Synthesis and bulk properties of poly(methyl methacrylate)-*b*-poly(isooctyl acrylate)-*b*-poly(methyl methacrylate)

J.D. Tong[a], Ph. Leclère[b], C. Doneux[b], J.L. Brédas[b], R. Lazzaroni[b], R. Jérôme[a],*

[a]*Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, B-4000 Liège, Belgium*
[b]*Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc, 20, B-7000 Mons, Belgium*

Abstract

A series of well-defined poly(methylmethacrylate) (PMMA)-*b*-poly(isooctylacrylate) (PIOA)-*b*-PMMA triblock copolymers (MIM) has been synthesized by transalcoholysis of PMMA-*b*-poly(*tert*-butylacrylate) (PtBA)-*b*-PMMA precursors (MTM) by isooctyl alcohol. Phase separation is observed for all the investigated triblock copolymers, thus containing PMMA outer blocks in the 3500–50,000 molecular weight (MW) range and PIOA inner block with MW in the 100,000–300,000 range. The ultimate tensile properties of these MIM triblock copolymers are poor even when PMMA blocks of 50,000 MW are associated with an inner PIOA block of 300,000 MW. A reasonable explanation should be found in the molecular weight between chain entanglements (M_e), which has been estimated at 60,000 for PIOA, much higher than M_e for the traditional polydiene central blocks in the well-known thermoplastic elastomers of the triblock type. The tensile behavior of MIM copolymers has been successfully accounted for by a simple elastomer model free from chain entanglements, supporting the view that the lack of entanglements in the central block is very detrimental to the mechanical properties of the investigated fully (meth)acrylate triblock copolymers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(methyl methacrylate-*b*-poly(isooctyl acrylate)-*b*-poly(methyl methacrylate); Bulk properties; Synthesis
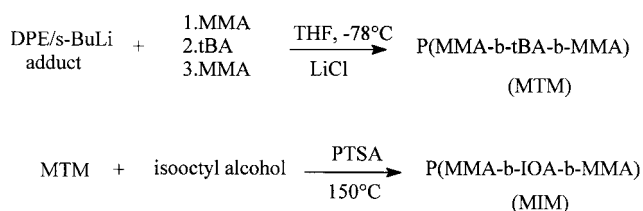
1. Introduction

SBS and SIPS triblock copolymers consisting of polystyrene blocks (S) and a central rubbery polybutadiene (B) or polyisoprene (IP) block are well-known thermoplastic elastomers (TPEs). They are used in a large range of applications such as adhesives, footwear, medical devices, automobile parts and asphalt modification. Their unique thermomechanical properties are associated with a phase morphology of PS domains dispersed in a continuous rubbery phase. This physical network of flexible chains combines the mechanical performance of vulcanized rubbers and the straightforward processing of thermoplastics. The use of diene-based TPEs is, however, limited by the poor oxidation resistance of the unsaturated central block and the relatively low upper service temperature (60–70°C), controlled by the glass transition of polystyrene. Accordingly, efforts have been made to improve the performances of TPEs by changing either the outer [1–5] or the inner [2,6] blocks. Another valuable alternative considered

in this paper is fully (meth)acrylate TPEs, in relation to the large range of properties of this family of polymers. Indeed, depending on the alkyl substituent of the ester group, the glass transition temperature (T_g) can be changed over a very large temperature range (e.g. from −50°C for poly(isooctyl acrylate) up to 190°C for poly(isobornyl methacrylate)). Furthermore, immiscibility of alkyl polymethacrylates and polyacrylates is the rule, although some exceptions are found in the case of small alkyl groups and low molecular weight [7]. The much better resistance of poly(meth)acrylates to oxidation compared with polydienes is an additional advantage. Finally, recent progress in the controlled/living radical polymerization of alkyl (meth)acrylates has raised an optimistic forecast in the direct synthesis of polymethacrylate-*b*-polyacrylate-*b*-polymethacrylate triblock copolymers [8] which remains a challenge in anionic polymerization.

Nevertheless, the previous study of PMMA-*b*-poly(alkyl acrylate)-*b*-PMMA triblocks [9,10], [PMMA-*b*-poly(alkyl acrylate)]$_n$X and [PS-*b*-poly(alkyl acrylate)]$_n$X star-shaped copolymers [9], and poly(methacrylic acid) (PMAA)-*b*-poly(2-ethylhexyl methacrylate) (P2EHMA)-*b*-PMAA and the neutralized version [11] has shown that (meth)acrylate

---

* Corresponding author. Tel.: +32-4-366-3565; fax: +32-4-366-3497.
E-mail address: rjerome@ulg.ac.be (R. Jérôme).

