Poly[poly(isobornyl methacrylate-*co*-methyl methacrylate) (poly(IBMA-*co*-MMA))-*b*-polybutadiene-*b*-poly(IBMA-*co*-MMA)] Copolymers: Synthesis, Morphology, and Properties

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Received December 17, 1996; Revised Manuscript Received June 30, 1997[⊗]

ABSTRACT: Anionic random and block copolymerization of isobornyl methacrylate (IBMA) and methyl methacrylate (MMA) has been studied in THF at −78 °C by using (1,1-diphenyl-3,3-dimethylbutyl)lithium (DDBLi) as initiator in the presence of LiCl. The random copolymerization of MMA and IBMA has also been carried out at 0 °C, all the other conditions being kept unchanged. Poly[poly(IBMA)-*b*-poly(BD)-*b*-poly(IBMA)] (IBI), poly[poly(IBMA-*co*-MMA)-*b*-poly(BD)-*b*-poly(MMA-*co*-IBMA)] (I/MBM/I), and poly[poly(IBMA)-*b*-poly(MMA)-*b*-poly(BD)-*b*-poly(MMA)-*b*-poly(IBMA)] (IMBMI) block copolymers have been synthesized by sequential anionic polymerization of butadiene, MMA, and IBMA initiated by the *m*-diisopropenylbenzene (*m*-DIB)/*tert*-butyllithium (*t*-BuLi) diadduct. These block copolymers of a monomodal and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.1$) have been analyzed by size exclusion chromatography (SEC), NMR, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and transmission electron microscopy (TEM). Stereocomplexation of IMBMA and I/MBM/I with iPMMA has also been studied by DSC. Although IBI triblock copolymers show a lamellar morphology even for relatively low hard block content (33 wt %), cylindrical and lamellar morphologies have been observed for the other block copolymers under consideration. These new block copolymers exhibit high ultimate tensile strength (30 MPa), elongation at break (1000%), and upper service temperature (140−200 °C).

Introduction

Living anionic polymerization allows one to design the molecular architecture and molecular parameters of polymers, and particularly to synthesize well-defined block copolymers. A typical example of very useful block copolymers is the poly[poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene)] copolymers (SBS) known as thermoplastic elastomers. These materials exhibit the melt processing characteristics of thermoplastics together with the mechanical properties of vulcanized rubbers. This behavior results from a unique morphology, which consists of a continuous rubbery polybutadiene (PBD) phase in which dispersed polystyrene (PS) microdomains act as thermoreversible cross-linkers. The thermal stability of this physical cross-linking is controlled by the glass transition temperature of PS (T_g = 100 °C), and is thus much lower than chemically cross-linked rubbers. It is therefore valuable to increase the upper service temperature of these materials in order to compete with vulcanized rubbers. Two main strategies have been used for that purpose. One is to cross-link the PS microdomains by appropriate chemical modification of the PS outer blocks.[1,2] Another consists of substituting the PS outer blocks by a polymer of a higher T_g, such as poly(α-methylstyrene),[3] poly(ethylene sulfide),[4] and poly(*p*-methylstyrene).[5]

Recently, special attention has been paid to poly(alkyl methacrylate)s (PAMA) as substitutes for the PS outer blocks.[6−11] Indeed, a large range of T_g can be made available from 110 °C for poly(cyclohexyl methacrylate) to 199 °C for poly(bornyl methacrylate).[12] However, synthesis of triblock copolymers containing PAMA hard blocks was a challenge for a long time due to the difficult purification of the monomers and the occurrence of side reactions above −65 °C.[13,14] Furthermore, PAMA anions are unable to initiate the polymerization of dienes, which requires the availability of difunctional initiators soluble in apolar solvents for the diene polymerization into a high cis-1,4 polymer. Poly[poly(*tert*-butyl methacrylate) (tBMA)-*b*-polybutadiene (BD)-*b*-poly(tBMA)] triblock copolymers were synthesized earlier by McGrath et al.[7,8,11] with a difunctional initiator soluble in apolar solvents based on 1,3-bis(1-phenylethenyl)benzene. Synthesis of poly[poly(MMA-*b*-poly(isobutylene)-*b*-poly(MMA)] triblock copolymers has also been reported by combining anionic and cationic techniques.[9,10] Recently, we have reported on the successful synthesis of poly[poly(MMA)-*b*-poly(BD)-*b*-poly(MMA)], or MBM, of high mechanical properties.[15] These materials have been proved to retain high tensile properties at higher temperatures compared to styrenic triblock copolymers not only when in bulk[16] but also when transformed into gels by mixing with a selective solvent for the midblock, e.g., a nonvolatile hydrocarbon oil.[17] Very recently, even higher thermoresistant materials have been synthesized by substituting PIBMA for PMMA (IBI triblocks),[18] since PIBMA has a much higher T_g (195 °C) than PMMA (125 °C). Although these IBI triblock copolymers show quite the same tensile properties as MBM in bulk, the mechanical properties of gels are degraded when IBI is substituted for MBM, because of the solvation of the PIBMA phase by the hydrocarbon oil. This drawback might be alleviated by using random or block copolymers of IBMA and MMA instead of PIBMA, so as to improve the oil resistance of the hard blocks while maintaining a high T_g. The purpose of this paper is thus to focus on the random and block copolymerization of IBMA and MMA and the synthesis of poly[poly(IBMA)-*b*-poly(BD)-*b*-poly(IBMA)] (IBI), poly[poly(IBMA-*co*-MMA)-*b*-poly(BD)-*b*-poly(MMA-*co*-IBMA)] (I/MBM/I), and poly[poly(IBMA)-*b*-poly(MMA)-*b*-poly(BD)-*b*-poly(MMA)-*b*-poly(IBMA)] (IMBMI) block copolymers.

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S0024-9297(96)01849-9 CCC: $14.00

Table 1. Block and Random Copolymerization of Methyl Methacrylate (M) and Isobornyl Methacrylate (I) with DDBLi as an Initiator in THF in the Presence of LiCl ([LiCl]/[Active Sites] = 4)

sample code	polymer[a] code	T (°C)	MMA/IBMA (wt/wt)		yield (%)[c]	$10^{-3}\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[e]	T_g (°C)[f]
			theor	exp[b]				
A1	MI	−78	0.49/0.51	0.52/0.48	90	12−12	1.05 (1.05)	143−182
A2	IM	−78	0.49/0.51	0.51/0.49	90	10−10	1.1 (1.05)	180−140
A3	I	−78	0/1	0/1	88	14	1.05	195
A4	M/I	−78	0.16/0.84	0.19/0.81	90	14	1.05	167
A5	M/I	−78	0.33/0.67	0.37/0.63	94	12	1.1	156
A6	M/I	−78	0.49/0.51	0.51/0.49	90	23	1.05	148
A7	M/I	−78	0.66/0.34	0.63/0.37	95	13	1.1	140
A8	M/I	−78	0.83/0.17	0.85/0.15	92	18	1.05	136
A9	M	−78	1/0	1/0	95	16	1.1	122
A10	M	0	1/0	1/0	50	12	1.75	117
A11	M/I	0	0.33/0.67	0.34/0.66	86	13	1.45	154

[a] MI = poly(MMA-*b*-IBMA), M/I = poly(MMA-*co*-IBMA). [b] Calculated from the ^{1}H NMR spectrum. [c] Weight ratio of recovered polymer compared to monomer. [d] SEC analysis with polystyrene calibration; $\bar{M}_n$ of the second block was calculated from the copolymer composition (^{1}H NMR) and $\bar{M}_n$ of the first block (SEC). [e] SEC analysis; values in parentheses are for the first block. [f] DSC analysis, heating rate of 20 °C/min.

