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Synthesis of poly(methyl methacrylate)-b-poly(*n*-butyl acrylate)-b-poly(methyl methacrylate) triblocks and their potential as thermoplastic elastomers

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Abstract

A series of well defined poly(methyl methacrylate) (PMMA)-b-poly(n-butyl acrylate) (PnBA)-b-PMMA triblock copolymers (MnBM) has been synthesized by transalcoholysis of PMMA-b-poly(*tert*-butylacrylate) (PtBA)-b-PMMA precursors (MTM) by *n*-butanol. Phase separation is observed for all the investigated triblock copolymers, which contain PMMA outer blocks in the 5000–50 000 molecular weight (MW) range and PnBA inner blocks with MW in the 100 000–200 000 range. Although the ultimate tensile properties of these MnBM triblock copolymers are poor compared to traditional diene-based TPEs (SBS and SIS), they are much better than those ones reported for PMMA-b-poly(isooctyl acrylate) (PIOA)-b-PMMA triblocks (MIM). A reasonable explanation for this observation is found in the average molecular weight between chain entanglements (M_e) that has been estimated to be 28 000 for the central PnBA rubbery block, which is consistently much smaller than for PIOA (59 000) and substantially higher than M_e for polybutadiene (1700) and polyisoprene (6100). The tensile behavior of MnBM copolymers cannot be fitted by either a simple elastomer model free from chain entanglements (suitable to MIM) or by a "filler" modified rubber model (suitable for diene-based TPEs), supporting the hypothesis that the mechanical properties of the investigated (meth)acrylate thermoplastic elastomers are significantly affected by any change in M_e of the central acrylate block. Viscoelastic analysis shows that MnBM triblocks are of higher complex viscosity than the SBS and SIS analogs, leading to a shift in the order–disorder transition temperature to much higher temperature, unless the outer PMMA blocks are of very low molecular weight (5000).

Keywords: Thermoplastic elastomers; Triblock copolymers; Transalcoholysis

1. Introduction

SBS and SIS triblock copolymers, consisting of outer polystyrene blocks (PS) and inner rubbery polybutadiene (PB) or polyisoprene (PIP) blocks, are very well known thermoplastic elastomers (TPEs). Their unique thermomechanical properties are associated with multi-phase morphology of PS microdomains dispersed in a continuous rubbery matrix. This physical network of flexible chains combines the mechanical performances 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 service temperature (60–70°C) in relation to the glass transition temperature of polystyrene. Accordingly, efforts have been made to improve the properties of the outer [1-6] and/or the inner [2,7] blocks. Substitution of fully (meth)acrylate TPEs for the traditional SBS and SIS copolymers would be potentially beneficial due to the large range of properties of poly(meth)acrylates. Indeed, depending on the alkyl substituent of the ester group, the glass transition temperature (T_g) can be tuned 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 may be found in the case of small alkyl substituents and low molecular weight [8]. The much better resistance of poly(meth)acrylates to UV and oxidation compared to polydienes is an additional advantage. Finally, the recent progress in the "controlled" radical polymerization of alkyl (meth)acrylates [9] suggests the possibility of the direct synthesis of polymethacrylate-b-polyacrylate-b-polymethacrylate triblock copolymers, which remains a challenge in anionic polymerization.

Previous studies of (meth)acrylate triblock [10-13] and star-shaped copolymers [10] have shown that (meth)acrylate block copolymers have rather poor ultimate mechanical properties compared to traditional diene-based TPEs. This issue has been recently addressed in the case of poly(MMA)-b-poly(isooctyl acrylate)-b-poly(MMA), or MIM, and the very large molecular weight between chain entanglements (M_e) for the polyacrylate rubbery block has been found responsible for this problem [13]. This paper deals with the properties

of poly(MMA)-b-poly(nBA)-b-poly(MMA) copolymers, or MnBM, whose central block has a lower M_e (although similar T_g) compared to the poly(isooctyl acrylate). A series of triblock copolymers of various molecular weights and compositions has been prepared by sequential anionic polymerization of MMA, *tert*-butyl acrylate (tBA) and MMA, respectively, followed by the selective transalcoholysis of the central PtBA block by *n*-butanol.

2. Experimental section

2.1. Materials

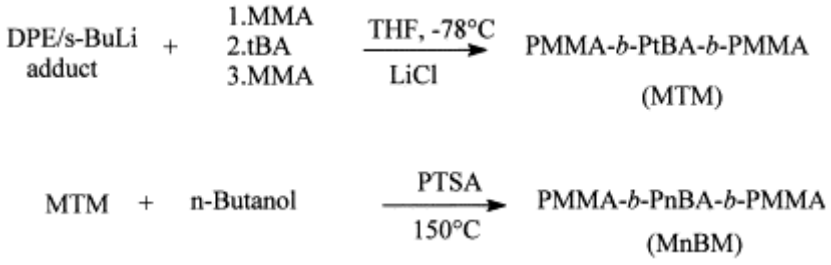
THF and toluene were purified by refluxing over the deep purple sodium–benzophenone complex. MMA and tBA (Aldrich) were refluxed over CaH_2, vacuum distilled and stored under nitrogen at −20°C. Before polymerization, they were added with 10 wt.% $AlEt_3$ solution in hexane until a persistent yellowish 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). *n*-Butanol (Janssen) was used as received. LiCl (99.99%, Aldrich) was dried under vacuum at 130°C.

2.2. Synthesis of poly(MMA)-b-poly(tBA)-b-poly(MMA) (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 rubber septa and stainless steel capillaries or syringes. A three-fold molar excess of DPE and a 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 experimental 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 poly(MMA)-b-poly(nBA)-b-poly(MMA) (MnBM) copolymers

On the basis of preliminary experiments, the best conditions for the transalcoholysis of the tBA units of MTM copolymers involved dissolving the copolymers in an excess of *n*-butanol in the presence of *p*-toluenesulfonic acid (PTSA; 10 mol% with respect to tBA units). After reflux at 130°C for 48 h, the copolymer was recovered by precipitation into methanol and dried under vacuum at 80°C overnight. Scheme 1 summarizes the overall synthesis of the MnBM copolymers.



Scheme 1. Synthesis of MnBM triblock copolymers.