DPE/s-BuLi adduct + 1.MMA 2.tBA 3.MMA $\xrightarrow[\text{LiCl}]{\text{THF, -78°C}}$ P(MMA-b-tBA-b-MMA) (MTM)

MTM + isooctyl alcohol $\xrightarrow[\text{150°C}]{\text{PTSA}}$ P(MMA-b-IOA-b-MMA) (MIM)

Scheme 1.

based triblock copolymers have rather poor ultimate mechanical properties ($\sigma_B < 10$ MPa and $\varepsilon < 500\%$) compared to traditional diene-based TPEs ($\sigma_B \approx 30$ MPa and $\varepsilon \approx 800$–1000%). Several reasons have been proposed to account for the poor mechanical properties of these fully (meth)acrylate triblocks, such as (partial) miscibility of the constitutive blocks [12], sample preparation by compression molding at a temperature at which melt viscosity remains very high [9,13], too short outer blocks [11] and poor control of the block copolymer structure [10]. Actually, except for the synthesis, little is known about the properties of this kind of materials. The main pending question is certainly to know whether the poor mechanical performances are intrinsic to this type of triblock copolymers or result from lack of control in the synthesis and/or processing of the samples. In order to answer this question, a series of PMMA-*b*-poly-(isooctyl acrylate)-*b*-PMMA, or MIM, triblock copolymers has been synthesized by sequential living anionic polymerization of MMA, *tert*-butyl acrylate (tBA) and MMA, followed by the selective transalcoholysis of the central PtBA block by isooctyl alcohol. All these triblocks have been characterized by size exclusion chromatography (SEC), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA) and atomic force microscopy (AFM). Although the molecular structure is well-controlled (e.g. $M_w/M_n < 1.1$) and the phase separation is clearly observed, the ultimate tensile properties of these physically vulcanized rubbers remain much lower than the traditional styrene–diene counterparts. So, the origin for this disappointing observation should be found in the chemical composition of the triblocks, as will be discussed further.

2. Experimental section

2.1. Materials

THF and toluene were purified by refluxing over the deep purple sodium-benzophenone complex. MMA and tBA (Aldrich) were refluxed over CaH$_2$, vacuum distilled and stored under nitrogen at $-20°C$. Before polymerization, they were added with a 10 wt% AlEt$_3$ solution in hexane until a persistent yellowish green color was observed, and distilled under reduced pressure just prior to use (tBA was diluted by the same volume of toluene before distillation). *sec*-Butyllithium (s-BuLi) (Aldrich, 1.3 M solution in cyclohexane) was diluted by cyclohexane (ca. 0.25 N).

1,1-diphenylethylene (DPE, Aldrich) was vacuum distilled over s-BuLi and diluted by toluene (ca. 0.3 N). Isooctyl alcohol (3 M) was used as received. LiCl (99.99%, Aldrich) was dried under vacuum at 130°C.

2.2. Synthesis of polyMMA-b-polytBA-b-polyMMA (MTM) precursors

A known amount of LiCl was added to a glass reactor that was flamed under vacuum and purged with nitrogen. THF and DPE were transferred into the glass reactor by using rubbery septa and stainless steel capillaries or syringes. Three-fold molar excess of DPE and five-fold molar excess of LiCl were used with respect to s-BuLi. The initiator solution was then added dropwise until a red color persisted, followed by the desired amount of initiator. The solution was cooled down to $-78°C$ and added with the required amount of MMA. The polymerization was conducted at $-78°C$ for 1 h. Upon MMA addition, the deep red color of the initiator immediately disappeared, indicating an instantaneous initiation. The sequential addition and polymerization of tBA and MMA were carried out under the same conditions. The copolymerization product was quenched by degassed methanol and the final solution was concentrated before being precipitated into an excess of 90/10 (v/v) methanol/water mixture under stirring. The crude copolymer was dried under vacuum at 60–80°C overnight.

2.3. Derivatization of polyMMA-b-polyIOA-b-polyMMA (MIM) copolymers

On the basis of preliminary experiments, the best conditions for the transalcoholysis of the tBA units of MTM copolymers consisted in dissolving the copolymers in an excess of isooctyl alcohol in the presence of *p*-toluenesulfonic acid (PTSA; 10 mol% with respect to tBA units). After reflux at 150°C for 48 h, the copolymer was recovered by precipitation in methanol and dried under vacuum at 80°C overnight. Scheme 1 (synthesis of MIM triblock copolymers) summarizes the main steps for the synthesis of the MIM copolymers.

PIOA of the same microstructure as the central PIOA block in the MIM triblocks was also prepared by transalcoholysis of PtBA homopolymer by isooctyl alcohol as detailed above. PtBA was synthesized by anionic polymerization of tBA in THF in the presence of LiCl([LiCl]/[Li] = 5) at $-78°C$ for 30 min.

2.4. Sample preparation.

Films were prepared by casting a copolymer solution (8 wt%; 160 ml) in a 100 mm diameter polyethylene dish. The solvent was evaporated over 3–4 days at room temperature. Films were dried to constant weight in a vacuum oven at 80°C for ca. 1 day. They were colorless, transparent and elastomeric, with a smooth surface.

2.5. Analysis

Molecular weight and molecular weight distribution were measured by size exclusion chromatography (SEC) in THF with a Hewlett-Packard 1090 apparatus equipped with linear styragel columns. PMMA standards were used for calibration.

^{1}H NMR spectra were recorded with a Bruker AM-250 spectrometer by using $CDCl_3$ as solvent at 25°C. Composition of the diblock and the final MTM triblocks was calculated from the relative intensity of the signals for the O–CH$_3$ protons in PMMA (3.6 ppm), and the –C(CH$_3$)$_3$ protons in PtBA (1.4 ppm). M_n of the PtBA block (in the intermediate diblock) and the final MTM triblock was calculated from the copolymer composition and molecular weight of the first PMMA block.

DSC analysis was carried out with a DuPont 910 calorimeter at heating rates of 10–20°C/min.

