Synthesis and Properties of Poly[isobornyl methacrylate (IBMA)-*b*-butadiene (BD)-*b*-IBMA] Copolymers: New Thermoplastic Elastomers of a Large Service Temperature Range

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ABSTRACT: Anionic polymerization of isobornyl methacrylate (IBMA) has been studied in THF and toluene in a temperature range from −78 to +40 °C by using (1,1-diphenyl-3,3-dimethylbutyl)lithium (DDBLi) as an initiator in the presence of LiCl or not. Effect of solvent and polymerization temperature on tacticity has been studied. The reactivity of IBMA is comparable to *tert*-butyl methacrylate (tBMA), and polymers of a very narrow molecular weight distribution (<1.10) have been synthesized at room temperature, in THF, in the presence of LiCl. The T_g of PIBMA is found to vary from 170 to 206 °C with chain tacticity. Poly(isobornyl methacrylate) (PIBMA)−polybutadiene (PBD)−PIBMA triblock copolymers have been synthesized by using the *m*-diisopropenylbenzene (*m*-DIB)/*tert*-butyllithium (*t*-BuLi) diadduct as an initiator. The PBD midblock has been prepared in a cyclohexane/diethyl ether (100/6, v/v) mixture at room temperature. THF has been added [cyclohexane/diethyl ether/THF (100/6/100, v/v/v)] before the IBMA polymerization takes place at either −78 or +25 °C. Triblock copolymers of a very narrow molecular weight distribution (1.10) have been synthesized even at 25 °C, and no gel formation has been observed. These new triblock copolymers exhibit high tensile strength (30 MPa), high ultimate elongation (1000%), and high upper service temperature (160 °C).

Introduction

Styrene−butadiene−styrene (SBS), styrene−isoprene−styrene (SIS), and styrene−(ethylene-*co*-1,2-butene)−styrene (SEBS) triblock copolymers are known for unique combination of elasticity and thermoplasticity. These materials consist of polystyrene (PS) microdomains phase separated in a continuous rubbery diene phase, which results in a physical network of flexible chains. This remarkable behavior persists over a limited range of service conditions. The upper service temperature is limited by the approach to the glass transition temperature of PS (100 °C). It is therefore a major concern to increase the service temperature range of these thermoplastic elastomers in order to compete with vulcanized rubbers. Among several known examples,[1−9] Morton et al.[1] have explored the use of poly(α-methylstyrene) the T_g of which is higher than polystyrene by 70 °C. The low ceiling temperature of this polymer, however, makes the synthesis of triblock copolymers less attractive. Poly(ethylene sulfide)[2] has also been considered as a substitute for polystyrene, but the related triblock copolymers have poor ultimate mechanical properties. Triblock copolymers with poly(*p*-methylstyrene) hard blocks have also been considered by Quirk.[9]

Poly(alkyl methacrylate) (PAMA) is a possible candidate for the hard block. Indeed, T_g varies from 110 °C for poly(cyclohexyl methacrylate) to 194 °C for poly(bornyl methacrylate).[10] However, synthesis of triblock copolymers with PAMA hard blocks was a considerable challenge for a long time because of the difficult purification of the monomers and side reactions during propagation above −65 °C.[11,12] Furthermore, PAMA anions are unable to initiate polymerization of dienes, which requires the availability of a difunctional initiator soluble in apolar solvents for the diene polymerization into a high cis 1,4 polymer. Although syndiotactic poly(methyl methacrylate) (sPMMA)−polyisobutylene−sPMMA triblock copolymers have been reported earlier[5,6] by combining anionic and cationic techniques, only very recently sPMMA−polybutadiene−sPMMA, or MBM, have been successfully synthesized and characterized[15] in our laboratory. Although MBM triblock copolymers have a high thermal resistance (T_g sPMMA = 125 °C) which can be further extended to 180 °C by stereocomplexation with isotactic poly(methyl methacrylate) (iPMMA), some problems must be pointed out: (i) MBM must be polymerized at a low temperature (−78 °C) in the presence of large amounts of THF; (ii) the monomer concentration must be kept low enough for avoiding gelation; (iii) the T_g of sPMMA is only 25 deg higher than polystyrene, and the tensile strength decreases upon stereocomplexation with iPMMA.[14] Furthermore, crystallization of the stereocomplex in the melt is very slow (2 days at 100 °C).[16] This paper deals with the possible substitution of isobornyl methacrylate (IBMA) for MMA, since the poly(isobornyl methacrylate), or PIBMA, is known for a T_g as high as 200 °C.[10,17,18] To our knowledge, anionic polymerization of IBMA has not been reported yet. In order to fill in this gap, anionic polymerization of IBMA has been studied under different experimental conditions and a series of PIBMA-PBD−PIBMA triblock copolymers have been prepared and their thermal and mechanical properties investigated.