PnBA of the same microstructure as the central PnBA block in the MnBM triblocks was also prepared by transalcoholysis of PtBA homopolymer by *n*-butanol 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 in toluene (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 distributions 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. The universal calibration method by Benoit et al. [14] was used to calculate the molecular weight of homo-PMMA and homo-PtBA, with the following viscosimetric relationships:PMMA in THF [15]

$$[\eta]=1.298\times10^{-4}M^{0.688} \quad (1)$$

PtBA in THF [16]

$$[\eta]=3.30\times10^{-3}M^{0.80} \quad (2)$$

^{1}H NMR spectra were recorded with a Bruker AM-250 spectrometer by using $CDCl_3$ as solvent at 25°C. The compositions of the diblocks and the final MTM triblocks were 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). The M_n of the PtBA block (in the intermediate diblock) and the parent 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 MnBM copolymers were measured with the RSI ARES rheometer. Samples with a diameter of 7 mm 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 were measured by using the RSI ARES rheometer with 25 mm diameter parallel plates or cone-plate.

Tensile properties were measured using a Adamel Lhomargy tensile tester. Micro-dumbbells were cut from solution cast films and extended at 100 mm/min at room temperature. Strain was measured from the crosshead displacement. The 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

Nucleophilic side reactions are known to perturb the anionic polymerization of primary acrylates even at low temperature. This situation is however improved by the addition of chelating μ–σ dual ligand, such as polydentate lithium alkoxide particularly in case of 2-ethylhexyl acrylate [17] and *n*-butyl acrylate [18]. Nevertheless, this improvement is not good enough to allow well controlled (meth)acrylate block copolymers, e.g. poly(MMA)-b-poly(2EHA)-poly(MMA) [19] and poly(MMA)-b-poly(nBA)-b-poly(MMA) [20], to be synthesized. Therefore, the MnBM triblock block copolymers were synthesized indirectly, i.e. by the sequential living anionic copolymerization of MMA, tBA and MMA, followed by the selective acid-catalyzed transalcoholysis of the *tert*-butyl ester groups of the PMMA-b-PtBA-b-PMMA precursors by *n*-butanol. Well defined poly(MMA)-b-poly(isooctyl acrylate)-b-poly(MMA) triblocks, MIM, were previously synthesized according to this strategy [13]. Table 1 lists the precursors and the final MnBM triblock copolymers that were synthesized. Fig. 1 illustrates the typical SEC traces of the first PMMA block, the PMMA-b-PtBA diblock, and the final MTM triblock, respectively (sample 2 in Table 1). Molecular weight distributions are monomodal, symmetrical and narrow (M_w/M_n ≈ 1.1). Furthermore, molecular weight increases with the progress of the

sequential block copolymerization, in good agreement with the values calculated from the monomer–initiator molar ratios. Monomer conversion is close to completion. The sequential polymerization is thus perfectly controlled, which is consistent with the livingness of each step and the suitable cross-reactivity of the monomers. The accordingly synthesized MTM triblock copolymers cover a large range of molecular weight (PMMA from 5000 to 50 000; PtBA from 50 000 to 210 000) and composition (PMMA content: 9–50%). The MTM precursors were then converted into the expected MnBM triblocks by the acid catalyzed transalcoholysis of the PtBA block by *n*-butanol. This reaction must however be selective in the presence of PMMA [10,21]. ^{1}H NMR analysis of the original MTM and the final MnBM copolymers shows that there are no residual tBA groups in MnBM, although some of them have been hydrolyzed rather than transalcoholyzed (2–5%). Fig. 1 shows that transalcoholysis of MTM (sample 2, Table 1) into MnBM does not change the molecular weight distribution significantly. It may thus be concluded that fully acrylic analogs 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 low T_g PnBA block.

Table 1. Molecular characteristics of triblocks synthesized in this work

Sample	PMMA-b-PtBA-b-PMMA		Yield (%)	PMMA-b-PnBA-b-PMMA	
	M_n (10^{-3})	M_w/M_n		M_n (10^{-3})	M_w/M_n
1	5–100–5	1.04	93	5–100–5	1.04
2	10–80–10	1.06	97	10–80–10	1.07
3	15–100–15	1.04	95	15–100–15	1.05
4	20–166–20	1.05	96	20–166–20	1.06
5	20–100–20	1.05	97	20–100–20	1.06
6	20–50–20	1.04	94	20–50–20	1.05
7	30–150–30	1.04	95	30–150–30	1.05
8	30–100–30	1.11	97	30–100–30	1.13
9	40–210–40	1.06	96	40–210–40	1.07
10	50–100–50	1.05	94	50–100–50	1.05

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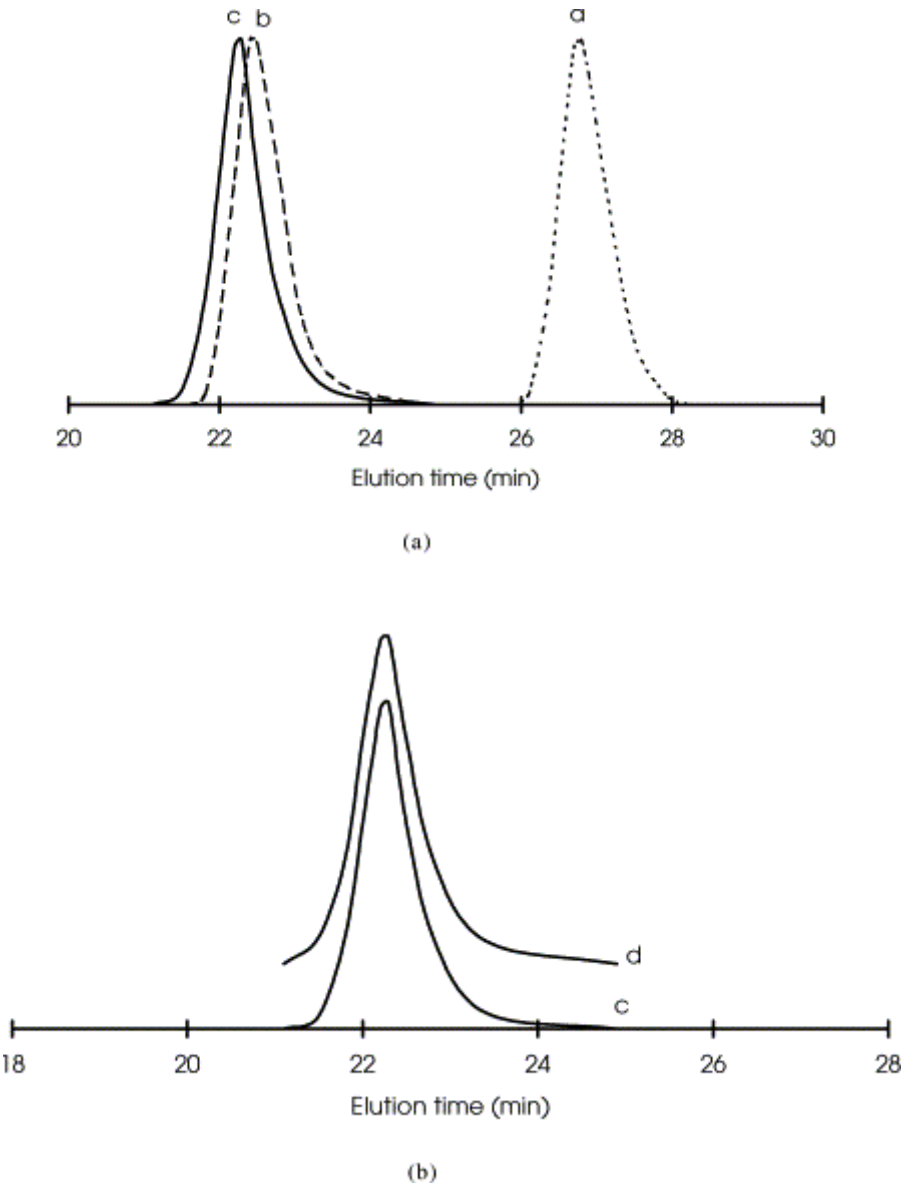

