unrecoverable deformation at break over the initial length.

copolymers[27]. σ_b of MBM triblock copolymers of a total molecular weight higher than 80 000 and a hard block content higher than 30 wt % exceeds 30 MPa, whereas it is smaller than 5 MPa for sPMMA−PBD diblock copolymers. Contamination of triblock copolymers by diblocks thus results in a decrease in σ_b depending on the diblock content. For instance, contamination of a MBM triblock (σ_b = 35 MPa) by 40 wt % diblock triggers a decrease of σ_b by a factor of ca. 2 (15 MPa),[32] which is consistent with the estimation of 40 wt % diblock in sample A3. The tensile properties are clearly improved when DLi II is substituted for DLi I, because then the triblock copolymers are no longer contaminated by diblocks, as discussed in a previous section.

The tensile properties of the thermoplastic elastomers of the SBS type are known to depend directly on the characteristics of the physical network which is formed as result of the immiscibility of the constitutive blocks. The higher the degree of phase separation the better the mechanical properties are. The next sections report on the properties of a series of MBM triblock copolymers in relation to their molecular weight and composition, and the sample preparation as well.

Effect of the Casting Solvent. The solvent casting technique with a slow solvent evaporation has been reported to yield reproducible phase morphology for SBS block copolymers.[14] Morphology and bulk properties of a solvent cast film however depend on the casting conditions, and particularly on the casting solvent, as discussed above.[23,24] Table 5 and Figure 8 illustrate the dependence of the mechanical properties of the B15 sample on the casting solvent: toluene, cyclohexane/THF (90/101 v/v), and MEK/THF (90/10 v/v). The sample cast from toluene (common solvent for PBD and PMMA) exhibits the highest ultimate tensile strength and elongation at break. When a THF/MEK mixture is used, the highest modulus and permanent set (i.e. irreversible deformation) together with a yield point are observed, which is indicative of the formation of a semicontinuous PMMA phase when a selective solvent for it (MEK) is used (see Figure 6c). Casting the copolymer film from a solvent mixture rich in cyclohexane (a selective solvent for PBD) results in a very soft material, since the initial modulus is the lowest and the ultimate properties are poorer compared to the toluene cast copolymer.

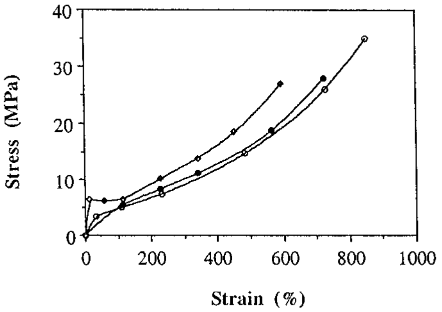


Figure 8. Stress−strain curves for the B15 MBM triblock copolymer cast from toluene (○), cyclohexane/THF (10/90, v/v) (●), and MEK/THF (10/90, v/v) (◇).

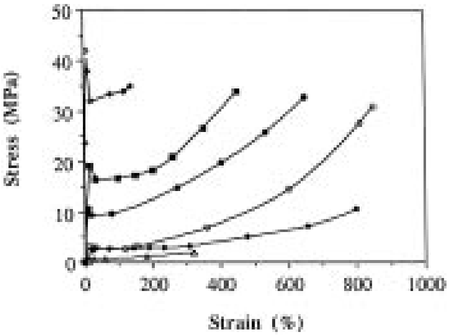


Figure 9. Effect of the PMMA content on the stress−strain curves for MBM triblock copolymers containing the same PBD block (36 000) and cast from toluene: B1 (△); B2 (♦); B3 (○); B4 (●); B5 (■); B6 (◇).