Experimental Section

Materials. IBMA (Acros Chimica) was first refluxed over CaH_2 under a nitrogen atmosphere. It was then distilled under reduced pressure and stored under nitrogen at −20 °C. Just before polymerization, it was added to a mixture of diisobutyl aluminum hydride (DIBAH: 0.1 M in toluene) and triethylaluminum (TEA: 0.1 M in toluene) (50/50, v/v) until a persistent yellowish green color was observed. It was then redistilled under reduced pressure and polymerized.

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LiCl (99.99% purity, Aldrich) was dried overnight at 130 °C and dissolved in dry THF (0.2 M solution). Cyclohexane 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 immediately before use. *tert*-Butyllithium (*t*-BuLi) (Aldrich, 1.3 M in cyclohexane) was diluted with cyclohexane into a 0.2 M solution, as determined by double titration.[27] *m*-Diisopropenylbenzene (m-DIB, Aldrich) was first distilled over CaH_2 for 24 h and then from fluorenyllithium before use. 1,1-Diphenylethylene (DPE, Aldrich) was dried over *s*-BuLi and distilled from diphenylmethyllithium before use. Butadiene was dried over *n*-BuLi.

Initiators. (1,1-Diphenyl-3,3-dimethylbutyl)lithium (DDBLi) was used as a monofunctional initiator and prepared by addition of *t*-BuLi to DPE (monoadduct). The *t*-BuLi/*m*-DIB diadduct was prepared in cyclohexane at 50 °C for 2 h and used as a difunctional initiator. Solutions of these mono- and difunctional initiators were homogeneous with a deep red color.

Polymerization. Homopolymerization of IBMA and block copolymerization of butadiene and IBMA were carried out in a glass reactor equipped with a magnetic stirrer under an inert atmosphere. Solvent, initiator, and monomers were transferred with a syringe and/or capillaries. Details for the experimental techniques used in the synthesis of triblock copolymers were reported elsewhere.[13,15] Briefly, the synthesis consisted of three steps: (1) butadiene was polymerized in a cyclohexane/diethyl ether mixture (100/6, v/v) at room temperature for one night; (2) PBD dianions were end-capped with diphenylethylene (DPE) at room temperature for 30 min; (3) THF was added at 0 °C with formation of a 50/50 cyclohexane/THF (v/v) mixture, to which IBMA was finally added and polymerized at either low or room temperature. Triblock copolymers were recovered by precipitation in methanol and dried at room temperature for 2 days in vacuum.

Hydrogenation. An alkylmetal/transition metal salt complex was used as the homogeneous hydrogenation catalyst. The metal alkyl was triethylaluminum (1 M in toluene) and the metal salt was cobalt 2-ethylhexanoate (0.2 M in toluene). The catalyst complex was prepared by adding dropwise the transition metal salt solution to the metal alkyl solution under nitrogen. The molar ratio of the two constitutive components (alkyl/salt) was 3/1. Hydrogenation was conducted in a 5 L autoclave, equipped with a mechanical stirrer. A solution of 20 g of block copolymer in 3 L of dry toluene was first mixed with the catalyst complex (about 0.03 mol of transition metal/mol of double bonds) and then injected. After closing, the reactor was purged with nitrogen. The reactor was heated to 60 °C and purged with hydrogen, and the reaction was allowed to proceed for ca. 3 h under a 6 bars hydrogen pressure. After hydrogenation, the catalyst was decomposed with dilute HCl. The copolymer was precipitated in methanol, washed and redissolved in toluene, reprecipitated, and dried under vacuum.

Film Preparation. Block copolymers were added with 1 wt % hindered phenol antioxidant (tetrakis[1-methoxy 3-(3′,5′-di-*tert*-butyl-4′-hydroxylphenyl) propionyl]methane, Irganox 1010, Ciba-Geigy Corp.) and dissolved in toluene. This solution (8 wt % copolymer) was poured into a Petri dish, and the solvent was allowed to evaporate slowly over 3−4 days at room temperature. Films were dried to constant weight in a vacuum oven at 40 °C; they were elastomeric, transparent, and colorless with a smooth surface.