Fig. 1. Typical SEC traces for the three-stage synthesis of MTM copolymer: (a) first PMMA block; (b) PMMA-b-PtBA; (c) MTM (sample 2, Table 1); (d) MIM.

3.2. Dynamic mechanical properties (DMA)

Fig. 2 illustrates the temperature dependence of the dynamic shear modulus (G') from −100 to 200°C for a series of MnBM triblocks of increasing PMMA content (9–50%) and PMMA molecular weight (5000–50 000). Two glass transitions and an intermediate rubbery plateau are observed for all copolymers, which is in agreement with extended phase separation. The transition at low temperature (T_{gL}) is assigned to the glass transition temperature of the soft PnBA block, whereas T_g at high temperature (T_{gH}) is typical of the PMMA blocks.

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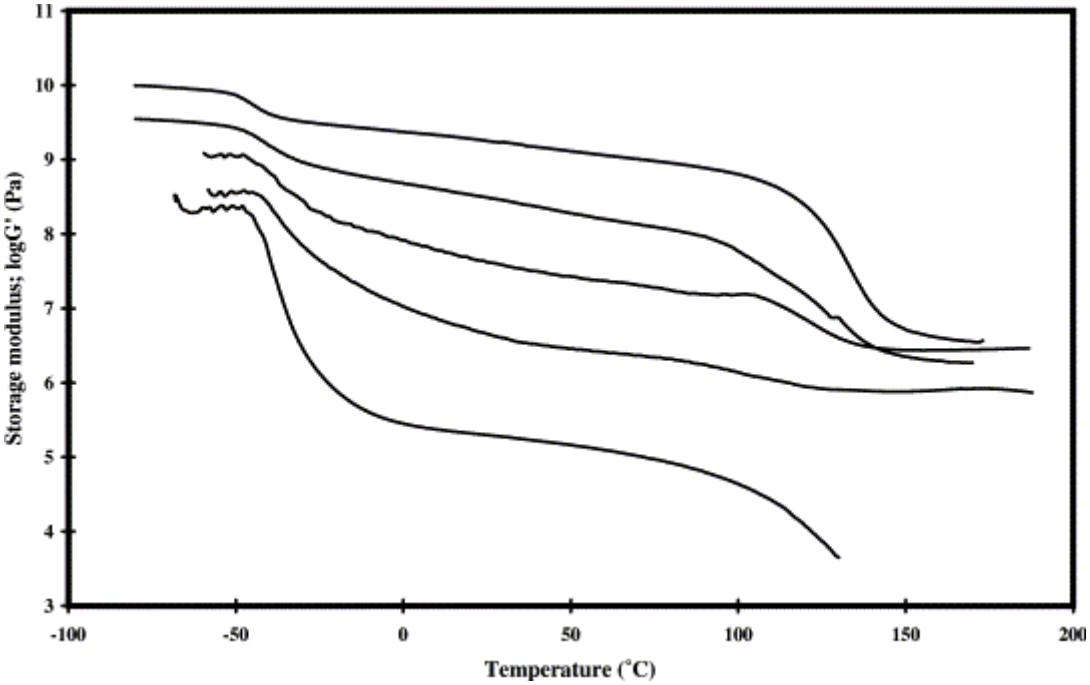

Fig. 2. Shear modulus (G') vs. temperature at 1 Hz. From bottom to top: samples 1, 3, 5, 8, and 10 (Table 1). Heating rate: 2°C/min. For sake of clarity, curves have been vertically shifted with respect to sample 1 (sample 3 by 0.4; sample 5 by 0.6; sample 8 by 1.0; sample 10 by 1.4 units).

Fig. 3 illustrates how the glass transition temperature (the temperature at the maximum of tan δ) of the PnBA and PMMA blocks depends on the molecular weight of the outer blocks, the inner block being unchanged (10^5 MW). As the PMMA molecular weight is increased from 5000 to 50 000 and the PMMA content from 9 to 50%, T_{gL} decreases from −34 to −43°C and T_{gH} increases from 60 to 137°C. This observation is consistent with the increasingly more complete phase separation in relation to the PMMA molecular weight [22] and volume fraction [23]. It is worth pointing out that when the PMMA MW exceeds 15 000, G' tends to level off beyond T_g of PMMA indicating that the triblock does not flow (or the phase separation persists) at least in the investigated temperature range. This question will be discussed further in the last section of this paper.

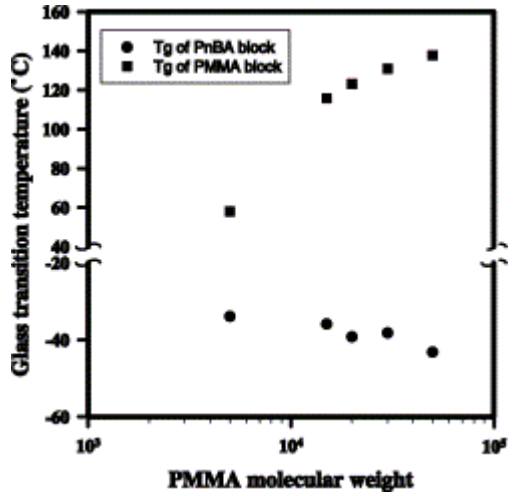

Fig. 3. Dependence of T_g of the PnBA and PMMA blocks on the PMMA MW for MnBM triblocks (samples 1, 3, 5, 8, 10 in Table 1). T_g is assumed to be the temperature at maximum tan δ. T_g for the 5000 MW PMMA block has been measured by DSC, being undetectable by DMA.