Dynamic mechanical properties of the MIM copolymers were measured with a Polymer Laboratory DMTA. 7 mm diameter samples were cut from 1–2 mm thick solution cast films. They were tested in the shear mode (1 Hz frequency; 1% strain) at a scanning rate of 2°C/min.

Viscoelastic properties of PIOA were measured by using the RSI ARES rheometer equipped with the cone-plate geometry (25 mm diameter, 4° cone angle and 56 μm gap between the cone tip and the plate).

AFM images were recorded with a Nanoscope IIIa microscope from Digital Instruments Inc. Details were reported elsewhere [13].

Tensile properties were measured with an Adamel Lhomargy tensile tester. Microdumbells were cut from solution cast films and extended at 100 mm/min at room temperature. Strain was measured from the crosshead displacement. Sample thickness and width were 1.5 and 4 mm, respectively. At least three independent measurements were recorded for each sample.

3. Results and discussion

3.1. Synthesis

The prerequisite for drawing fundamental structure-property relationships for triblock type TPEs 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 length. Living anionic polymerization is certainly a valuable way to achieve this target in case of fully acrylic triblocks. Syndiotactic PMMA has been selected as the hard block, because of a T_g close to 130°C when MMA is anionically polymerized in THF at low temperature. In contrast to the anionic polymerization of MMA and bulky acrylates, such as tBA [14], which is living in THF at -78°C, that of long-chain acrylates (e.g. *n*-butyl
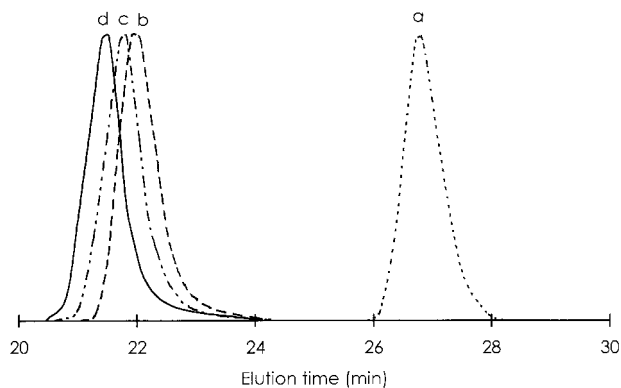

Fig. 1. Typical SEC traces for the three-stage synthesis of MTM copolymers. (a) first PMMA block; (b) PMMA-*b*-PtBA; (c) MTM (sample 3, Table 1); (d) MIM.

acrylate, isooctylacrylate) is usually out of control as result of nucleophilic side reactions. Therefore, the central PtBA block has been originally synthesized because of the ability of the *tert*-butyl ester group to undergo selective acid-catalyzed transalcoholysis by long-chain alcohols, with formation of low T_g polyacrylate. Thus, a three-stage synthesis of MTM triblocks has been initiated by s-BuLi in THF at -78°C. Fig. 1 illustrates the typical SEC traces of the PMMA first block, the intermediate PMMA-*b*-PtBA diblock and the final MTM triblock, respectively (sample 3 in Table 1). Molecular weight distribution is and remains monomodal, symmetrical and narrow ($M_w/M_n \sim 1.1$). Furthermore, molecular weight increases with sequential block copolymerization, in good agreement with the value calculated from the monomer/initiator molar ratio. The sequential polymerization is thus perfectly controlled consistently with the livingness of each step and the reactivity matching of the two co-monomers. Table 1 lists the series of MTM triblock copolymers that have been prepared in a large range of molecular weight (PMMA MW from 3500 to 50,000; PtBA MW from 50,000 to 210,000) and composition (PMMA content: 9–50 wt%). Monomer conversion is usually close to completion and polydispersity narrow ($M_w/M_n < 1.2$). The MTM precursors have been converted into triblocks containing a central PIOA block of low T_g. The acid catalyzed transalcoholysis of PtBA by alkyl alcohol in the presence of PMMA is selective [9,15] and highly quantitative (95–98%). ^{1}H NMR analysis of the original MTM and the final MIM copolymers shows that no tBA group can be detected in MIM although some of them have been hydrolyzed rather than transalcoholyzed. Indeed, the signal at 1.4 ppm for the –C(CH$_3$)$_3$ protons of PtBA has completely disappeared upon transalcoholysis. In parallel, the signal at 4.0 ppm for the –O–CH$_2$– protons of PIOA is observed in the case of MIM triblocks. The transalcoholysis yield is calculated from the relative intensity of the signals for the –O–CH$_2$– protons of PIOA and the –O–CH$_3$ protons of PMMA at 3.6 ppm, compared to the original molar composition of the MTM precursors. The SEC trace
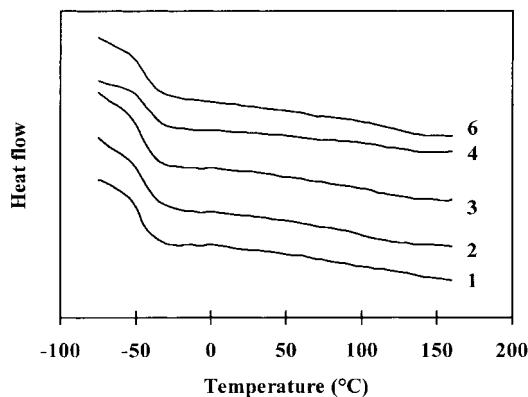
Fig. 2. DSC traces for samples 1–4 and 6 (Table 2). Heating rate: 20°C/min. Samples have been annealed at 140°C for 5 h. Curves have been vertically shifted for the sake of clarity.

of sample 3 after transalcoholysis, thus of the MIM triblock, is shown in Fig. 1. Table 1 shows that the transalcoholysis of MTM into MIM triblocks does not change the MW distribution significantly. It may thus be concluded that fully acrylic analogues of the traditional TPEs of the SBS type can be tailored by sequential anionic polymerization of MMA and tBA, followed by the selective transalcoholysis of the PtBA central block into a low T_g PIOA block.