Analysis. Molecular weight and molecular weight distribution were measured by size exclusion chromatography (SEC) with a Waters GPC 501 apparatus equipped with linear Styragel columns. THF was the eluent (flow rate of 1 mL/min), and polystyrene standards were used for calibration. The method by Benoit et al.[25] for the universal calibration was used with the following viscosimetric relationships:

$$[\eta] = 1.36 \times 10^{-4} M^{0.714} \qquad \text{(PS in THF)}^{22}$$

$$[\eta] = 3.68 \times 10^{-5} M^{0.730} \qquad \text{(PIBMA in THF)}^{18}$$

^{1}H NMR spectra were recorded with a Bruker AN-400 spectrometer, by using $CDCl_3$ as solvent. The content of the PBD 1,2-units was calculated by ^{1}H NMR from the relative intensity of the signal at 4.9 ppm (CH=: 1,2 double bond), and 5.4 ppm (CH=: 1,2 plus 1,4 double bond). The tacticity of PIBMA was calculated by quantitative ^{13}C NMR recorded at 20 °C by using an inverse-gated proton decoupling technique. Composition of the copolymer was calculated by ^{1}H NMR from the signal for the 1,2-units of PBD and the signal at 4.4 ppm for the O−CH< carbon of the IBMA units. $\overline{M}_n$ for PIBMA was calculated from composition and PBD molecular weight.

IR spectra were recorded with the 600 FT-IR Perkin-Elmer spectrometer.

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 as the inflection point of the heat capacity jump. The width of the glass transition (ΔT_g) was defined as 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 (DuPont). Samples (8 × 10 × 2 mm) were deformed at constant frequency (1 Hz).

Tensile measurements were conducted with an Adamel Lhomargy tensile tester. Testing samples (microdumbells) cut from solution-cast films were extended at 200 mm/min at room temperature. Reported data are the average of three measurements.

Results and Discussion

Synthesis of Poly(isobornyl methacrylate) (PIBMA). Monomer purification is a key issue in living polymerization of methacrylic esters. In the case of branched alkyl methacrylates, residue of the parent branched alcohol is the main impurity, whose complete elimination is a problem compared to normal alcohols because of a lower reactivity toward triethylaluminum (TEA). An efficient purification technique has been proposed and applied to *tert*-butyl methacrylate (tBMA),[19,20] that consists of the addition of diisobutylaluminum hydride (DIBAH) to the TEA solution. This method has been successfully used for the purification of isobornyl methacrylate (IBMA) in this work, since polymerization of accordingly purified IBMA has provided a polymer of a narrow molecular weight distribution (<1.25), as shown in Table 1. Nevertheless, IBMA must be separated from the DIBAH/TEA mixture by distillation prior to polymerization. The high boiling point of IBMA (245 °C/760 mmHg) is responsible for the partial polymerization even when distillation is conducted at 110 °C under reduced pressure. McGrath et al.[21] have purified methacrylates of a high boiling point by using a column technique. In order to avoid these problems, IBMA has been tentatively polymerized in the presence of the residual DIBAH/TEA mixture. Table 1 shows that samples P3 and P8 that have been prepared with the nondistilled monomer show a slight increase in syndiotacticity and a quite comparable molecular weight distribution with respect to the P1 and P4 samples prepared with previously distilled IBMA.

It is worth noting that initiation of the IBMA polymerization by DDBLi in THF and in toluene is slower compared to MMA. Indeed, the red color of the initiator does not disappear immediately but slowly when the monomer is added, in sharp contrast to what happens when MMA is the monomer.

The polymerization temperature of MMA is known to have a critical effect on the stability of the enolate form of the active species and thus to affect deeply the polymer yield and chain tacticity.[19] The temperature effect is usually of a decreasing importance when the

Table 1. Polymerization of Isobornyl Methacrylate (IBMA) with (1,1-Diphenyl-3,3-dimethylbutyl)lithium (DDBLi) as Initiator

sample	solvent[a]	A[b]	T (°C)	reactn time (h)	polym yield(%)	$\overline{M}_n$cal[c]	$\overline{M}_n$ SEC[d]	$\overline{M}_w/\overline{M}_n$	microstructure (%)[e]			T_g[f] (°C)
									s	h	i	
P1	THF		−78	2	100	14 700	19 000	1.25	66	34	0	196
P2	THF		0	2	100	14 700	16 000	1.25	58	39	3	199
P3[g]	THF		−78	2	100	19 800	27 000	1.30	74	26	0	206
P4	THF	LiCl	−78	1	85	12 000	19 000	1.05	70	27	3	202
P5	THF	LiCl	0	1	88	12 000	19 000	1.05	61	37	2	195
P6	THF	LiCl	25	1	91	13 000	19 000	1.15	55	43	2	198
P7	THF	LiCl	40	1	93	13 000	19 000	1.15	50	45	5	196
P8[g]	THF	LiCl	−78	1	90	13 000	19 000	1.05	73	27	0	197
P9	Tol		25	12	100	29 000	72 000	2.25	2	33	65	174
P10	Tol/THF	LiCl	25	1.5	100	29 000	26 000	1.25	37	41	22	194
P11	CH		25	12	100	29 000	33 000	5.05	8	32	60	177
P12	CH/THF	LiCl	25	1.5	100	29 000	31 000	1.20	34	46	20	192

[a] Tol = toluene, CH = cyclohexane, Tol/THF and CH/THF are 9/1 (v/v) mixtures. [b] [LiCl]/[Li$^+$] = 5. [c] Calculated for a living polymerization. [d] Calculated in reference to a polystyrene calibration. [e] ^{13}C NMR. [f] DSC: heating rate 20 °C/min. [g] Monomer is contaminated by residues of the DIBAH/Et$_3$Al purification agents.