3.3. Stress–strain behavior

Early analysis of SBS and SIS block copolymers reported ultimate tensile strength and elongation at break as high as 30 MPa and 800%, respectively [24] (Fig. 4). These properties, particularly tensile strength, are much higher than those observed for unreinforced vulcanizates of SBR and polybutadiene. A possible explanation is that the hard polystyrene domains act as reinforcing filler particles, whereas the slippage of the entangled rubbery blocks contribute to the high ultimate tensile strength [25-26]. A previous paper from this laboratory has reported that the mechanical properties of PMMA-b-poly(isooctylacrylate)-b-PMMA copolymers (MIM) [13], are generally poor compared to traditional diene-based TPEs. Although partial miscibility of low molecular weight PMMA and PIOA blocks might partly explain this disappointing observation, the most reasonable explanation has to be found in the average molecular weight between chain entanglements, M_e, of the polyacrylate central block. Indeed, M_e is much higher for PIOA than for polydienes (Table 2). Since the number of chain entanglements are very limited in the MIM triblocks, the deformation stress is not dissipated by the central block, but directly transferred to the PMMA microdomains. M_e for PIOA and for PnBA has been calculated from rheological measurements [27-30], on the basis of Eq. (3) (Table 2):

$$M_e = \rho R T / G_{0N} \quad (3)$$

where ρ is the polymer density, R the gas constant, T the temperature and G_{oN} the shear modulus of the rubbery plateau (i.e. G' value at the minimum of tan δ [31]). M_e for PnBA is approximately half the value for PIOA, although much higher compared to the diene polymers. It may, therefore, be anticipated that the mechanical properties for MnBM should be intermediate between those of MIM and SBS (or SIS) of comparable molecular weight and composition. The stress–strain curves (Fig. 4) confirm this expectation. Table 3 lists the ultimate tensile properties and tensile modulus for a series of MnBM. The initial modulus of MnBM triblocks is essentially higher compared to MIM triblocks of similar PMMA content [13], which is consistent with the smaller M_e of the MnBM central block. The ultimate tensile strength of MnBM triblocks is also 30–100% higher than for the MIM counterparts [13], so confirming the key effect of M_e of the polyacrylate block on the mechanical properties. It must be noted that PnBA and PIOA have essentially the same T_g (−35 to −40°C, DMTA), so that this property has nothing to do with the very significant difference in the stress–strain behavior of MIM and MnBM.

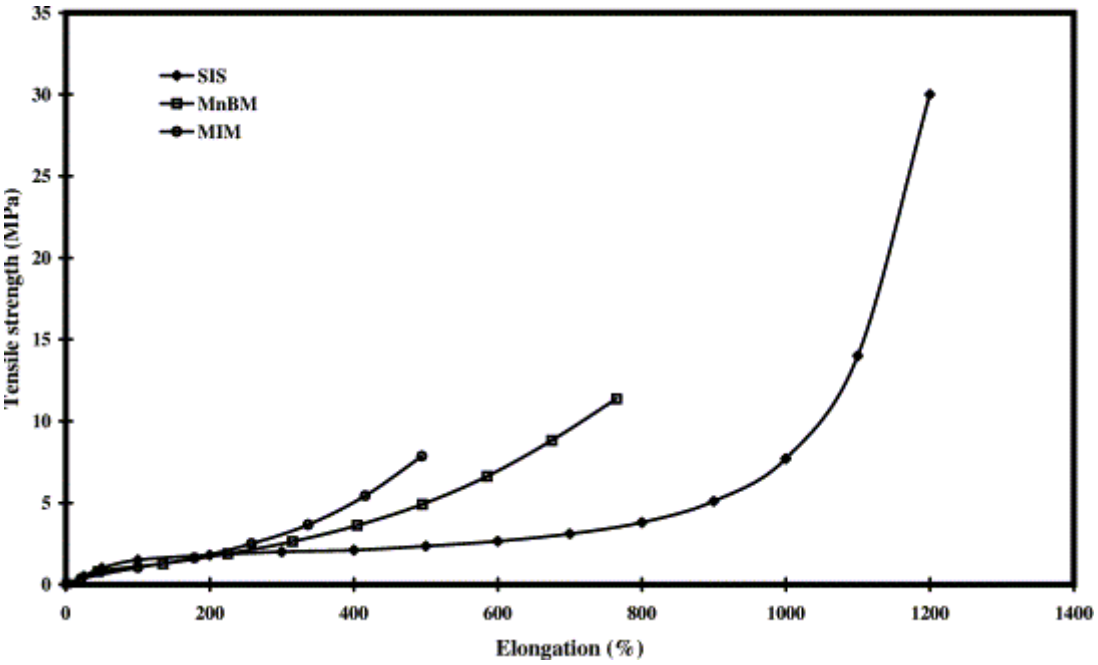

Fig. 4. Stress–strain curves for SIS (14K–109K–14K), MIM (20K–140K–20K) and MnBM (20K–166K–20K) triblocks.

Table 2. Average molecular weight between chain entanglements (M_e) for a series of polymers

Polymer	M_e (dynamic)
Polybutadiene [24]	1700
Polyisoprene [24]	6100
Poly(*n*-butyl acrylate)[a]	28 000
Poly(isooctyl acrylate)[a]	59 000

[a] From this work.

The main consequence of the large difference in M_e between a polydiene and a polyacrylate block in TPEs is that the tensile behavior of fully (meth)acrylic TPEs should be accounted for by the classical theory of rubber elasticity [32] at low to moderate elongations (Eq. (4)), rather than by the "rubber+filler" model that fits the behavior of polydiene-based TPEs. The SIS tensile behavior is indeed properly explained by the classical law of rubber elasticity modified by the filler effect [33] (Eq. (5)):

$$\sigma = \frac{\rho RT}{M_c}\left(\lambda - \frac{1}{\lambda^2}\right), \tag{4}$$

$$\sigma = \left(\frac{\rho RT}{M_c} + \frac{2C_2}{\lambda}\right)\left(\lambda - \frac{1}{\lambda^2}\right)(1 + 2.5\phi_s + 14.1\phi_s^2) \tag{5}$$

where σ is the applied tensile strength, λ the extension rate, ρ the density, R the gas constant, T the absolute temperature, M_c the average molecular weight between the crosslinks of the rubber, C_2 a constant that expresses the deviation from the ideal elastic behavior, and ϕ_s the volume fraction of the PS domains.