The phase morphology of these multiblock copolymers and the effect of molecular weight of the outer block on the upper service temperature of IBI will also be investigated.

Experimental Section

Materials. Purification of monomers, solvents, and other reagents has been reported in a previous paper.[18]

Random and Block Copolymerization of MMA and IBMA. Polymerization was carried out in a previously flamed glass reactor equipped with a magnetic stirrer under an inert atmosphere. Solvent, initiator, and monomers were transferred into the reactor with a syringe and/or stainless steel capillaries. THF containing LiCl ([LiCl]/[active sites] = 4) was first introduced into the reactor. (1,1-Diphenyl-3,3-dimethylbutyl)lithium (DDBLi) was used as an initiator.[14] The reaction medium was cooled to −78 °C, and a mixture of MMA and IBMA was then added and polymerized for 1 h with formation of the poly(MMA-*co*-IBMA) random copolymer (M/I). Poly[poly(MMA)-*b*-poly(IBMA)] copolymer (MI) was prepared by sequential polymerization of MMA and IBMA initiated by DDBLi at −78 °C; the reaction time was 1 h for each monomer. Polymers were recovered by precipitation in heptane. They were then dried at 80 °C until constant weight.

Multiblock Copolymerization. Detailed experimental techniques and conditions used in the synthesis of methacrylate-containing triblock copolymers were reported elsewhere.[15,28] Butadiene was first polymerized in a cyclohexane/diethyl ether mixture (100/6, v/v) at room temperature for one night, using the diadduct of *tert*-butyllithium (*t*-BuLi) onto *m*-diisopropenylbenzene (*m*-DIB) as the initiator.[18] When the polymerization of butadiene was complete, an aliquot of the solution was picked out and PBD was precipitated into acidified methanol for characterization. The PBD dianions were end-capped with 1,1-diphenylethylene (DPE) at room temperature for 30 min. LiCl containing THF ([LiCl]/[living sites] = 5) was then added to the reactor at 0 °C, with formation of a cyclohexane/THF (30/70, v/v) mixture (deep red color), to which either IBMA, or a MMA/IBMA mixture, or MMA followed by IBMA was added and polymerized at −78 °C. Block copolymers were recovered by precipitation in methanol. They were dried at room temperature in vacuum until constant weight.

iPMMA was synthesized by anionic polymerization of MMA initiated by (*tert*-butylMgBr in toluene at −78 °C.[20] The molecular characteristics were as follows: $\bar{M}_n = 30\,000$; $\bar{M}_w/\bar{M}_n = 1.1$; isotactic triad content = 90%; $T_g = 50$ °C.

Analysis. Film preparation was reported elsewhere.[18] In the case of stereocomplexation, block copolymer and iPMMA were separately dissolved in toluene at room temperature.

Molecular weight and molecular weight distribution were measured by size exclusion chromatography (SEC) with a HP GPC 1090 apparatus equipped with linear Styragel columns. THF was the eluent (flow rate of 1 mL/min) and polystyrene standards were used for calibration.

^{1}H NMR spectra were recorded with a Bruker AM-400 spectrometer, by using $CDCl_3$ as a solvent. The content of the PBD 1,2-units was calculated by ^{1}H NMR from the relative intensity of the signals at 4.9 ppm ($CH_2=$ 1,2 double bond) and at 5.4 ppm ($CH=$ 1,2 plus 1,4 double bond). Composition of the copolymers was calculated by ^{1}H NMR from the relative intensity of the signal of the PBD 1,2 units, the OCH_3 group of the MMA units at 3.6 ppm, and the $-OCH<$ group of the IBMA units at 4.4 ppm, respectively.

Differential scanning calorimetry (DSC) was carried out with a DuPont 910 instrument, as previously reported.[18]

Dynamic mechanical analysis (DMA) was carried out with a TA 983 dynamic mechanical analyzer. Samples (8 × 10 × 1 mm) were deformed at a constant frequency (1 Hz) and strain amplitude (0.2 mm). The heating rate was 5 °C/min.

For transmission electron microscopy (TEM), toluene-cast films were microtomed into 70 nm thick sections and exposed to a 1% aqueous solution of OsO_4 for 30 min. A transmission electron microscope (model Philips CM-12) was used with an accelerating voltage of 100 kV.

Tensile measurements were conducted with an Adamel Lhomargy tensile tester. Microdumbell-shaped testing samples (30 × 3.6 × 1 mm) were cut from toluene-cast films and extended at 200 mm/min at room temperature. Reported data are the average of three independent measurements.

Results and Discussion

Synthesis of MMA/IBMA Block and Random Copolymers. The nucleophilicities of most methacrylic esters are similar enough for block and random copolymers of two methacrylic esters to be synthesized anionically, as has been shown for MMA/glycidyl methacrylate,[21] MMA/ethyl methacrylate, and MMA/butyl methacrylate[22,23] pairs. Therefore, block and random copolymerizations of MMA and IBMA have been considered in this study. The molecular characteristics of the synthesized copolymers are reported in Table 1. Typical SEC traces for the MI diblock A1 are shown in Figure 1a. The molecular weight distribution (1.05) is narrow for both the PMMA block and the final diblock, indicating that the PMMA anions quantitatively initiate the IBMA polymerization. In parallel, the IM diblock copolymer A2 has also a narrow molecular weight distribution for both the PIBMA block and the final diblock (Table 1), showing again a quantitative cross-reaction when the addition order of the two monomers is reversed. This observation is a good indication for quite a comparable electroaffinity of the two comonomers and thus for a random distribution of MMA and IBMA in copolymers synthesized from previously prepared comonomer mixtures. Consistently, these copoly-