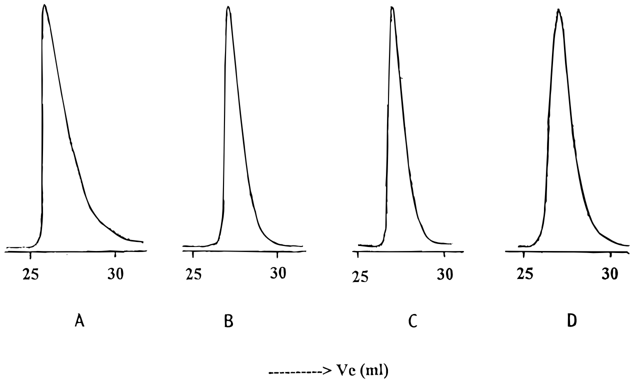

Figure 1. Typical SEC traces for poly(isobornyl methacrylate) (PIBMA): P1 (A); P4 (B); P5 (C); P6 (D).

bulkiness of the ester alkyl group is increased, since the stability of the enolate is accordingly improved. In this regard, samples P1 and P2 are convincing examples, since molecular weight, molecular weight distribution, and monomer conversion are the same although the polymerization temperature is very different, i.e. −78 °C for P1 and 0 °C for P2, except for a slightly lower syndiotacticity at 0 °C. This observation is in complete agreement with results reported by McGrath et al.[19] for the anionic polymerization of tBMA.

It has been reported from our laboratory[12] that μ-type ligands, such as LiCl, are quite efficient in promoting the living polymerization of (meth)acrylic esters. Although PIBMA prepared in THF (P1 to P3 samples) has a rather narrow molecular weight distribution (<1.30), a small tail is observed on the low molecular weight side (Figure 1A). The anionic polymerization of IBMA has been repeated in THF in the presence of LiCl with a [LiCl]/[initiator] molar ratio of 5. Table 1 shows that the molecular weight distribution becomes narrower (1.05), and Figure 1B−D for the P4 to P6 samples confirms that the low molecular weight tail has disappeared. This series of anionic polymerization of IBMA added with LiCl provides additional evidence that the polymerization temperature has limited effect on the polymerization reaction. Indeed, when the polymerization temperature is increased from −78 to 40 °C (samples P4 to P7 in Table 1), the molecular weight distribution is slightly increased from 1.05 to 1.15 and initiation efficiency, which is the ratio between the theoretical molecular weight and the experimental value is not significantly different. Nevertheless, the chain tacticity is affected, since the syndiotacticity of PIBMA is decreased from 70% to 50% in favor of the hetero triads. Thus, compared to the anionic polymerization of MMA, which is adversely affected by the polymerization exotherm (>10 °C) at −78 °C, no side reaction occurs in the course of the anionic polymerization of IBMA in a large temperature range. So a careful control of the reaction exotherm, e.g. by very slow monomer addition, is not required.

In addition to polymerization temperature and ligand, solvent polarity also has an effect on the polymer tacticity and the livingness of polymerization. The stereochemical addition of the incoming monomer to the propagating enolate is indeed strongly dependent on the presence or not of peripheral solvation. Table 1 reports polymerization experiments not only in THF but also in apolar solvents such as toluene and cyclohexane and in 9/1 (v/v) mixtures of these solvents with THF in which LiCl has a limited solubility compared to complete insolubility in the pure apolar solvents. Similarly to tBMA, polymerization of IBMA is not controlled in an apolar solvent at room temperature and a broad molecular weight distribution is observed, 2.25 in toluene and 5.05 in cyclohexane, as shown in Table 1. This situation is, however, significantly improved by addition of 10% THF, since the molecular weight distribution dramatically decreases down to 1.25 in the 9/1 (v/v) toluene/THF mixture and to 1.20 in the cyclohexane/THF mixture of the same composition. The effect of solvent polarity on chain tacticity is clearly illustrated by comparison of samples P6 (55% syndiotactic triads in THF), P9 (65% isotactic triads in toluene), and P10 [37% syndiotactic triads in toluene/THF (9/1, v/v)] at 25 °C (Table 1). Thus, combination of polar and apolar solvents allows us to control tacticity over a wide range.