Fig. 5 and Fig. 6 illustrate how the tensile properties for SIS, MnBM and MIM block copolymers are fitted by (4) and (5), respectively. Although the $\sigma/(\lambda-1/\lambda^2)(1+2.5\phi_s+14.1\phi_s^2)$ versus $1/\lambda$ plot is linear for the SIS copolymer, Eq. (5) completely fails in the case of the MIM triblock (Fig. 6). Consistently, the tensile properties for MIM comply with the classical rubber elasticity law (Eq. (4)), since a linear relationship is found when σ is plotted against $(\lambda-1/\lambda^2)$, in contrast to what happens in case of SIS copolymers (Fig. 5. Finally, none of the two models account for the tensile behavior of the MnBM triblock, in line with the few entanglements of the PnBA central block which is an intermediate situation between PIOA (very limited number of entanglements) and polydiene (large number of entanglements) of the same molecular weight.

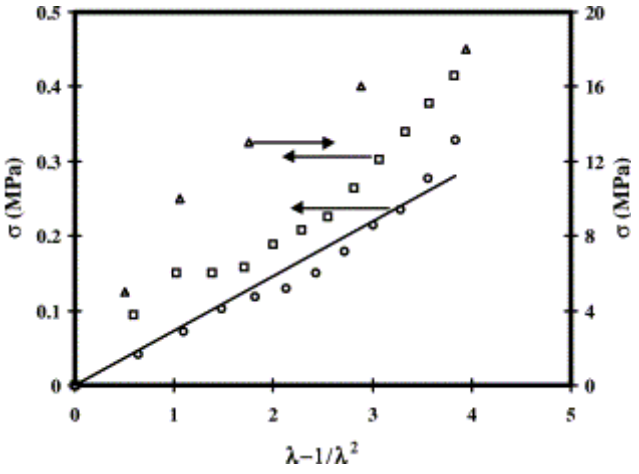

Fig. 5. Stress–strain data for MIM triblock (○: 3.5K–100K–3.5K), SIS triblock (△: 14K–109K–14K),and MnBM triblock (□: 5K–100K–5K), plotted according to the classical rubber elasticity law (Eq. (4)).

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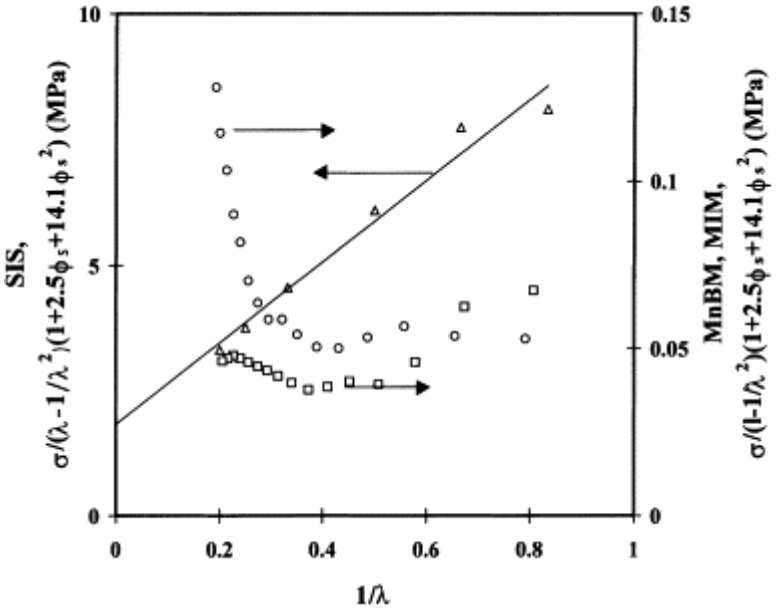

Fig. 6. Stress–strain data for MIM triblock (○: 3.5K–100K–3.5K), SIS triblock (△: 14K–109K–14K), and MnBM triblock (□: 5K–100K–5K), plotted according to the "rubber+filler" model (Eq. (5)).

3.4. Effect of the PMMA chain length and the PMMA content

Fig. 7 compares the stress–strain curves for a series of MnBM triblock copolymers (samples 1, 3, 5, 8, and 10 in Table 3) consisting of the same PnBA block (100 000) associated with PMMA blocks of increasing molecular weight (5000–50 000). An increase of the elastic modulus (Table 3) and a decrease in the elongation at break is observed as the PMMA content is increased, as it is the case for most TPEs. The dependence of the ultimate tensile strength on PMMA chain length up to 20 000 PMMA molecular weight suggests partial miscibility of the two poly(meth)acrylate blocks. However, when PMMA MW exceeds 20 000, the ultimate tensile strength of MnBM becomes independent of PMMA block length and content. This observation might indicate that the PMMA and PnBA phase separation is complete when PMMA blocks of MW higher than 20 000 are associated with PnBA blocks of 10^5 MW or higher. Yielding behavior is distinctly observed at ca. 38% PMMA, due to at least partial continuity of the PMMA phase. It is increasingly more pronounced as the PMMA content is increased further, exceeding the ultimate tensile strength at 50% PMMA. Fig. 8 compares the stress–strain curves for MnBM triblocks of different MW but comparable composition. The tensile behavior is essentially the same, which indicates that it is driven by M_e rather than by the total length of the central block. The same situation is observed for SIS copolymers [26], in contrast to what happens in case of the MIM copolymers whose modulus and elongation at break depend on the length of the central block [13]. The exceedingly high M_e of PIOA is at the origin of this apparent disagreement.