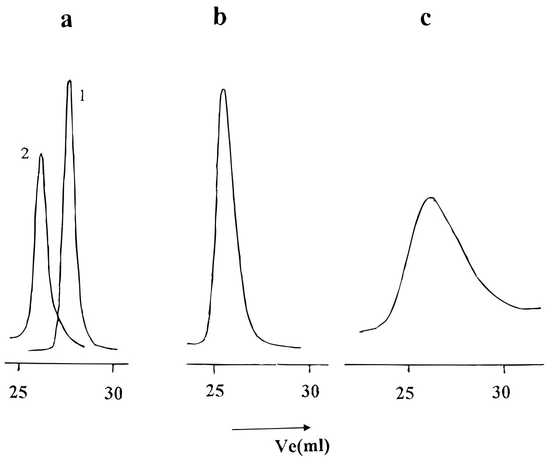

Figure 1. SEC traces for (a) poly[poly(MMA)-*b*-poly(IBMA)] diblock A1 [(1) MMA block, (2) final diblock], (b) poly(MMA-*co*-IBMA) random copolymer A6, and (c) poly(MMA-*co*-IBMA) random copolymer A11.

mers show one single T_g, as observed by DSC and discussed hereafter. Figure 1b shows the typical SEC trace for the random copolymer A6, whose molecular weight distribution is very narrow. For all the copolymers prepared, the total comonomer conversion is in the range of 90% (as calculated from the weight of the copolymer recovered by precipitation) and the weight composition is in good agreement with the initial comonomer weight ratio (Table 1).

Figure 2 shows the ^{13}C NMR spectrum for the carbonyl carbons in the MI diblock sample A1 (Figure 2a) and the M/I random copolymer sample A6 (Figure 2b) of a very close to 50/50 wt composition. The peak assignments are based on the comparison of the copolymer spectra with the spectra of both PMMA[24] and PIBMA homopolymers.[18] So, the ^{13}C NMR spectrum for the diblock copolymer A1 (Figure 2a) essentially combines the signals characteristic of the PMMA and PIBMA constitutive components, i.e., signals at 178.1 ppm for syndiotactic pentads and at 177.1 and 178.3 ppm for heterotactic pentads of PMMA[24] and signals at 176.5 and 177.2 ppm for heterotactic and syndiotactic triads of PIBMA.[18] In contrast, the ^{13}C NMR spectrum of the random copolymer A6 shows carbonyl signals intermediate between the resonances of PMMA and PIBMA, respectively. This observation confirms the randomness of the comonomer distribution in the copolymer chains.

It is known that in polymerization of MMA at a temperature higher than −40 °C, side reactions are a problem, resulting in broad molecular weight distribution and low polymer yield.[13,14,19] Indeed, when homoPMMA (A10, Table 1) is prepared at 0 °C, all the other conditions being the same, the molecular weight distribution is 1.75, and the polymerization yield is low (50%). In contrast, the anionic polymerization of IBMA has been shown to be controlled in a much larger temperature range and very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.1$) has been obtained even at room temperature with a yield of ca. 90%.[18] In the case of random copolymerization of MMA with IBMA, the side reactions known for the anionic polymerization of MMA at high temperature might be less effective and possibly prevented from occurring. This expectation is at least qualitatively confirmed by the "random" copolymerization of MMA and IBMA carried out at 0 °C (sample A11, Table 1), since the molecular weight distribution is relatively narrow (1.45) and monomodal (Figure 1c), the comonomer conversion is high (86%). Homopolymers A3 and A9 have been synthesized for the sake of comparison, and particularly for comparing T_g.

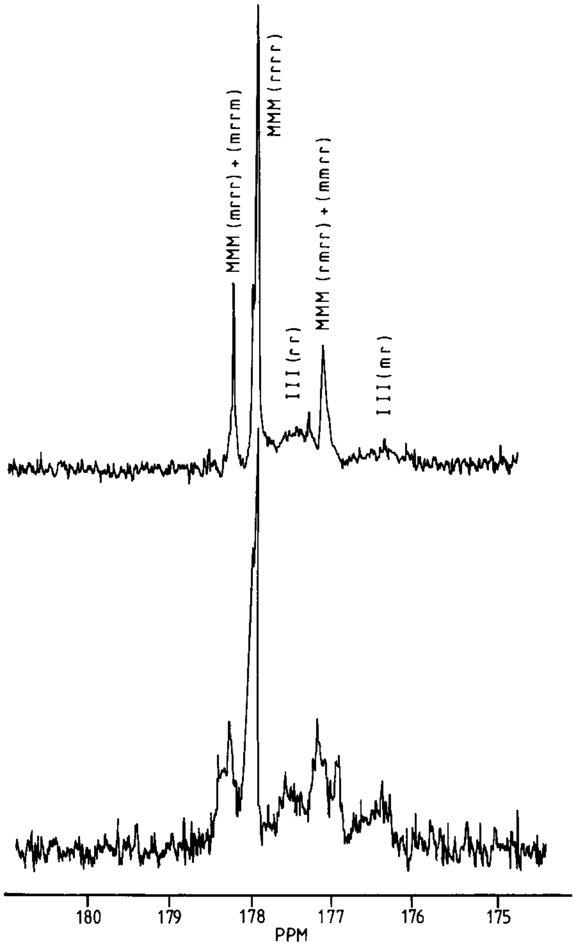

Figure 2. ^{13}C NMR spectra for poly[poly(MMA)-*b*-poly(IBMA)] copolymer A1 (a) and poly(MMA-*co*-IBMA) random copolymer A6 (b) in $CDCl_3$ at 25 °C (100 Hz).

Synthesis of Multiblock Copolymers with a PBD Midblock. The main characteristic features of these triblock copolymers are listed in Table 2. Molecular weight and the weight content of the PBD midblock are quite comparable, and the molecular weight distribution is very narrow. Block copolymers in which poly(IBMA-*co*-MMA) or poly[poly(IBMA)-*b*-poly(MMA)] blocks are substituted for the PIBMA outer blocks of the B1 and B2 triblocks have been similarly synthesized (Table 2). The poly[poly(IBMA-*co*-MMA)-*b*-poly(BD)-*b*-poly(MMA-*co*-IBMA)] triblocks B3 and B4 have been synthesized by addition of a MMA/IBMA mixture to the polybutadienyl dianions previously end-capped by 1,1-diphenylethylene (DPE). No gelation of the reaction medium has been observed during the polymerization of methacrylates, as usually happens when MBM triblock copolymers of a PMMA content higher than 20 wt % are prepared as a result of the strong association of the PMMA anions.[15] The narrow molecular weight distribution of the PBD midblock is preserved for the final block copolymer ($\bar{M}_w/\bar{M}_n = 1.1$). When the poly[poly(IBMA)-*b*-poly(MMA)-*b*-poly(BD)-*b*-poly(MMA)-*b*-poly(IBMA)] pentablock B5 is prepared, the deep red color of the polybutadienyl dianions previously end-capped by DPE disappears upon the addition of MMA, which indicates a fast initiation of the MMA polymerization. The reaction medium becomes also rapidly viscous as a