Synthesis of Triblock Copolymers. Synthesis of well-defined PMMA−PBD−PMMA (MBM) triblock copolymers has been reported from this laboratory by using the *m*-DIB/*t*-BuLi diadduct as a difunctional initiator for the butadiene polymerization.[15] Table 2 shows that this technique is also successful for the preparation of triblock copolymers in which PIBMA is substituted for PMMA. Typical SEC traces are illustrated in Figure 2. A symmetric and very narrow molecular weight distribution is observed for both the PBD midblock and the triblock copolymer (1.10), which indicates that the polybutadienyl dianions end-capped by DPE quantitatively initiate the IBMA polymerization. The major advantage of IBMA over MMA is that copolymerization of the methacrylic monomer can be conducted at 25 °C and no longer at −78 °C while the

Table 2. Synthesis of Poly(alkyl methacrylate) (PAMA)−Polybutadiene (PBD)−PAMA Triblock Copolymers with the *m*-Diisopropenyl Benzene (*m*-DIB)/*t*-BuLi Diadduct as Difunctional Initiator

				PBD				PAMA		
sample	PAMA	T (°C)[a]	total yield (%)	$\overline{M}_n$ cal[b]	$\overline{M}_n$ SEC[c]	1,2 (%)[d]	$\overline{M}_w/\overline{M}_n$[c]	$\overline{M}_n$[e]	content (%)[d]	$\overline{M}_w/\overline{M}_n$
C1	PIBMA	−78	100	50 000	60 000	43	1.10	2 × 15	33	1.10
C2[f]	PIBMA	−78	100	50 000	60 000	45	1.10	2 × 15	33	1.10
C3	PIBMA	25	100	50 000	60 000	43	1.10	2 × 15	33	1.10
M	PMMA	−78	100	50 000	60 000	43	1.10	2 × 16	34	1.10

[a] Polymerization temperature for the methacrylate monomer. [b] Calculated from the monomer weight/ initiator mole ratio. [c] Calculated in reference to a polystyrene calibration. [d] ^{1}H NMR analysis. [e] $\overline{M}_n$ calculated from the copolymer composition and the PBD molecular weight. [f] No previous distillation of IBMA from the purification agents (see Experimental Part).

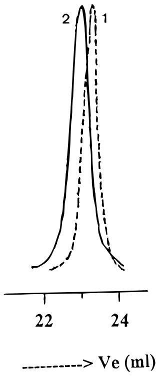

Figure 2. Typical SEC traces for (1) the PBD precursor and (2) the PIBMA−PBD−PIBMA triblock copolymer.

control on the molecular structure of the triblock is kept intact. The C3 sample synthesized at 25 °C has indeed the same molecular characteristics as the C1 sample prepared at −78 °C for the IBMA polymerization (Table 2). As in the case of IBMA homopolymerization, the use of IBMA containing the purification agents (DIBAH/TEA mixture) (sample C2) rather than the corresponding distilled monomer (samples C1 and C3) does not perturb the copolymerization course. In all the cases, a very narrow molecular weight distribution is observed (1.10). It is worth pointing out that no gelation occurs upon addition and polymerization of IBMA even at −78 °C in cyclohexane/THF (60/40, v/v) at a 7 wt % polymer concentration, although in the case of MMA, a gel is immediately formed when the monomer is added to a 50/50 (v/v) cyclohexane/THF at a 3 wt % polymer concentration.[15] Thus a smaller THF content, a higher monomer concentration, and a much higher temperature for the IBMA polymerization compared to MMA make the PIBMA−PBD−PIBMA triblock copolymers very promising materials for industrial production.

In order to illustrate the range of end products that can be made available by living block copolymerization of IBMA, a triblock copolymer has been hydrogenated by a Co/Al catalyst.[23,28] FTIR and ^{1}H NMR analysis confirm the quantitative conversion of the PBD to the saturated counterpart which is much more resistant to oxidation and better suited to high-temperature applications. Figure 3 shows that the IR absorptions at 960 and 910 cm^{-1} for 1,4- and 1,2-units, respectively, and at 1640 cm^{-1} for the C=C stretching of cis-1,4-units have disappeared, in contrast to the absorption of PIBMA at 1725 cm^{-1}, which remains unchanged after hydrogenation, although this polymethacrylate is known for propensity to hydrolysis in the presence of an acid.[26] SEC analysis (Figure 4) shows that the molecular weight distribution remains narrow: 1.15 instead of 1.10 before hydrogenation. A small shoulder on the high molecular weight side of the elution peak is, however, detected, the origin of which is still unclear.