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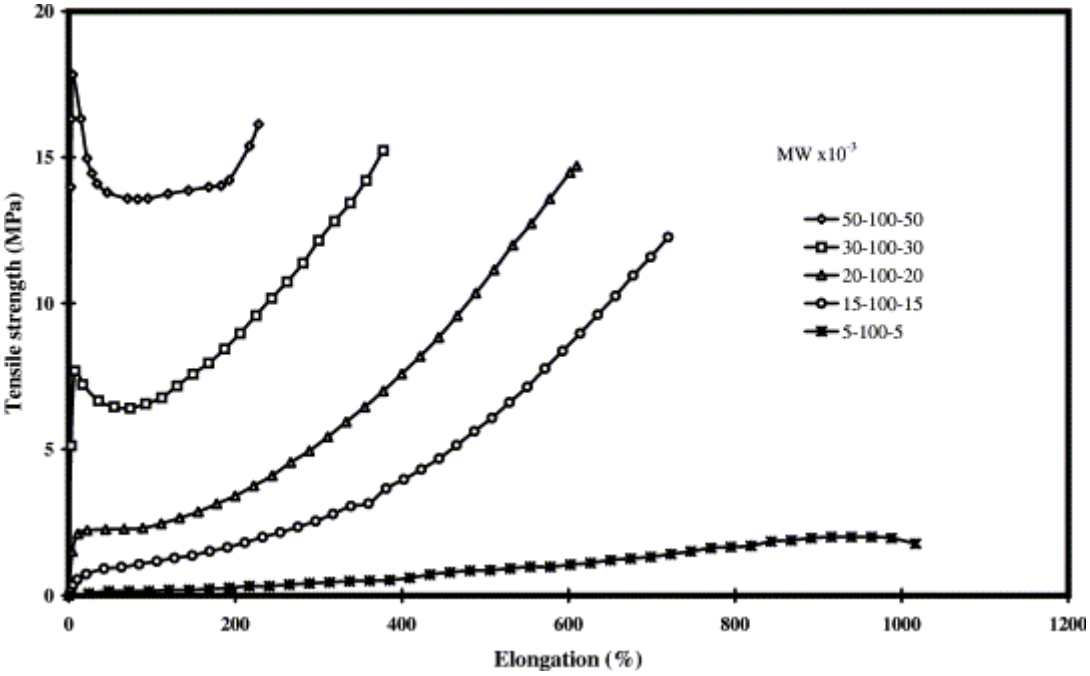

Fig. 7. Stress–strain curves for MnBM triblocks containing the same PnBA central block (100K).

Table 3. Mechanical properties of MnBM triblock copolymers

Sample[a]	PMMA (wt.%)	MW	Ultimate tensile strength (MPa)	Elongation at break (%)	Initial modulus (MPa)
1	9.1	5–100–5	1.8	1016	0.31
2	20.0	10–80–10	9.3	712	3.6
3	23.1	15–100–15	12.3	720	6.9
4	19.4	20–166–20	11.4	765	3.7
5	28.6	20–100–20	14.7	610	30.9
6	44.4	20–50–20	17.2	283	310.0
7	28.6	30–150–30	15.0	700	25.0
8	37.5	30–100–30	15.2	378	181.0
9	27.6	40–210–40	15.2	701	25.6
10	50	50–100–50	16.1	228	573.4

[a] All samples are toluene cast films (three days casting, and drying in vacuum at 80°C for 24 h).

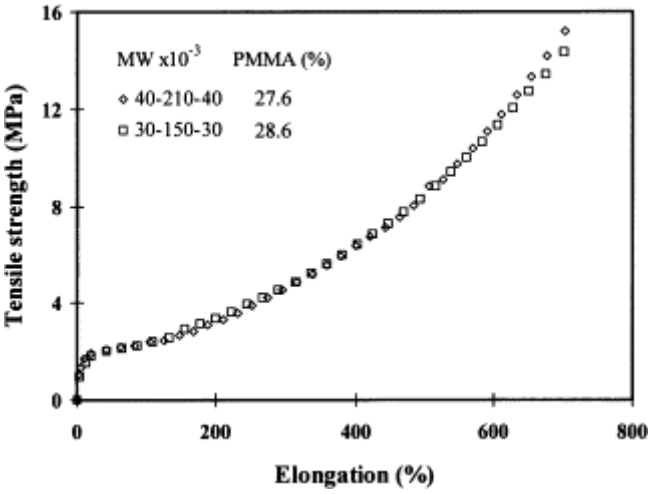

Fig. 8. Stress–strain curves for MnBM triblocks of comparable PMMA content.

3.5. Effect of crosslinking

The central PnBA block that contains 2–5 mol% COOH groups as result of the incomplete transalcoholysis reaction was selectively crosslinked using a multifunctional aziridine containing crosslinker. Actually, the MnBM block copolymer (sample 4, Table 1) has been added with 2 wt.% crosslinker before being cured at 80°C, thus below T_g of PMMA, so that the phase morphology is not expected to change. Fig. 9 compares the stress–strain curves for sample 4 before and after curing. The stress–strain curves are essentially identical at low extension rate, indicating that the crosslinking density of the central block is very low. The decrease in the ultimate tensile strength observed for the chemically crosslinked triblock is more likely due to the chemical crosslinks that prevent stress distribution within the entangled chain network [26].

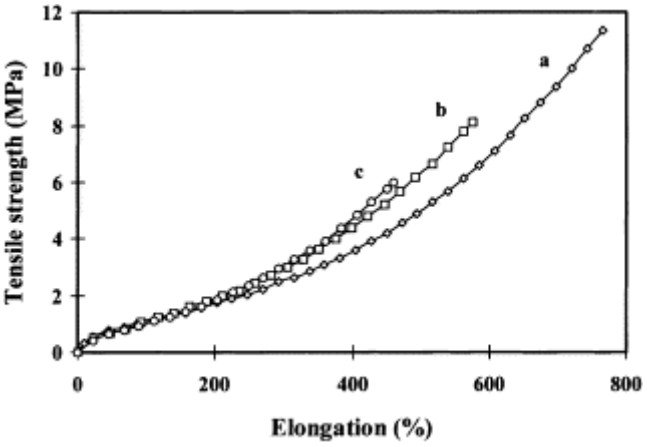

Fig. 9. Stress–strain curves for MnBM (20K–166K–20K) before and after crosslinking: (a) original; (b) crosslinking at 80°C for 2 h; (c) crosslinking at 80 °C for 4 h.