Table 2. Main Characteristics of the X−PBD−X Block Copolymers Synthesized in This Work

sample	outer block[a] X	PBD $10^{-3}\bar{M}_n$[b]	PBD $\bar{M}_w/\bar{M}_n$[b]	PBD 1,2 (%)[c]	outer block $10^{-3}\bar{M}_n$	composition (%)[c] B	composition (%)[c] M	composition (%)[c] I	copolymer $\bar{M}_w/\bar{M}_n$[b]
B0	PMMA	55	1.1	41	18	60	40	0	1.1
B1	PIBMA	60	1.1	43	15	67	0	33	1.1
B2	PIBMA	57	1.1	45	20	59	0	41	1.1
B3	poly(MMA-*co*-IBMA)	56	1.1	42	15	66	18	16	1.1
B4	poly(MMA-*co*-IBMA)	56	1.1	44	12	69	18	13	1.1
B5	poly(MMA-*b*-IBMA)	57	1.1	42	63	76	16	8	1.1

[a] PIBMA = poly(isobornyl methacrylate), MMA = methyl methacrylate, IBMA = isobornyl methacrylate. [b] Measured by SEC with a polystyrene calibration; all the experimental values were found in the 1.07(5)−1.12(5) range and rounded to 1.10. [c] Measured by ^{1}H NMR.

Table 3. Thermal and Mechanical Properties of Block Copolymers

sample	DSC (°C) T_{g1}	DSC (°C) T_m	DSC (°C) ΔH[b]	DMA[c] T_{g1}	DMA[c] T_{g2}	DMA[c] T_{g3}	tensile properties at 25 °C σ_y (MPa)	tensile properties at 25 °C σ_b (MPa)	tensile properties at 25 °C ϵ_b (%)	tensile properties at 25 °C set (%)
B0	−60			−55	122		5.2	35	870	100
B1	−58			−54	155			30	1000	40
HB1[d]	−53	−7	15	−40	180		5.0	33	560	50
B2	−56			−53	202		9.6	35	650	160
B3	−58			−55	132			24	1000	50
HB3	−50	−5	16	−47	138		5.1	29	720	66
B4	−56			−55	130			27	1000	50
B5	−58			−51	149	176		30	1100	40
CB3[d]	−58			nd[e]	nd	nd	nd	nd	nd	nd
CB5	−59	180	20	nd	nd	nd	nd	nd	nd	nd

[a] Heating rate: 20 °C/min. [b] Unit is J/g of PEB for samples HB1 and HB3, J/g of PMMA for sample CB5. [c] Heating rate: 3 °C/min. [d] HBi and CBi refer to the hydrogenated and complexed (with iPMMA) versions of Bi. [e] Not determined.

result of strong interactions of PMMA anions. The relatively low PMMA content together with a low polymer concentration (<2 wt %) and a high THF content in the cyclohexane/THF mixture, however, prevent the reaction solution from forming a gel. No aliquot of the MBM triblock solution has been withdrawn due to an exceedingly high viscosity. MMA was allowed to polymerize for 1 h although the polymerization is known to be very fast and quantitative within several minutes under similar conditions.[14] When the second IBMA comonomer is added, the viscosity of the reaction medium rapidly decreases, as a result of the cross-addition of IBMA to the PMMA anions, and formation of less associated PIBMA anions in relation to the bulkiness of the isobornyl substituent. A very narrow molecular weight distribution is again observed for both the PBD midblock and the final pentablock copolymer ($\bar{M}_w/\bar{M}_n = 1.1$), which confirms, if necessary, the quantitative cross-addition of MMA to the polybutadienyl dianions end-capped by DPE and that of IBMA to the living PMMA anions, respectively.

Samples HB1 and HB3 (Table 3) are the hydrogenated versions of the block copolymers B1 and B3 (Table 2). The quantitative hydrogenation of the PBD midblock has been ascertained by ^{1}H NMR and FTIR as reported elsewhere for MBM triblocks.[30]

Differential Scanning Calorimetry (DSC). DSC is a useful technique to study phase separation in binary blends and block copolymers of two immiscible components, provided that the individual glass transition temperatures (T_g) are sufficiently different from each other and the weight composition is far from the extreme values. T_g values for all the MMA/IBMA copolymers are listed in Table 1. Two T_g's are observed for the block copolymers A1 and A2, which indicates a phase separation and thus the immiscibility of the PMMA and PIBMA blocks. However, T_g of the PMMA microphase is higher compared to homoPMMA, and T_g of the PIBMA microphase is slightly lower than homoPIBMA, which might suggest a partial phase mixing.

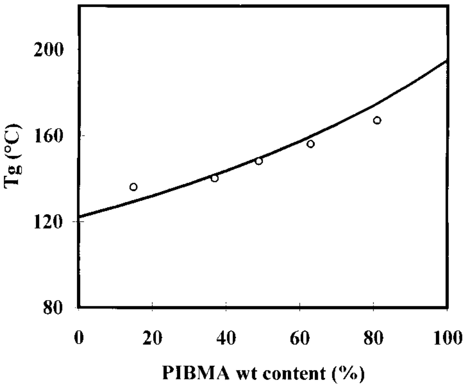

Figure 3. Dependence of T_g of poly(MMA-*co*-IBMA) copolymers on the weight composition. The solid line is the Fox prediction.

In contrast, a single T_g is observed for all the random copolymers analyzed in this study, whose MMA content is in the range 19−85% (Table 1). According to Figure 3 and Table 1, this single T_g changes with composition, as predicted by the Fox equation. This experimental observation is in favor of the copolymer randomness, consistently with the ^{13}C NMR analysis (Figure 2).

Multiblock copolymers containing a PBD or a hydrogenated PBD midblock, i.e., poly(ethylene-*co*-1,2-butene) (PEB), have also been analyzed by DSC (Table 3). A transition is clearly observed at low temperatures for all the samples and is assigned to the glass transition (T_{g1}) of the soft PBD (or PEB) phase. T_{g1} varies from −56 to −60 °C for the PBD-containing triblock copolymers, in a possible relationship with the content of the 1,2-units in the PBD midblock (Table 2). T_{g1} is slightly increased upon hydrogenation of samples B1 (+5 °C) and B5 (+8 °C). The second transition temperature (T_{g2}) characteristic of the hard phase is so faint that it cannot be reported in a reliable way. Nevertheless, samples B0 and B1 (Table 3) show that T_{g1} is independent of the hard block [122 °C for PMMA (A9), and 195 °C for PIBMA (A3)], which is a clear indication of the immiscibility of the hard and the soft blocks.

When samples B1 and B3 are hydrogenated (HB1 and HB3: Table 3), a broad, ill-defined melting endotherm is observed above T_{g1}, with a maximum close to −7 °C. So the PEB component can crystallize, although with formation of a small number of poorly defined crystalline domains as previously reported,[29] and discussed elsewhere.[30] The melting enthalpy is quite comparable for HB1 and HB3, thus unaffected by the hard block content.