3.2. DSC and DMTA studies

Measurement of glass transition temperature is a common way to detect phase separation in multicomponent organic materials. As many glass transitions as immiscible components in a block copolymer are predicted at temperatures that however depend on the extent of phase separation. Fig. 2 shows typical DSC traces for a series of MIM triblock copolymers of increasing PMMA content (6.5–22%) and MW (3500–20,000). In each case, a glass transition at ca.
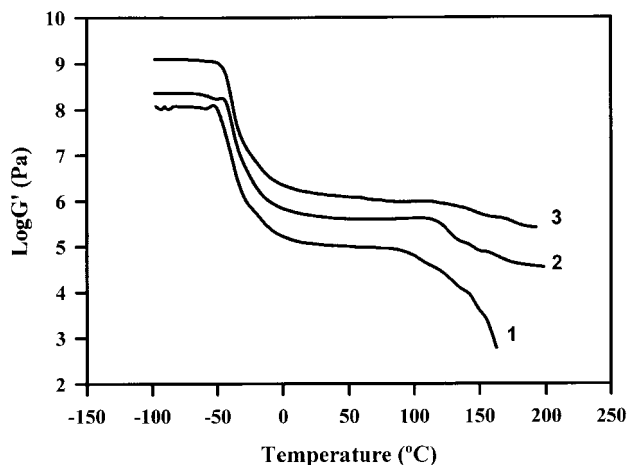

Fig. 3. Shear modulus (G') vs. temperature at 1 Hz for samples 1–3 (Table 2). Heating rate: 2°C/min. For the sake of clarity, curves have been shifted upwards with respect to sample 1 (sample 2 by 0.5 unit; sample 3 by 1.0 unit).

−45°C is clearly detected and assigned to PIOA. The independence of this T_g of the PMMA content and MW is indicative of extensive phase separation. However, observation of T_g for PMMA microphases is a problem except for sample 6, more likely due to low PMMA contents. Since DSC analysis is not sensitive enough to confirm unambiguously the two-phase morphology of the MIM triblock copolymers, the temperature dependence of the dynamic shear modulus (G') has been measured for three MIM triblocks (samples 1–3). Fig. 3 shows a sharp drop of G' at ca. −50°C, which is characteristic of the PIOA glass transition. A rubbery plateau observed between ca. 0 and 100°C for all the samples can only be explained by a three-dimensional network of rubbery chains, as is observed for styrene–diene triblocks. In their study of binary blends of SIPS triblocks with either SIP diblocks or PIP homopolymers, Berglund and Mckay have shown that G' of the triblocks decreases in the plateau region as rapidly as the content of SIP or PIP is increased [16]. The very flat plateau in the temperature dependence of G' observed for the MIM samples (Fig. 3) indicates that the physical network of PIOA chains is essentially free from undesirable diblocks (PMMA–PIOA) or homopolymers, which might have a detrimental effect on the ultimate mechanical properties of the triblocks. At ca. 100°C, G' for the MIM with the shortest PMMA block (sample 1) drops rapidly, which corresponds to the terminal zone, as is commonly observed for the traditional SBS and SIPS thermoplastic elastomers. The increase of the PMMA MW from 3.5K to 7K dramatically changes this situation. The onset of the terminal zone is observed at ca. 120°C, thus ca. 30°C higher than for sample 1. This temperature is also 30–40°C higher than the value reported for the commercially available Kraton 1107 (SIPS, 10 K–120 K–10 K), which is thus a substantial improvement of the upper service temperature. Nevertheless, sample 2 is not in the flow regime above 120°C, since an additional plateau extending up to at least 200°C is rapidly observed. This new characteristic feature, which is more pronounced for sample 3 of higher PMMA MW, indicates that the ordered phase structure is maintained at high temperatures.