Effect of Length of the PMMA Block at Constant $\bar{M}_n$(PBD). Figure 9 compares the stress−strain curves for a series of six triblock copolymers (B1 to B6, Table 1) containing a PBD block (36 000) associated with PMMA blocks of increasing molecular weight (7000−46 000). A very small tensile strength is observed for the B1 sample that contains the shortest PMMA block. An increase in tensile strength and elongation at break is observed when $\bar{M}_n$ PMMA is increased up to a PMMA content of 40 wt %. At this composition, yielding occurs as result of at least partial continuity of the PMMA phase. Beyond 40 wt % MMA, the elongation at break regularly decreases with increasing PMMA content, whereas the ultimate tensile strength does not change very much. In parallel, yielding is steadily more pronounced, and at 72 wt % PMMA the yield stress exceeds the ultimate tensile strength. As expected, the initial modulus and the permanent set at break, which is a measurement of the unrecovered deformation, increase with increasing PMMA content. In this series of triblock copolymers, a PMMA molecular weight of $\bar{M}_n$ = 12 000 associated with a PBD block of 36 000 appears to be the best thermoplastic elastomer. In agreement with the similar entanglement molecular weight for PMMA (12 000) and PS (10 000),[15] the $\bar{M}_n$ of the PMMA end block that suits to good elastomeric properties is quite comparable to SBS containing a PBD block of the same length.[1]

Figure 10 refers to another series of MBM triblock copolymers, in which $\bar{M}_n$(PBD) is maintained constant at a higher value (80 000), whereas the $\bar{M}_n$(PMMA)

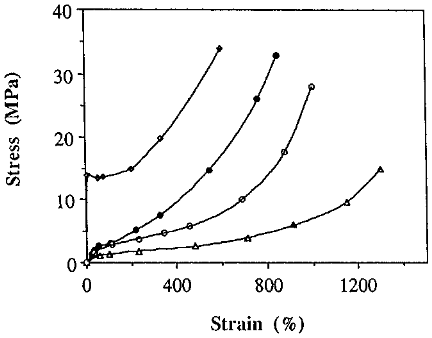


Figure 10. Effect of the PMMA content on the stress−strain curves for MBM triblock copolymers cast from toluene ($\bar{M}_n$ PBD = 80 000): B7 (△); B9 (○); B10 (●); B12 (◇).

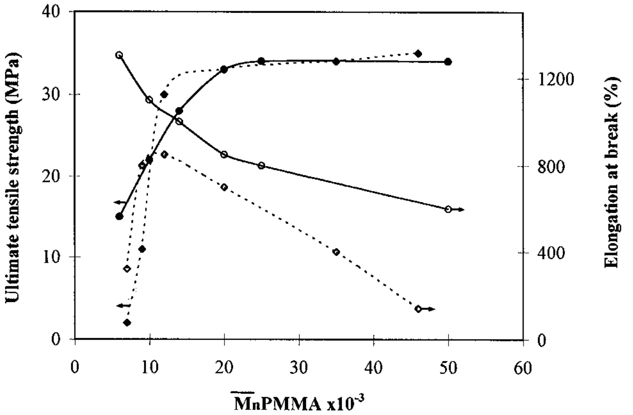


Figure 11. Ultimate tensile strength and elongation at break vs PMMA content for MBM triblock copolymers: $\bar{M}_n$ PBD = 36 000 (◆, ◇); $\bar{M}_n$ PBD = 80 000 (●, ○).

varies from 6000 to 50 000. The same general modification is observed in the stress−strain curves when $\bar{M}_n$(PMMA) is increased for the two series of triblocks. When $\bar{M}_n$(PBD) is increased, $\bar{M}_n$(PMMA) also has to be increased (20 000 in the second series compared to 12 000 in the first one) for the ultimate tensile strength to be the highest. As shown in table 5, samples B1 and B7 are of a comparable $\bar{M}_n$(PMMA). However, the ultimate tensile strength and elongation at break are higher for B7 (15 MPa, 1300%) than for B1 (2 MPa, 320%), which more likely results from a more complete phase separation as a result of a much higher molecular weight for the PBD block. It is indeed well-known that polymer immiscibility increases with molecular weight.[1]

Figure 11 summarizes the effect of the PMMA length on the ultimate tensile strength and elongation at break of MBM triblock copolymers. At low $\bar{M}_n$(PMMA) (<10 000), $\bar{M}_n$(PBD) significantly affects the tensile properties of the triblocks. At higher $\bar{M}_n$(PMMA) (>15 000), this effect on the ultimate tensile strength becomes completely negligible, whereas a difference in elongation at break persists in favor of the copolymers containing the longest PBD block. The B12 sample has been annealed at 120 °C for 15 h (sample B12* in Table 5) without a significant effect on the tensile properties (Table 5).