Stereocomplexation of iPMMA with the sPMMA outer blocks of MBM triblocks and MSBSM pentablocks has been reported to occur with a melting temperature of ca. 180 °C and a melting enthalpy of ca. 30 J/g of PMMA.[25] In order to confirm that stereocomplexation can occur independently of the location of the sPMMA block in a multiblock copolymer, the IMBMI pentablock copolymer B5 (Table 1), in which sPMMA is inserted between the PIBMA and the PBD blocks, has been blended with isotactic PMMA (iPMMA) in a 2/1 syndio/iso mixing ratio (sample CB5, Table 3). As reported in the Experimental Section, copolymer B5 and iPMMA were separately dissolved in toluene at room temperature, and the two solutions were then mixed at 100 °C. When the mixed solution is cooled to room temperature, a gel is formed as a result of stereocomplexation between the sPMMA block and iPMMA. Indeed, a well-defined endotherm is clearly observed at 180 °C by DSC (sample CB5, Table 3), which is the signature of the sPMMA/iPMMA stereocomplex. The melting temperature is indeed the same as in the case of the MBM triblocks, whereas the melting enthalpy (20 J/g of PMMA) is relatively lower due to the low molecular weight of the sPMMA block (6000, Table 2) and possibly to the capping of the sPMMA block by other blocks at both ends. Therefore, the capping of sPMMA by a PIBMA block at one end and a PBD block at the other end does not prevent stereocomplexation with iPMMA. Triblock copolymer B3, in which the hard block is a random copolymer of MMA and IBMA, has also been blended with iPMMA (CB3, Table 3). No gelation is, however, observed when the blend solution is cooled to room temperature, so that no stereocomplexation occurs. This is confirmed by DSC analysis, since no melting endotherm is observed. Thus stereocomplexation does not occur as a consequence of the random distribution of the MMA and IBMA units in the hard block.

Dynamic Mechanical Analysis (DMA). Figure 4 shows the temperature dependence of the dynamic shear storage modulus (G') and loss tan δ ($=G''/G'$) from −100 to +250 °C for the IBI copolymers B1 and B2, and the hydrogenated B1 sample (HB1, Table 3). In contrast to DSC analysis, the glass transition of the hard phase is now clearly observed in addition to T_{g1}, which confirms the two-phase morphology of these copolymers. From Figure 4A, it appears that G' in the glassy plateau is not significantly dependent on the hard block content (33 and 41 wt %) since G' of sample B1 is quite similar to that of B2, whereas hydrogenation (HB1) seems to result in a decrease of G' in the glassy plateau. In contrast, G' in the rubbery plateau is strongly dependent on the hard block content, at least in the range investigated in this study (33−44 wt %). Indeed, G' of sample B2 is much higher than sample B1 in the rubbery plateau. Furthermore, G' is steadily decreasing when the temperature of B1 is increased in this plateau region, until T_{g2} is observed above 100 °C. Conversely, G' of sample B2 decreases much more slowly with increasing temperature, until a much sharper glass transition is observed at a much higher temperature (160 °C). The damping of the lower temperature transition is more important for sample B1 compared to B2 although the temperature at the peak maximum is the same. This observation is consistent with G' that starts to decrease as soon as the temperature exceeds T_{g1} for sample B1 in contrast to what happens for B2. The transition at the higher temperature shows a very broad distribution of relaxation times for the PIBMA phase of sample B1, with a maximum at 155 °C. A much narrower damping peak is observed for sample B2 at a much higher temperature of 202 °C. The difference in the DMA properties of samples B1 and B2 can only be accounted for by a much larger interphase in sample B1 in relation to the relatively low molecular weight of the PIBMA blocks. The large interphase that is thought to dominate in sample B1 appears to be reduced by hydrogenation of the midblock if one compares the damping characteristic of the hard phase, which is narrow and observed at a higher temperature for HB1 compared to B1 (Figure 4B).

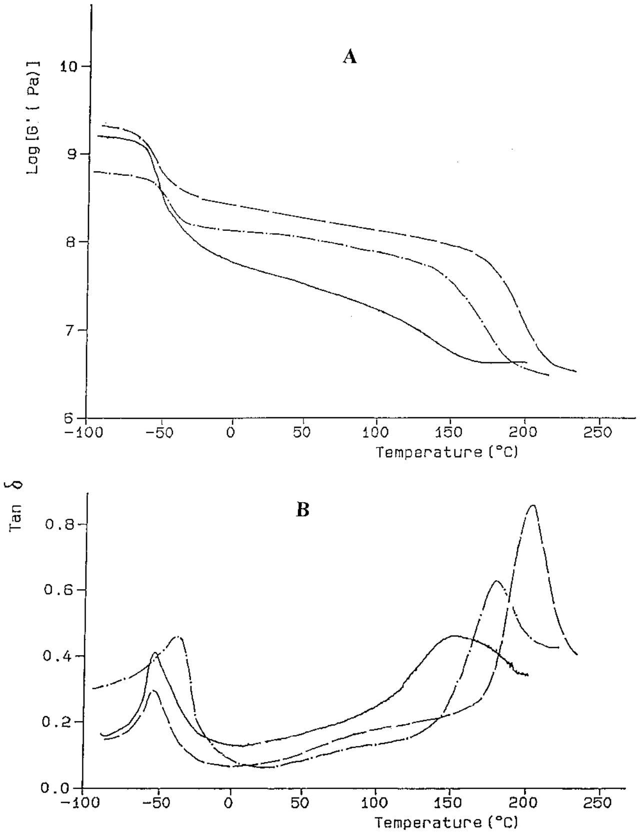

Figure 4. Shear storage modulus (G') (A) and loss tan δ ($=G''/G'$) (B) vs temperature at 1 Hz for the IBI sample B1 (—), the hydrogenated counterpart HB1 (—•—), and the IBI sample B2 (– –).

Figure 5 compares the dynamic mechanical properties of the copolymer B3, the hydrogenated counterpart HB3, the pentablock copolymer B5, and the MBM triblock copolymer B0. Two transitions are observed, which confirms the two-phase morphology previously suspected by DSC. The low-temperature transition (T_{g1}) for B3 that contains a poly(IBMA-*co*-MMA) outer block is the same as for the MBM copolymer B0. However, the high-temperature transition (T_{g2}) of the hard phase is higher for sample B3 (132 °C) than for B0 (122 °C), in line with the modification of PMMA by IBMA units whose polymer is of a higher T_g.[12,18] It is worth noting