3.3. Morphology

Although DSC and DMTA strongly suggest that the PMMA and PIOA blocks are microphase separated, the most convincing evidence for a two-phase morphology is the direct observation on the nanometer scale. Although the phase morphology of fully (meth)acrylate block copolymers cannot be detected by transmission electron microscopy because of lack of electronic contrast, atomic force microscopy (AFM) used in the tapping mode has proved highly efficient [13]. A previous paper has indeed reported that the well-known spherical, cylindrical and lamellar microphase structures were observed for MIM triblocks covering a large range of composition [13]. As an example, Fig. 4 shows two typical AFM images for samples 2 and 6 (Table 2), which
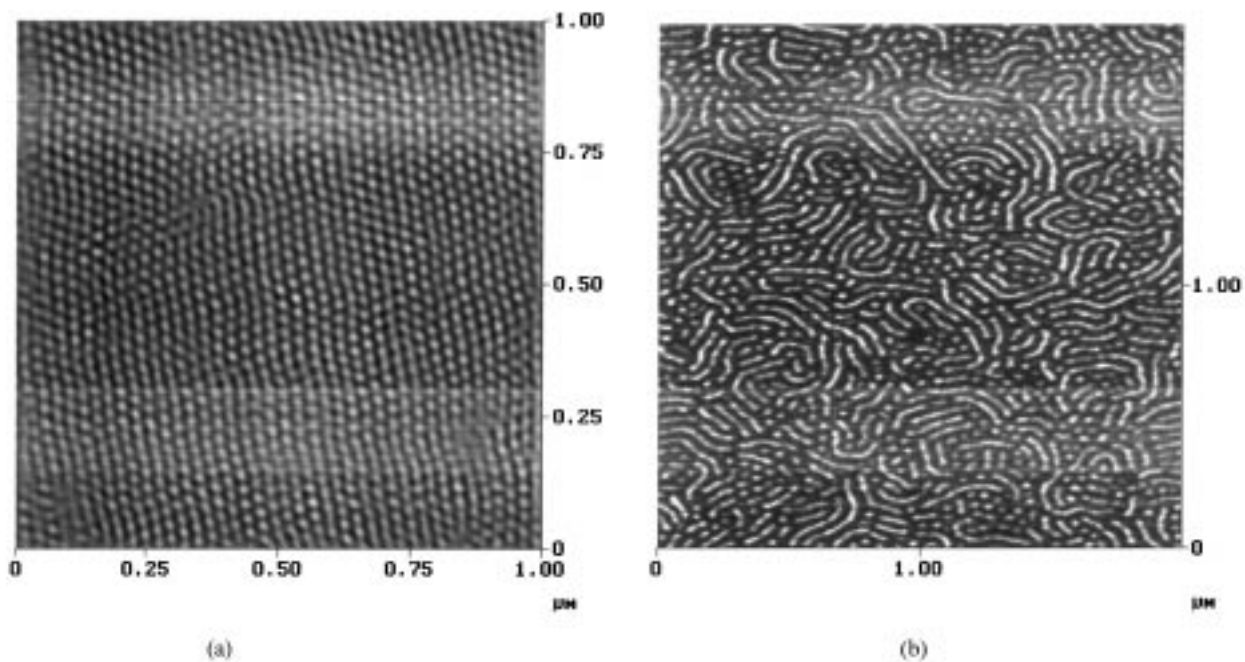
Fig. 4. AFM images for (a) sample 2 in Table 2; (b) sample 6 in Table 2. The white area is characteristic of PMMA microphases.

exhibit spheres and cylinders of PMMA (white micro-domains), respectively. It is worth noting that MIM with very short PMMA blocks (sample 1 [13] and sample 2 (Fig. 4a)) are phase separated, in contrast to the SBS and SIPS analogues, which are monophase materials [17].

3.4. Mechanical properties

Although the MIM triblocks of this series have well-defined molecular structure, exhibit distinct phase-separated morphology and show no evidence of contamination by diblock or homopolymer, their ultimate tensile properties (Table 2), particularly tensile strength (σ_B), are much lower compared with the SBS and SIPS analogues

(30 MPa and 800%) [18]. Fig. 5 shows typical stress–strain curves for a series of MIM triblocks of increasing PMMA MW containing the same PIOA block. Even though the very low σ_B observed for triblocks containing short PMMA blocks (samples 3–5 in Table 2) might be tentatively explained by the very partial miscibility of the constitutive blocks, this explanation does not hold any more for samples with PMMA blocks of higher MW, whose σ_B does not exceed ca. 12 MPa. In this respect, the comparison of the stress–strain curves for MIM and SIPS is very clear, when one knows that the polystyrene/polyisoprene immiscibility is less sharp compared to the PMMA and PIOA pair (cf. the previous section about phase separation in MIM and SIPS). Indeed, Fig. 6 confirms the tremendous superiority of SIPS
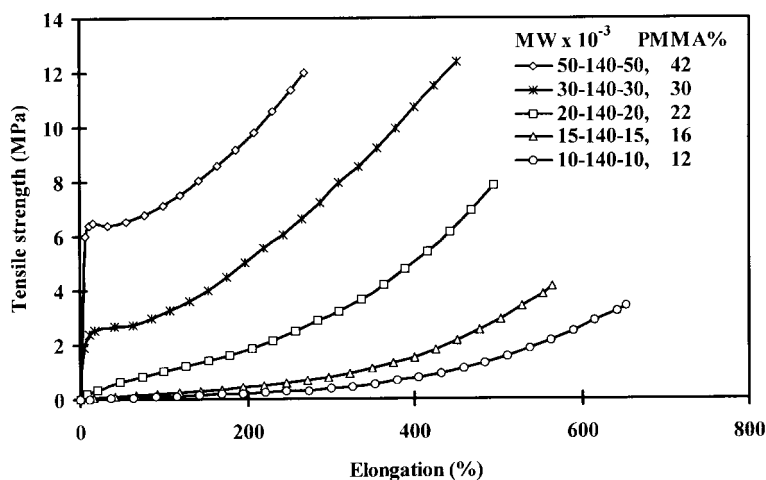