3.6. Viscoelastic properties

It is well established that phase separation characteristic of the SBS and SIS thermoplastic elastomers persists beyond the upper (PS) glass transition temperature. These block copolymers are thus non-Newtonian, with viscosity increasing as the shear rate decreases [34-35]. However, when temperature exceeds a critical value, the microdomain structure disappears and a monophase fluid is formed. This transition is referred to as the order–disorder transition (ODT) and is the rule for most block copolymers [36-40]. Usually a transition from non-Newtonian to Newtonian behavior takes place at the order–disorder transition temperature (T_{ODT}). Fig. 10 shows the frequency dependence of the complex viscosity at several temperatures for the MnBM triblock with the shortest PMMA block (5K). Newtonian behavior is observed at low shear rates at 120°C (T_g+60°C), whereas this behavior dominates in the whole frequency range at 160°C (T_g+100°C). Thus, below a critical temperature (ca. 150°C), dependence of log η^* on frequency shows *yield* behavior at low frequencies, which was proposed to be the signature of a transition from ordered state to disordered state by Chung and Gale [41].

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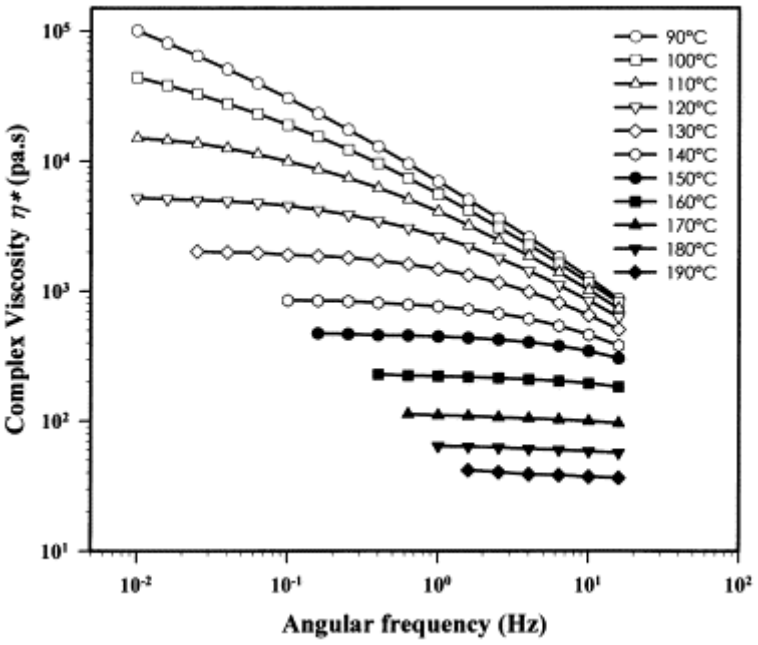

Fig. 10. Complex viscosity vs. frequency for MnBM 5K–100K–5K at different temperatures.

Han and co-workers [40-42] have recently demonstrated that T_{ODT} could be inferred from rheological measurements, particularly from the log G' vs. log G'' plot at several temperatures (Fig. 11). These authors have suggested that the threshold temperature at which the log G' vs. log G'' plot becomes linear with a slope (ca. 2) independent of temperature is T_{ODT}. This prediction is based on the validity of Eq. (6) for homogeneous polymers in the terminal viscoelastic zone:

$$\log G' = 2 \log G'' - \log(\rho R T/M_e) + \log(\pi^2/8) \quad (6)$$

where ρ is the polymer density, R the gas constant, T the absolute temperature and M_e average molecular weight between chain entanglements. This technique is very useful in case of fully (meth)acrylic block copolymers, whose phase morphology cannot be analyzed by SAXS because of the limited contrast between the phases. Fig. 11 shows that the log G' vs. log G'' data overlap at temperatures beyond 150°C, which is accordingly the T_{ODT} of sample 1, i.e. ca. 90°C higher than the glass transition temperature. So, the two rheological approaches lead to consistent T_{ODT} values for sample 1, even though some researchers [40-43] have pointed out that Chung's method is not reliable, or at least gives less accurate results. Fig. 12 and Fig. 13 illustrate the same dependence for MnBM block copolymers of higher PMMA MW (10K, 15K) and content (20–29%). Since the log G' vs. log G'' plots do not overlap each other, T_{ODT} must lie beyond the investigated temperature range. All these observations are consistent with previous DMTA analysis and indicate that MnBM triblock copolymers retain a microphase-separated structure up to temperatures close to degradation of PnBA (≈230°C by TGA) and that the flow remains typically non-Newtonian (at 190°C, Fig. 14) when the PMMA MW is higher than 10 000 and the PMMA content exceeds 10%. Fig. 14 compares the complex viscosity of a series of MnBM triblocks of increasing PMMA MW. The non-Newtonian behavior is more pronounced, since the PMMA MW is high as a result of the persistence of the phase separation. The behavior of a typical SIS thermoplastic elastomer (10K-100K-10K; M_w/M_n 1.1) is also shown for the sake of comparison. The MnBM counterpart (sample 2, Table 1) is clearly more viscous, particularly at low shear rates. This difference might result at least partly from the dehydration of the carboxylic acid groups of the central block into anhydrides, which is known to occur beyond 180°C. In order to know whether this potential crosslinking reaction occurs significantly during the rheological measurements, the tested MnBM block copolymers have been dissolved in THF, any gel fraction has been filtered off, and the soluble fraction has been analyzed by SEC. The gel content for all the samples is very limited (less than 1.5%) and the polydispersity of the soluble polymer remains essentially unchanged (i.e. 1.04, 1.08 and 1.06, for the MnBM samples of increasing PMMA content in Fig. 14), so that the MnBM block copolymers appear to be stable at least during the time required by the rheological measurements. Moreover, the MnBM block copolymer containing the shortest PMMA block (sample 1, Table 1) shows Newtonian behavior between 160 and 190°C. Thus, although crosslinking of MnBM triblocks by dehydration of residual COOH groups may not be completely disregarded, it cannot explain the fact that the flow behavior of MnBM triblocks is completely different from the SIS copolymers. Reasons for this difference might be found at least partly in (i) the higher temperature at which PMMA starts to flow compared to PS (by ca. 40°C) and (ii) the Me, which is at

least two times lower for PMMA than for PS. These assumptions deserve further investigation and will be discussed in a forthcoming paper.