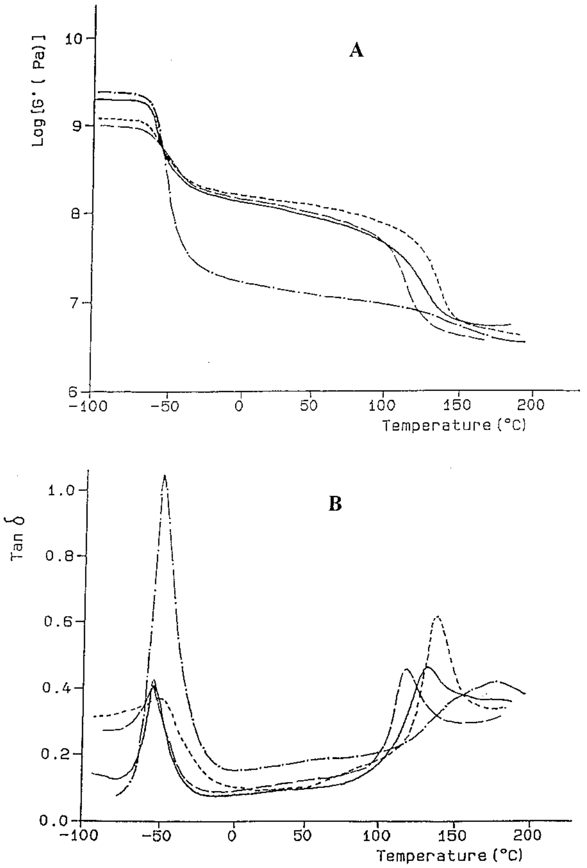

Figure 5. Shear storage modulus (G') (A) and loss tan δ ($=G''/G'$) (B) vs temperature at 1 Hz for the MBM sample B0 (– –), the I/MBM/I sample B3 (—), the hydrogenated counterpart HB3 (---) and the IMBMI pentablock B5 (—•—).

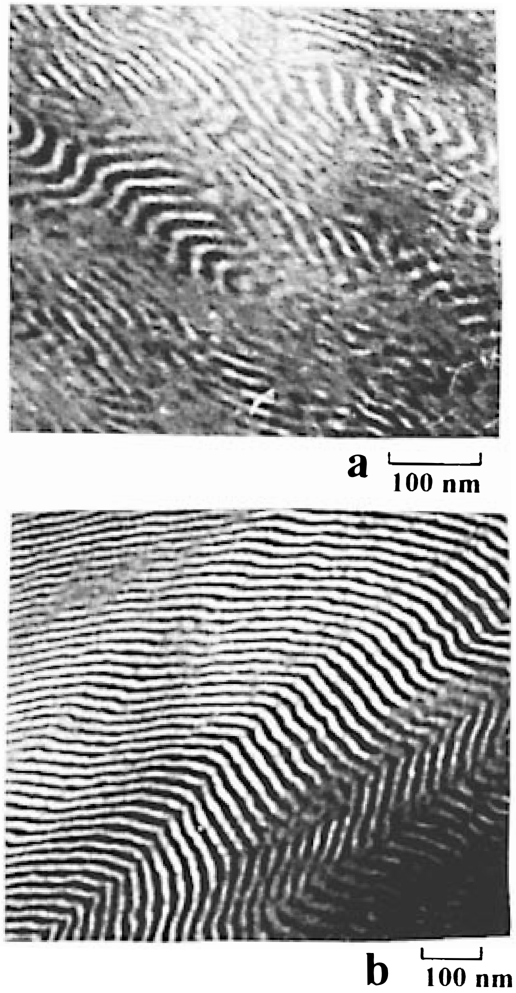

Figure 6. Transmission electron micrographs for block copolymers B1 (a) and B2 (b). PBD stained with OsO_4 is the black phase.

that T_g of the hard block in B3 containing a MMA and IBMA random copolymer does not obey the Fox equation, possibly due to the presence of the PBD midblock. T_{g2} of sample B3 is slightly increased by hydrogenation of the PBD midblock, as shown by tan δ vs temperature curves for B3 and HB3, more likely due to a sharper phase separation in the hydrogenated sample.[30] Hydrogenation of B3 also results in a decrease of G' in the glassy plateau, although G' is slightly increased in the rubbery plateau, in agreement with a change in the chemical structure of the midblock.

Two quite broad and superimposed transitions are observed for the hard phase of the IMBMI pentablock copolymer B5. The broadness of these transitions reflects a large distribution of relaxation times, which may be the signature of a partial phase mixing of the PMMA and PIBMA blocks. The transition at 148 °C is attributed to the rich-in PMMA phase, and conversely, the transition at 178 °C to the PIBMA-rich phase. The high damping of the PBD midblock for sample B5 at the lower transition temperature (−51 °C) is due to the high PBD content (76 wt %, Table 2).

Morphological Observations. Phase morphology has been analyzed by transmission electron microscopy (TEM), which confirms the phase separation shown by DSC and DMA analysis. Figures 6 and 7 show transmission electron micrographs of toluene-cast films annealed at 140 °C for 3 days under vacuum. PBD is observed as the dark phase as a result of selective staining by OsO_4. The equilibrium phase morphology of a binary block copolymer is known to be dictated by the copolymer composition, as reported for the SBS[26,27] and MBM triblock copolymers.[15] As a rule, a spherical morphology is observed for a PBD content in the range of 10−18 wt %. When the PBD content is as high as 18−38 wt %, a cylindrical morphology is observed, whereas a lamellar morphology is reported for 36−60 wt % PBD.[26] Figure 6 compares the phase morphology for the two IBI triblock copolymers B1 and B2. A lamellar morphology is clearly observed for both the B1 and B2 samples. Although this morphology may be expected for sample B2 that contains 59 wt % PBD, it is more surprising that sample B1 shows the same morphology since the PBD phase content is then 67 wt %. In this composition range, the PS blocks of SBS copolymers[26] and the PMMA blocks of MBM copolymers[15] typically form cylinders. Thus, when associated with PBD, PIBMA is prone to form a continuous phase at relatively low contents (33 wt %). A similar phenomenon has been reported for poly(ethyl methacrylate)-containing triblock copolymers.[16]

TEM of samples B3, B4, and B5 are shown in Figure 7 and confirm a two-phase morphology. A lamellar structure without any long range order is observed for samples B3 and B4 (figs.7a,b). Cylindrical poly[poly(IBMA)-*b*-poly(MMA)] hard phases are observed to be dispersed in a continuous PBD matrix in the case of the pentablock B5 (Figure 7c).