Fig. 5. Tensile curves for MIM triblock copolymers containing the same PIOA block (140,000).
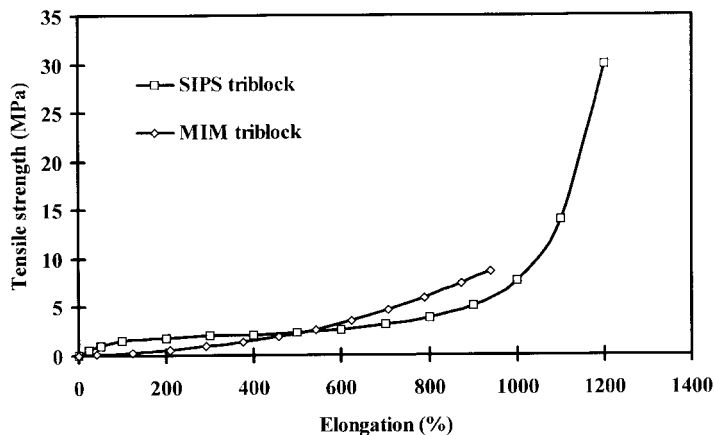
Fig. 6. Stress–strain behavior of SIPS (14K–109K–14K; 13 wt% PS) and MIM (40K–300K–40K; 21 wt% PMMA).

over MIM, which in this example, has, however, the advantage of higher MW and content of the hard block.

In order to explain the basic difference in the behavior of the diene-containing triblocks and the fully acrylic ones, it is worth referring to papers by Holden and Legge [18–20] and Quirk and Morton [19], who noted that the slippage of the entangled central blocks of triblocks could share the applied force so delaying the ductile failure of the hard microdomains. Furthermore, Ver State et al. reported that G_N^o (plateau modulus, see also Eq. (1)) has a dominant effect on the curemeter torque (M_H) for a series of vulcanized elastomers with the same chemical crosslinking density [21,22]. They pointed out that the mechanical properties (modulus and strength) of vulcanized elastomers are strongly influenced by chain entanglements. Therefore, it appears that the ability of the central block to form entanglements is essential for the parent triblock to be a good

thermoplastic elastomer. The average molecular weight between chain entanglements, M_e, is very low in the case of PBD (1700) and PIP (6100) [18]. M_e for PIOA has been determined from viscoelastic data according to Eq. (1) [23–26]

$$M_e = \rho RT/G_N^o \qquad (1)$$

where ρ is the polymer density, R is the gas constant, T is the absolute temperature and $G_N^o = G'(\tan \delta \rightarrow \text{min.})$ is the shear modulus of the viscoelastic plateau. Fig. 7 shows the master curves for homo-PIOA (210,000) at $-20°C$. Calculated from the G_N^o value, M_e is exceedingly high (ca. 60,000) compared to polydienes. Since the entanglement density for the central block is inversely proportional to M_e, it must be very limited in MIM triblocks compared to diene based TPEs, all other characteristics being the same (molecular weight and composition). Consistently, we have recently examined the ultimate mechanical properties of a series of PMMA–poly(alkyl acrylate)–PMMA triblock copolymers with alkyl groups ranging from 2–8 carbon atoms, thus M_e for poly(alkyl acrylates) ranging from 11,000 to 60,000. The ultimate tensile strength was found to increase linearly with $1/M_e$ [27].

The main consequence of the very significant increase in M_e when a rubbery polyacrylate block is substituted for the polydiene one in triblock TPEs is that the tensile behavior of the MIM triblocks should be accounted for by the rubber elasticity theory [28] at low to moderate elongations, rather than by the "rubber + filler" model which fits the behavior of the polydiene-based TPEs. The SIPS tensile behavior is indeed properly accounted for by the classical rubber elasticity law modified by the filler effect [29]:

$$\sigma = \left(\frac{\rho RT}{M_c} + \frac{2C_2}{\lambda} \right)\left(\lambda - \frac{1}{\lambda^2} \right)\left(1 + 2.5\phi_S + 14.1\phi_S^2 \right) \quad (2)$$

where σ is the applied tensile strength, λ is the extension rate; M_c is the average molecular weight between crosslinks (here close to M_e), C_2 is a constant related to deviation from the ideal elastic behavior, and ϕ_s is the volume fraction of
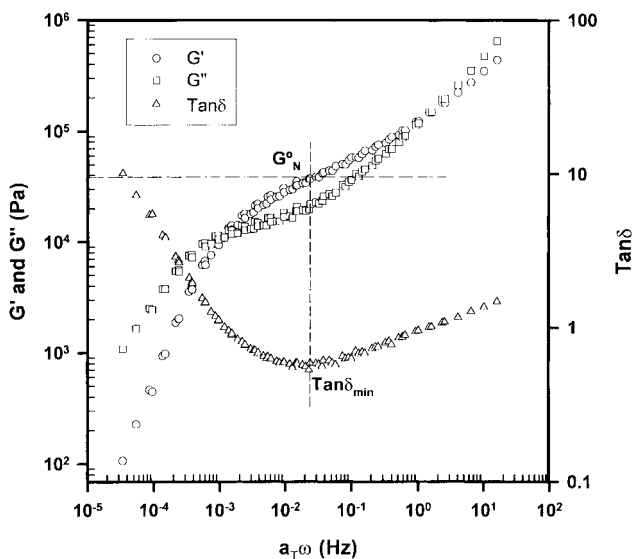