Effect of Molecular Weight at a Constant PMMA Content. Figure 12 compares stress−strain curves for a series of MBM triblock copolymers of different molecular weights at a comparable PMMA content (samples B13 to B16). The most characteristic data are listed in Table 5. $\bar{M}_n$(PBD) varies from 40 000 to 130 000 and $\bar{M}_n$(PMMA) from 13 000 to 40 000, respectively. Both the ultimate tensile strength and elongation at break do not depend on the block molecular weight, so that the stress−strain curves are quite similar (Figure 12). This observation is consistent with previous conclusions for SBS triblock copolymers.[1,21,22]

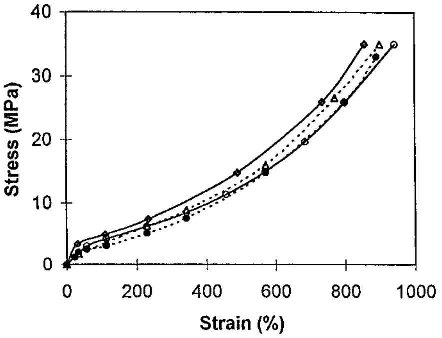


Figure 12. Stress−strain curves for MBM triblock copolymers of various molecular weights and comparable PMMA contents: B13 (◇); B14 (●); B15 (△); B16 (○).

Effect of PBD Microstructure. The B14 and B17 copolymer pair (Table 5) illustrates the effect of the PBD microstructure on the tensile properties of otherwise identical MBM triblocks. The B17 sample of a higher 1,2 content has a lower ultimate tensile strength, whereas the elongation and permanent set at break are comparable.

Conclusions

A series of syndiotactic poly(methyl methacrylate) (sPMMA)−polybutadiene (PBD)−sPMMA triblock copolymers (or MBM) has been synthesized by using two different dilithium initiators (DLi). These initiators have been prepared by addition of *t*-BuLi (2 equiv) to either 1,3-bis(1-phenylethenyl)benzene (PEB) (DLi I) or *m*-diisopropenylbenzene (*m*-DIB) (DLi II). The butadiene polymerization has been carried out in cyclohexane/diethyl ether at room temperature, whereas MMA has been polymerized in a second step in a cyclohexane/THF mixture at −78 °C. Although each block copolymer exhibits a symmetrical and very narrow molecular weight distribution, MBM copolymers prepared with DLi I are contaminated by MB diblocks and accordingly show poorer tensile properties than the pure triblocks initiated by DLi II.

Clear solution cast films of pure MBM triblocks (DLi II initiator) have been characterized by DSC, dynamic and static mechanical analysis, and transmission electron microscopy. All the investigated triblocks are phase separated with two transition temperatures at ca. −60 and +125 °C. The glass transition temperature for the PMMA microphases is not smaller than the T_g of the parent homoPMMA, which indicates a high degree of phase separation (even for $\bar{M}_n$(PMMA) as low as 6000). The casting solvent greatly affects the phase morphology. Annealed samples of a large composition range exhibit the well-known phase morphologies, i.e. a spherical morphology at low sPMMA content (13 wt %), followed by cylindrical and lamellar morphologies upon increasing the sPMMA content.

The effect of molecular weight, composition, and sample preparation on the tensile properties has been studied. A typical behavior of the thermoplastic elastomer is observed for a sPMMA molecular weight that depends on the length of the PBD block, i.e. 12 000 for $\bar{M}_n$(PBD) = 36 000 and 6000 for $\bar{M}_n$(PBD) = 80 000. The highest ultimate tensile strength is observed for $\bar{M}_n$(PMMA) = 15 000 independently of $\bar{M}_n$(PBD) in the studied range. The sPMMA content greatly affects the ultimate tensile strength up to ca. 35%. Beyond that content, the tensile strength remains constant and the elongation at break decreases, which agrees with a continuous thermoplastic phase.

Stereocomplexation of MBM triblock copolymers with isotactic PMMA has been discussed elsewhere.[33] Hydrogenation of MBM and temperature dependence of the tensile properties will be the topic of forthcoming papers.[34,35]

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