Stress-Strain Behavior. The IBI triblock copolymers exhibit a network structure as a result of block immiscibility and phase separation on a microscopic scale. The minor rigid blocks are thus expected to

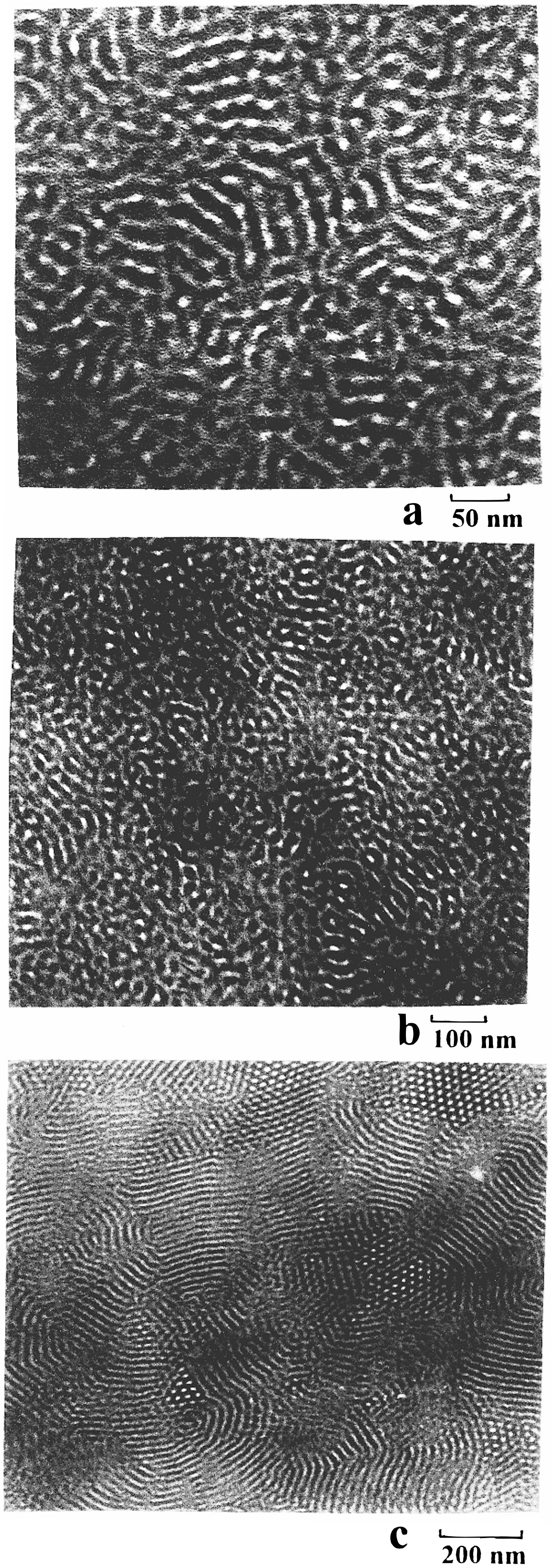

Figure 7. Transmission electron micrographs for block copolymers B3 (a), B4 (b), and B5 (c). PBD stained with OsO_4 is the black phase.

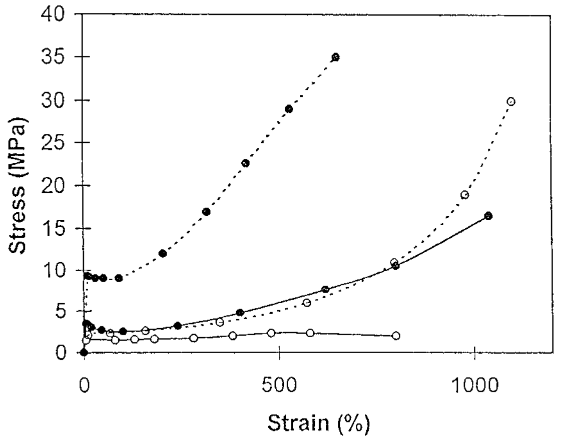

Figure 8. Stress–strain curves for the IBI triblock copolymer B1 (○) and B2 (●) at 25 °C (---) and 90 °C (—).

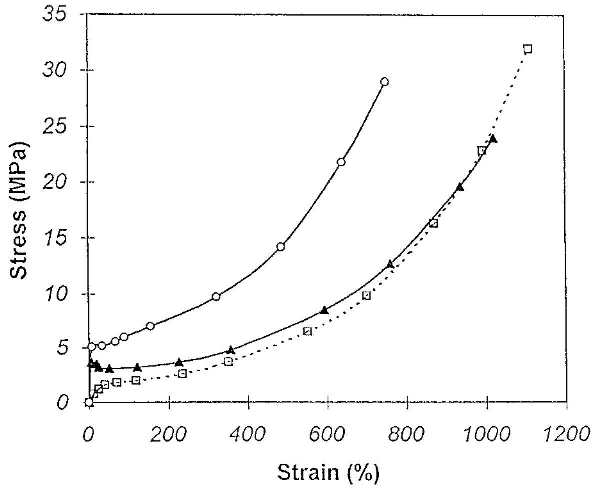

Figure 9. Stress–strain curves for the block copolymers B3 (▲), HB3 (○), and B5 (□) at 25 °C.

prevent viscous flow from occurring and to provide these two-phase materials with rubberlike properties at temperature well below the T_g of the hard phase. Indeed, high ultimate tensile strength and elongation at break are observed for both B1 and B2 samples at room temperature (Figure 8 and Table 3). This observation is indicative of phase separation and efficiency of the PIBMA microdomains in restricting the flow of the soft polybutadiene segments. A yield point is observed in spite of the relatively low hard block content (33 wt %), which is indicative of a semicontinuous PIBME phase in the PBD matrix, in agreement with the lamellar morphology observed by TEM (Figure 6a). The higher content of PIBMA in sample B2 (41 wt %) compared to B1 (33 wt %) accounts for the higher yielding shown by B2 and the smaller elongation at break (ϵ_b) for this sample. However, the network properties are decreased upon heating at 90 °C, particularly in the case of B1, whose T_{g2} is 155 °C. So, well below T_{g2}, the efficiency of the physical cross-linking in stabilizing the network structure is dramatically decreased. Figure 9 shows that more than 90% of the ultimate strength of B1 at 25 °C is lost at 90 °C, whereas the elongation at break is decreased from 1200% to 800%. In contrast, half the strength of sample B2 at 25 °C is maintained upon heating at 90 °C. The typical behavior of a thermoplastic elastomer is preserved at this temperature ($\sigma_b = 17$ MPa and $\epsilon_b = 1050\%$). Thus an increase in the molecular weight of the PIBMA outer block from 15 000 to 20 000 results in a significant increase in T_g (202 °C), which clearly improves the upper service temperature of the otherwise identical thermoplastic elastomer (Table 1).

Tensile properties of the block copolymer B3, the hydrogenated counterpart HB3, and the pentablock copolymers B5 are illustrated in Figure 9. Data for sample B4 are also reported in Table 3. The behavior of typical thermoplastic elastomers is observed for all these samples. A yield point is observed for both B3 and B4 samples, in agreement with the lamellar morphology observed by TEM. The tensile properties are significantly affected by hydrogenation of the PBD midblock, as in the case of MBM triblock copolymers. σ_b, the yield stress and the permanent set at break are indeed increased upon hydrogenation, whereas ϵ_b is decreased. In the case of the pentablock copolymer B5, no yield point is observed, the initial modulus is low compared to samples B3 and B4 as a consequence of a low hard block content, whereas the ultimate tensile strength and elongation at break are high.

All these copolymers will be used for gel formation by selective swelling of the midblock with an aliphatic and nonvolatile oil.