Fig. 7. Master curves (G', G'' and $\tan \delta$) for PIOA ($M_n = 210K$, $M_w/M_n = 1.10$) at $-20°C$. Dashed lines indicate the position of $\tan \delta_{min}$ and the value of G_N^o.
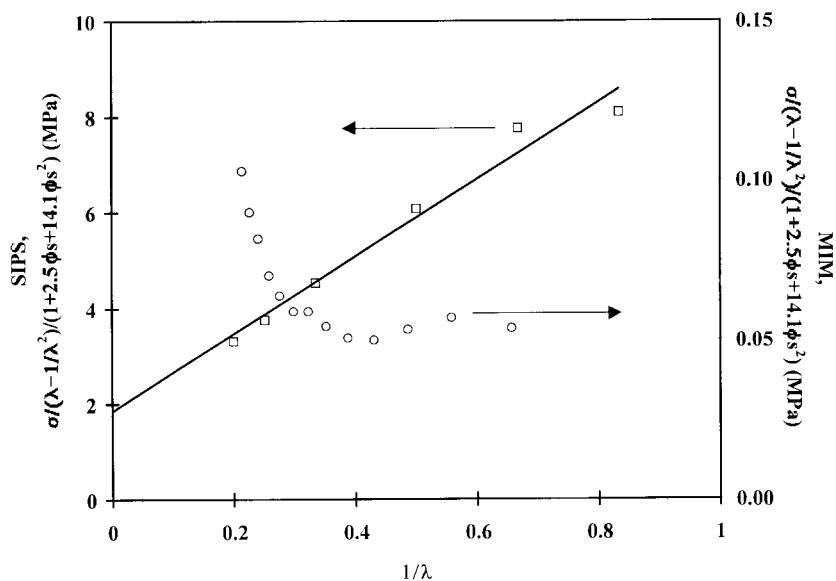
Fig. 8. Stress–strain data for MIM triblock (○, sample 1, Table 2) and SIPS triblock (□, 14K–109K–14K), plotted according to the "rubber + filler" model.

Table 1
Molecular characteristics of the triblock copolymers synthesized in this work

Sample	P(MMA-*b*-tBA-*b*-MMA)		Yield (%)	P(MMA-*b*-IOA-*b*-MMA)	
	M_n (10^{-3})	M_w/M_n		M_n (10^{-3})	M_w/M_n
1	3.5–70–3.5	1.04	95	3.5–100–3.5	1.04
2	7–70–7	1.06	95	7–100–7	1.07
3	10–100–10	1.05	96	10–140–10	1.05
4	15–100–15	1.05	96	15–140–15	1.06
5	20–150–20	1.05	94	20–210–20	1.05
6	20–100–20	1.04	93	20–140–20	1.04
7	40–210–40	1.12	95	40–300–40	1.13
8	30–100–30	1.06	96	30–140–30	1.07
9	20–50–20	1.05	92	20–70–20	1.05
10	40–100–40	1.07	93	40–140–40	1.08
11	50–100–50	1.07	95	50–140–50	1.07

Table 2
Mechanical properties of the MIM triblock copolymers

Sample[a]	PMMA wt%	MW	Ultimate tensile strength (MPa)	Elongation at break (%)	Initial modulus (MPa)
1	6.5	3.5–100–3.5	1.3	490	0.15
2	12.2	7–100–7	3.6	490	0.2
3	12.5	10–140–10	3.1	610	0.2
4	17.6	15–140–15	4.2	530	0.28
5	16.0	20–210–20	5.0	730	0.2
6	22.2	20–140–20	7.1	480	2
7	21.1	40–300–40	8.5	940	0.3
8	30.0	30–140–30	11.9	440	42
9	36.4	20–70–20	11.5	350	96
10	36.4	40–140–40	9.6	460	15
11	41.7	50–140–50	11.8	285	91

[a] All samples are toluene cast films (slow toluene evaporation for 4 days, followed by drying in vacuum at 80°C for 24 h).
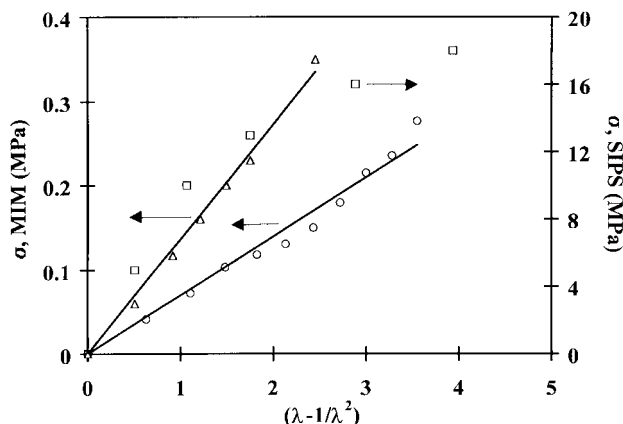
Fig. 9. Stress–strain data for MIM triblocks (○, sample 1 and △, sample 8, Table 2) and SIPS triblock (□, 14K–110K–14K), plotted according to the classical rubber elasticity law.

the PS domains. Although the $\sigma/(\lambda - 1/\lambda^2)(1 + 2.5\phi_s + 14.1\phi_s^2)$ versus $1/\lambda$ plot is linear for SIPS block copolymers, Eq. (2) completely fails in the case of MIM triblocks (Fig. 8). However, the tensile strength data reported for MIM comply with the classical rubber elasticity law:

$$\sigma = \frac{\rho RT}{M_c}\left(\lambda - \frac{1}{\lambda^2}\right) \tag{3}$$

Indeed a linear relationship is found when σ is plotted against $(\lambda - 1/\lambda^2)$ for MIM triblocks but not for the SIPS copolymer, which strongly supports the previous discussion (Fig. 9). Even when the PIOA molecular weight is high (300,000), the linear relationship persists at low extension ratios, indicating the very limited contribution of chain entanglements to the rubber elasticity of the MIM copolymers.