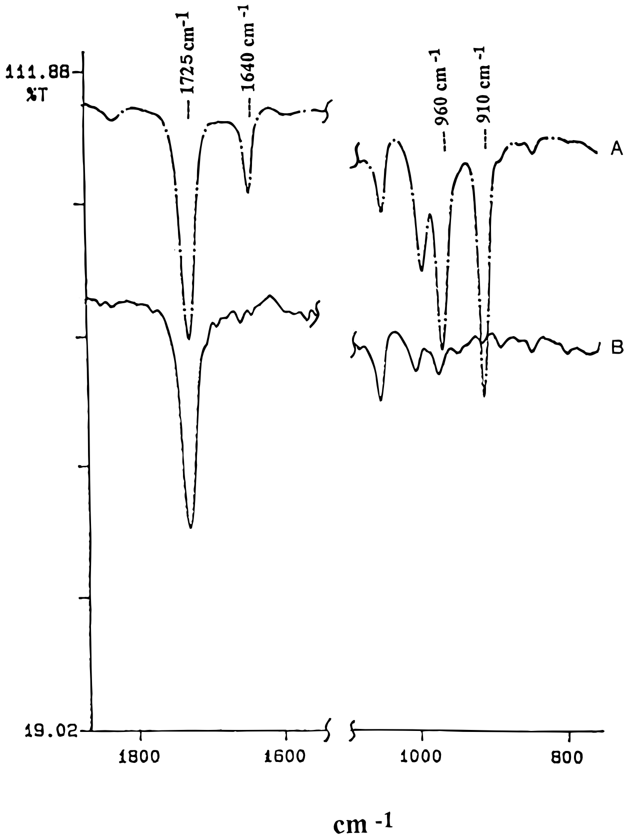

Figure 3. FTIR spectra for (A) the PIBMA−PBD−PIBMA triblock copolymer C1 and (B) the hydrogenated derivative C1H.

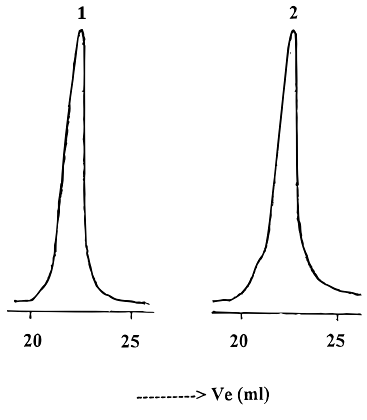

Figure 4. SEC traces for the PIBMA−PBD−PIBMA triblock copolymer C1 (trace 1) and the hydrogenated derivative C1H (trace 2).

Characterization of Homopolymers and Triblock Copolymers. Fourier transform infrared (FTIR) spectroscopy, NMR (^{13}C, ^{1}H), and DSC have been used as characterization techniques for PIBMA and the

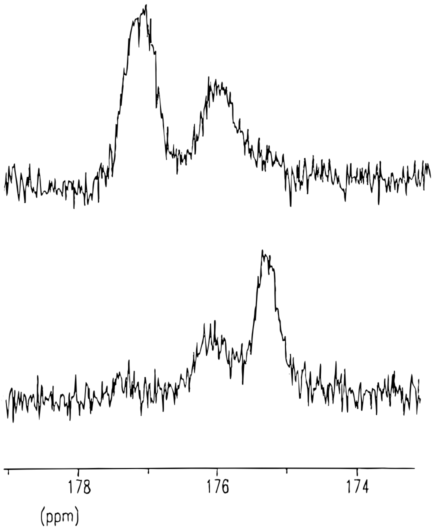

Figure 5. ^{13}C NMR of the carbonyl region for PIBMA samples: P4 (A); P9 (B).

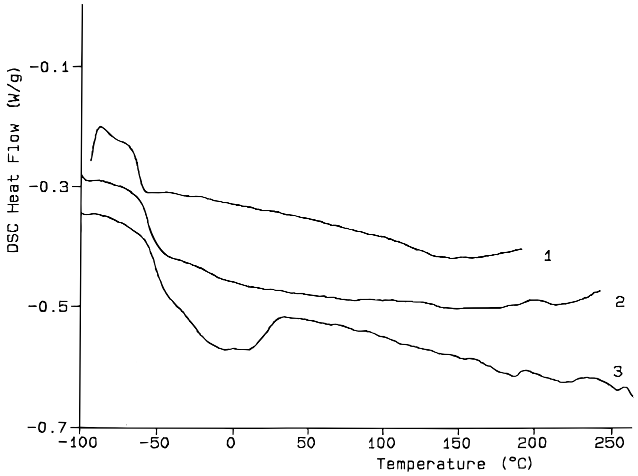

Figure 6. DSC traces for (1) the PIBMA−PBD−PIBMA sample C1, (2) the PMMA−PBD−PMMA sample M, and (3) the hydrogenated copolymer C1H.