Conclusion

Block and random copolymers of isobornyl methacrylate (IBMA) and methyl methacrylate (MMA) have been prepared in THF at −78 °C by using (1,1-diphenyl-3,3-dimethylbutyl)lithium as initiator in the presence of LiCl. Phase separation occurs in the MI block copolymer which shows two T_g's, whereas a single T_g is observed for the poly(MMA-*co*-IBMA) (M/I) random copolymers, which depends on the copolymer composition in agreement with the Fox equation. When prepared at 0 °C, random copolymers of MMA and IBMA still show a monomodal although broader molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.45$).

Poly[poly(IBMA)-*b*-poly(BD)-*b*-poly(IBMA)] (IBI), poly[poly(IBMA-*co*-MMA)-*b*-poly(BD)-*b*-poly(MMA-*co*-IBMA)] (I/MBM/I), and poly[poly(IBMA)-*b*-poly(MMA)-*b*-poly(BD)-*b*-poly(MMA)-*b*-poly(IBMA)] (IMBMI) block copolymers have been successfully synthesized by sequential anionic polymerization of butadiene, MMA, and IBMA. These block copolymers have a monomodal and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.1$). All these materials are phase separated. The degree of phase separation strongly depends on the molecular weight of the hard blocks (at a constant $\bar{M}_n$ for PBD), particularly at higher temperatures where a difference of up to 50 °C in the upper service temperature has been observed for two IBI triblock copolymers of different PIBMA molecular weights. Stereocomplexation also occurs when IMBMI copolymer and isotactic PMMA (iPMMA) are blended, in contrast to blends of I/MBM/I and iPMMA in which no stereocomplex is formed as a consequence of the random distribution of the MMA and IBMA units

IBI triblock copolymers have an essentially lamellar morphology, even for a copolymer containing a relatively low hard block content (33 wt %). Cylindrical and lamellar morphologies have been observed for the other materials. These new block copolymers typically behave as thermoplastic elastomers.

Acknowledgment. The authors are very much indebted to the IWT (Flemish Institute for the Promotion of Science-Technological Research in Industry) for the financial support of a joint research program with Raychem N.V. (Kessel-Lo, Belgium) and the Katholieke Universiteit Leuven (Prof. H. Berghmans and H. Reynaers). They warmly thank Dr. N. Overbergh (Raychem, Kessel-Lo), Dr. Ph. Hammond, and Dr. J. Hudson (Raychem, Swindon) for stimulating discussions. They are grateful to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" for general support in the frame of the "Pôles d'Attraction Interuniversitaires: Polymères". Ph.D. is "Chercheur Qualifié" of the Belgium FNRS.

References and Notes

(1) Weiss, R. A.; Sen, A.; Pottick, L. A.; Willis, C. L. *Polym. Commun.* **1990**, *31*, 220.
(2) Weiss, R. A.; Sen, A.; Willis, C. L.; Pottick, L. A. *Polymer* **1991**, *32* (10), 1867.
(3) Fetters, L. J.; Morton, M. *Macromolecules* **1969**, *2* (5), 453.
(4) Morton, M.; Mikesell, S. L. *J. Macromol. Sci., Chem.* **1993**, *A7* (7), 1391.
(5) Quirk, R. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (2), 14.
(6) Ladd, B. J.; Hogen-Esch, T. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 261.
(7) Long,T. E.; Broske, A. D.; Bradley, D. J.; McGrath, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 4001.
(8) DePorter, C. D.; Ferrence, G. M.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (2), 574.
(9) Kennedy, J. P.; Price, J. L. *Polym. Mater. Sci. Eng.* **1991**, *64*, 40.
(10) Kennedy, J. P.; Price, J. L.; Koshimura, K. *Macromolecules* **1991**, *24*, 6567.
(11) Loveday, D.; Wilkes, G. L.; Deporter, C.; McGrath, J. E. *Macromolecules* **1995**, *28*, 7822.
(12) Matsumoto, A.; Mizuta, K.; Otsu, T. *J. Polym. Sci., Part A: Chem. Ed.* **1993**, *31*, 2531.
(13) Wiles, D. M. In *Structure and Mechanism in Vinyl Polymerization*; Tsuruta, T., O'Driscoll, K. F., Eds.; Marcel Dekker: New York, 1969; p 233.
(14) (a) Jérôme, R.; Forte, R.; Varshney, S. K.; Fayt, R.; Teyssié, Ph. In *Recent Advances in Mechanistic and Synthetic Aspects of Polymeriztion*; Fontanille, M., Guyot, A., Eds.; NATO ASI series 215; Kluwer: Dordrecht, The Netherlands, 1987, p 101. (b) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 2618.
(15) Yu, J. M.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1996**, *29*, 6090.
(16) Yu, J. M.; Dubois, Ph.; Jérôme, R. *Macromolecules* **1996**, *29*, 8362.
(17) Yu, J. M.; Teyssié, Ph.; Jérôme, R.; Overbergh, N.; Hammond, Ph.; Hudson, J. Triblock Copolymer Based Thermoreversible Gels: Morphology, Viscoelastic and Mechanical properties. Manuscript in preparation.
(18) Yu, J. M.; Dubois, Ph.; Jérôme, R. *Macromolecules* **1996**, *29*, 7316.
(19) Long, T. E.; Allen, R. D.; McGrath, J. E. *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*; Fontanille, M., Guyot, A., Eds.; NATO ASI Series 215; Kluwer: Dordrecht, The Netherlands, 1987; p 79.
(20) Hatada, K.; Ute, K.; Tanaka, K.; kitayama, T.; Okamoto, Y. *Polym. J.* **1985**, *17* (8), 977.
(21) Hild, G.; Lamps, J. Ph.; Rempp, P. *Polymer* **1993**, *34* (13), 2875.
(22) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Macromol. Chem. Suppl.* **1989**, *15*, 167.
(23) Kitayama, T.; Ute, K.; Hatada, K. *Br. Polym. J.* **1990**, *23*, 5.
(24) Wang, J. S.; Jérôme, R.; Warin, R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 5984.
(25) Yu, J. M.; Yu, Y.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R. *Polymer* **1997**, *38*, 3091.
(26) Gallot, B. R. M. *Adv. Polym. Sci.* **1978**, *29*, 85.
(27) Holden, G.; Legge, N. R. In *Thermoplastic Elastomers*; Legge, N. R., Holden, G., Schroeder, H. E., Eds.; Hanser Publishers: Munich, Vienna, New York, 1987; p 47.
(28) Yu, Y.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, (a) 1753, (b) 2738.
(29) Cowie, J. M. G.; Lath, D.; McEwen, I. J. *Macromolecules* **1979**, *12*, 53.
(30) Yu, J. M.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R. Synthesis and characterization of hydrogenated poly[alkyl methacrylate(-*b*-styrene)-*b*-butadiene-*b*-(styrene-*b*-)alkyl methacrylate] triblock and pentablock copolymers. *Polymer*, in press.

MA961849W