4. Conclusions

A series of poly(methylmethacrylate) (MMA)-*b*-poly(i-sooctyl acrylate) (PIOA)-*b*-PMMA have been prepared by selective transalcoholysis of the central block of PMMA-*b*-poly(*tert*-butyl acrylate) (PtBA)-*b*-PMMA precursors by isooctyl alcohol. Solution cast films of MIM triblocks have been characterized by DSC, AFM, dynamic and static mechanical analysis. Distinct phase separation was found in all the investigated samples. Mechanical properties of these triblocks are much lower than the traditional diene-based TPEs, particularly the ultimate tensile strength. Although partial miscibility between the PMMA and PIOA blocks may not be disregarded, the much higher molecular weight between chain entanglements (M_e) for PIOA compared to polydienes is mainly responsible for the disappointing tensile properties. This explanation is supported by the fitting of the experimental data by the simple rubber elasticity law, which is not the case for the SIPS and SBS samples.

References

[1] Fetters LJ, Morton M. Macromolecules 1969;2(5):453.
[2] Morton M. In: Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers, Munich: Hanser, 1987. pp. 67.
[3] Morton M, Mikesell SL. J Macromol Sci—Chem 1993;A7(7):1391.
[4] Yu Y, Dubois Ph, Jérôme R, Teyssiè Ph. Macromolecules 1996;29:1753 see also p. 2738.
[5] Yu JM, Dubois Ph, Teyssié Ph. Macromolecules 1996;29:6090.
[6] Jérôme R, Fayt R, Teyssié Ph. In: Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers, Munich: Hanser, 1987. pp. 451.
[7] Cowie JMG, Ferguson R, Fernandez MD, Fernandez MJ, McEwen IJ. Macromolecules 1992;25:3170.
[8] Shipp DA, Wang JL, Matyjaszewski K. Macromolecules 1998;31:8005.
[9] Jerome R, Bayard Ph, Fayt R, Jacobs Ch, Varshney S, Teyssie Ph. In: Holden G, Legge NR, Quirk R, Schroeder HE, editors. Thermoplastic elastomers, 2. Munich: Hanser, 1996. pp. 521.
[10] Ihara E, Morimoto M, Yasuda H. Macromolecules 1995;28:7886.
[11] Venkateshwaran LN, York GA, Deporter CD, McGrath JE, Wilkes GL. Polymer 1992;33:2277.
[12] Soltani R, Laupretre F, Monnerie L, Teyssih Ph. Teyssie. Polymer 1998;39:3297.
[13] Tong JD, Leclère R, Rasmont A, Bredas JL, Lazzaroni R, Jérôme R. Macromol Chem Phys 1999, in press.
[14] Teyssié Ph, Fayt R, Hautekeer JP, Jacobs C, Jerôme R, Leemans L, Varshney SK. Macromol Chem, Macromol Symp 1990;32:61.
[15] Deporter CD, Long TE, McGrath JE. Polym Int 1994;33:205.
[16] Berglund CA, Mckay KW. Polym Engng Sci 1993;33:1195.
[17] Meier DJ. J Polym Sci—Part C 1969;26:81.
[18] Holden G, Legge NR. In: Holden G, Legge NR, Quirk PR, Schroeder HE, editors. Thermoplastic elastomers, 2. Munich: Hanser, 1996. pp. 47.
[19] Quirk PR, Morton M. In: Holden G, Legge NR, Quirk PR, Schroeder HE, editors. Thermoplastic elastomers, 2. Munich: Hanser, 1996. pp. 71.
[20] Holden G, Bishop ET, Legge NR. J Polym Sci—Part C 1969;V26:37.
[21] Ver State G, Graessley W, unpublished results. Presented in Ref. [22].
[22] Ver State G, Lohse DJ. In: Mark JE, Erman B, Erich FR, editors. Science and technology of rubber, 2. San Diego, CA: Academic Press, 1994.
[23] Ferry JD. Viscoelastic properties of polymers, 3. New York: Wiley, 1980.
[24] Graessley WW. Adv Polym Sci 1974;16:58.
[25] Xu Z, Hadjichristidis N, Fetters LJ, Mays JW. Adv Polym Sci 1995;120:1.
[26] Onogi S, Masuda T, Kitagawa K. Macromolecules 1970;3:109.
[27] Tong JD, Jérôme R. Macromolecules 1999, in press.
[28] Gumbrell SM, Mullins L, Rivlin RS. Trans Faraday Soc 1953;49:1495.
[29] Guth E. J Appl Phys 1945;16:20.