triblock containing them. FTIR shows that the carbonyl IR absorption of PIBMA (1725 cm^{-1}) is close to PtBMA (1723 cm^{-1}), but different from PMMA (1730 cm^{-1}), which illustrates the effect of the alkyl group on the carbonyl environment. Although ^{1}H NMR is a convenient technique for the analysis of the PMMA tacticity, it is not applicable to bulkier alkyl esters due to signal overlapping in the α-methyl region, as observed for PtBMA and poly(isopropyl methacrylate).[19] ^{13}C NMR is, however, sensitive to the stereochemical environment of the carbonyl carbon. Figure 5 shows that the ^{13}C chemical shifts characteristic of the carbonyl do not interfere with other resonances. Three resonances are observed: the downfield peak is assigned to the isotactic triads, the upfield peak to the syndiotactic triads and the intermediate peak to the heterotactic triads.[18]

The glass transition temperature (T_g) of PIBMA (Table 1) ranges from 174 to 206 °C depending on the chain tacticity. These values are in good agreement with the T_g of PIBMA of comparable tacticity,[10,18] but synthesized by a radical process. The T_g of PIBMA is much higher than that of highly syndiotactic PMMA, as a result of a reduced chain flexibility due to the steric hindrance of the large isobornyl side group.[17] The difference in T_g for syndiotactic and isotactic PIBMA is ca. 34 deg, thus comparable to poly(*tert*-butyl methacrylate). Figure 6 shows the DSC trace of toluene-cast films of triblock copolymers. As is usually reported for the DSC analysis of thermoplastic elastomers,[24] the glass transition of the hard block is quite a problem. The T_g of the polybutadiene block is clearly observed at ca. −60 °C, independently of the hard block PMMA or PIBMA. The hydrogenated sample (C1H) shows a very broad and ill-defined melting endotherm with a very diffuse maximum at ca. −7 °C, which indicates that the E/B central block tends to crystallize with formation of poorly organized crystalline microphases, as has been observed for SEBS triblock copolymers.[24]

The thermal dependence of the shear storage (G') and loss (G'') moduli from −100 to +200 °C for the PIBMA−PBD−PIBMA copolymer, C1, and the PMMA−PBD−PMMA copolymer, M, is compared in Figure 7 and Table 3. The glass transition temperature of the PBD midblock is consistently observed at ca. −50 °C; the glass transition of the hard PIBMA phase is observed at a much higher temperature (160 °C, Figure 7A) than that of the PMMA phase (130 °C, Figure7B), which supports the beneficial effect of the PMMA substitution by PIBMA on the upper service temperature. The high sensitivity of DMA with respect to DSC makes it clear that the PIBMA−PBD−PIBMA copolymers are two-phase separated materials, in spite of a small difference in the solubility parameter of PIBMA [8.1 (cal/cm^3)$^{1/2}$] and PBD [8.4 (cal/cm^3)$^{1/2}$].[22]

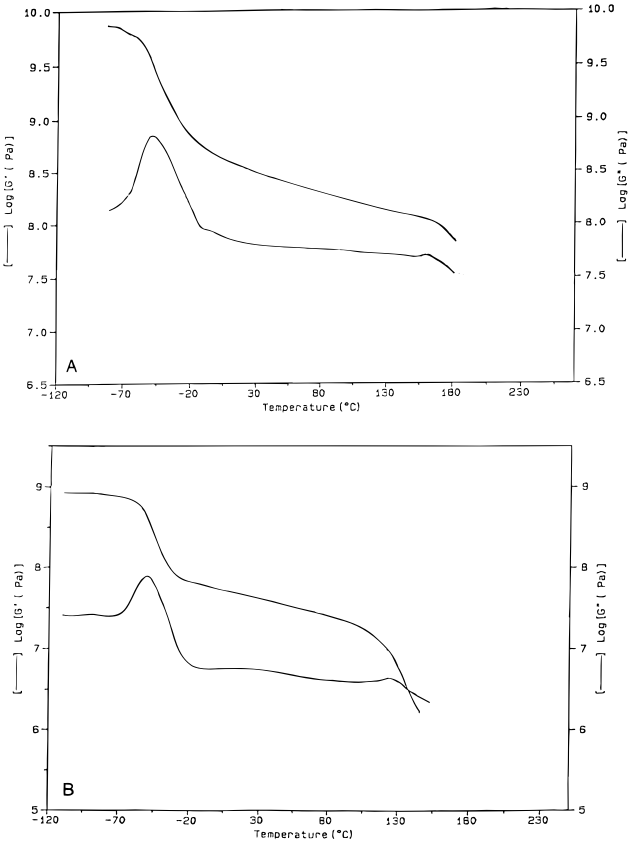

Figure 7. Shear storage (G') and loss (G'') moduli vs temperature for (A) sample C1, and (B) sample M. Heating rate: 5 °C/min; frequency: 1 Hz.