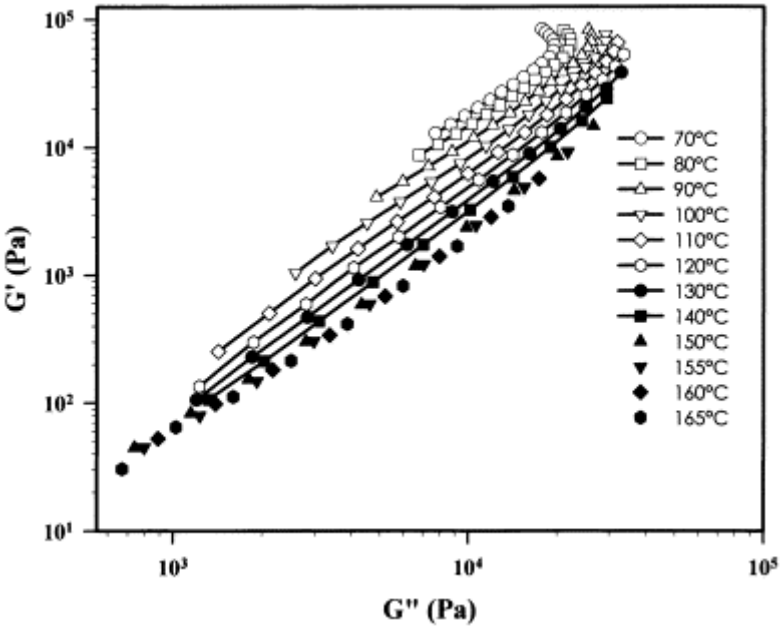

Fig. 11. Log G' vs. log G" for MnBM 5K–100K–5K at different temperatures.

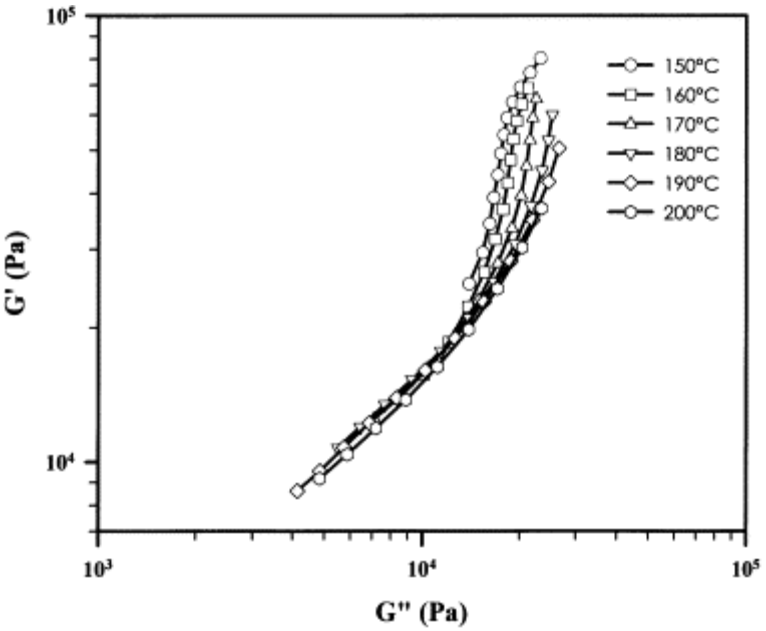

Fig. 12. Log G' vs. log G" for MnBM 10K–80K–10K at different temperatures.

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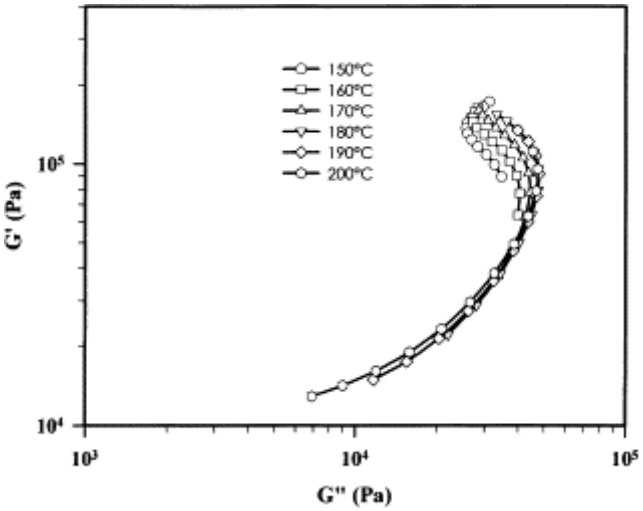

Fig. 13. Log G' vs. log G" for MnBM 15K–100K–15K at different temperatures.

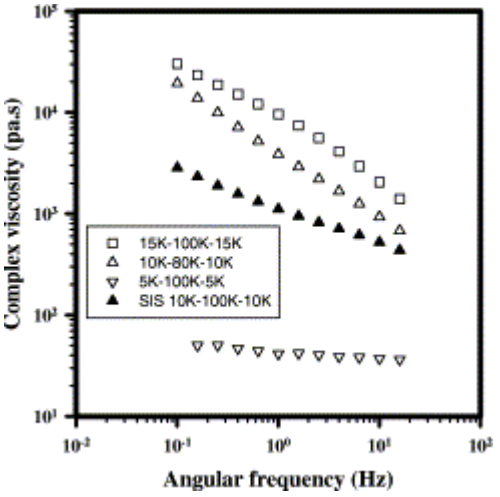

Fig. 14. Complex viscosity vs. frequency for MnBM and SIS triblocks at 190°C.

4. Conclusions

A series of poly(methyl methacrylate) (MMA)-b-poly(n-butyl acrylate) (PnBA)-b-PMMA triblock copolymers (MnBM) has been prepared by selective transalcoholysis of the central block of PMMA-b-poly(*tert*-butyl acrylate) (PtBA)-b-PMMA precursors by *n*-butanol. Solution cast films of MnBM triblocks have been characterized by dynamic and static mechanical analysis. All the investigated triblocks are phase separated with two transition temperatures. Although the mechanical properties of these triblocks are still lower than the traditional diene-based TPEs, they are much higher, particularly the ultimate tensile strength, compared to PMMA-b-poly(isooctyl acrylate)-b-PMMA. A lower molecular weight between chain entanglements (M_e) for PnBA compared to PIOA is mainly responsible for this improvement. In the case of a central block of 10^5 MW, the PIOA block (M_e=59 000) is essentially non-entangled and the stress–strain data are fitted by the simple rubber elasticity law. When the PnBA block is concerned (M_e=28 000), there are enough chain entanglements to make not only this simple law but also the "rubber+filler" model inappropriate to account for the stress–strain behavior of the MnBM triblocks. At a constant PnBA inner block of 10^5 MW, MnBM triblocks show the best ultimate mechanical properties when the PMMA block is of 10^4 MW and higher (Table 3). Under these conditions, the order–disorder transition temperature exceeds 200°C, which might be a problem for melt processing of these materials.

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