This conclusion is confirmed by stress−strain measurements. Indeed, Figure 8 shows stress−strain behavior typical of a cross-linked rubber, i.e., low initial modulus, high elongation at break, and high ultimate tensile strength. This observation is indicative of phase separation and efficiency of the PIBMA microdomains in restricting the flow of the soft butadiene segments.

Table 3. Thermal and Mechanical Properties of PIBMA−PBD−PIBMA and MBM Triblock Copolymers

sample	T_{g1}[a] (°C)	T_{g2}[a] (°C)	initial modulus (MPa)	ultimate tensile strength (MPa)	elongation at break (%)	permanent set at break (%)[b]
C1	−58 (−50)	(160)	19	30	1000	40
C2	−58		18	28	1000	53
C3	−58		18	30	1100	47
C1H	−53		90	33	560	50
M	−60 (−50)	(130)	6	31	990	35

[a] DSC heating rate 20 °C/min; values in parentheses were measured by DMA (1 Hz and 5 °C/min heating rate). T_{g1} corresponds to the maximum at low temperature and T_{g2} to the onset of the maximum at high temperature on the G'' vs temperature curve. [b] Ratio of the unrecoverable deformation at break to the initial sample length.

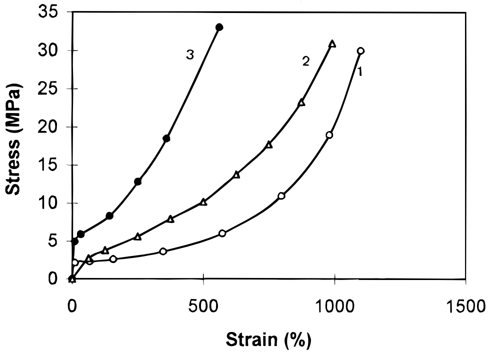

Figure 8. Stress-strain curves for (1) the PIBMA−PBD−PIBMA sample C1, (2) the PMMA−PBD−PMMA sample M, and (3) the hydrogenated sample C1.

Table 3 compares the tensile strength of PIBMA−PBD−PIBMA samples (C1, C2, C3) of the same composition and molecular weight although prepared under different experimental conditions, particularly the polymerization temperature and the purification procedure of IBMA (Table 1). Table 3 shows that these experimental modifications have no significant effect on tensile strength, elongation, and permanent set at break. In contrast to PIBMA which has a solubility parameter (δ) quite comparable to PBD, δ(PMMA) is much higher [9.3 (cal/cm^3)$^{1/2}$]. This difference might result in a better phase separation between the PBD midblock and the outer PMMA hard blocks. Some clues for this effect might be found in a smaller elongation at break and initial modulus when PMMA is the hard block. A reduction in elongation at break is consistent with a more efficient cross-linking. The observation of a yield point for the PIBMA-containing triblock copolymer is the signature for some PIBMA phase continuity. This characteristic feature is much less visible for the PMMA counterpart (curve 2, Figure 8) and points to a difference in the phase morphology. Continuity in the PIBMA phase agrees with a smaller interfacial area and thus a less extended phase separation. In the case of the hydrogenated PIBMA-containing sample C1H (curve 3, Figure 8), the ultimate tensile strength is slightly higher and the elongation at break is significantly smaller compared to the parent non-hydrogenated copolymer C1 (curve 1, Figure 8).

Conclusion

Isobornyl methacrylate (IBMA) has been shown to polymerize according to living mechanism in THF in a wide temperature range from −78 to +40 °C in the presence of LiCl by using (1,1-diphenyl-3,3-dimethylbutyl)lithium as initiator. Polymerization of IBMA in apolar solvents, such as toluene and cyclohexane, is not controlled. Although the reactivity of IBMA is comparable to *tert*-butyl methacrylate (tBMA), the syndiotactic triad content (71%) of PIBMA prepared in THF at −78 °C is slightly higher compared to the free radical polymerization, in contrast to the syndiotacticity of PtBMA which is smaller. The T_g of PIBMA is in the 170−206 °C range, depending on chain tacticity. The sequential polymerization of poly[isobornyl methacrylate (IBMA)-*b*-butadiene (BD)-*b*-IBMA] triblock copolymers has been initiated by the *m*-diisopropenylbenzene (*m*-DIB)/*tert*-butyllithium (*t*-BuLi) diadduct. This type of triblock copolymer with a very narrow molecular weight distribution (1.10) can be prepared even at room temperature in contrast to poly(MMA-*b*-BD-*b*-MMA) which must be synthesized at a low temperature (−78 °C). These materials and the hydrogenated counterparts exhibit high tensile strength (30 MPa), high ultimate elongation (1000%), and high upper service temperature (160 °C).

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