Poly[alkyl methacrylate-*b*-butadiene-*b*-alkyl methacrylate] Triblock Copolymers: Synthesis, Morphology, and Mechanical Properties at High Temperatures

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ABSTRACT: Block copolymers of the ABA type, where B is polybutadiene (PBD) and A is poly(ethyl methacrylate) (PEMA), poly(*tert*-butyl methacrylate) (P-t-BMA), poly(methyl methacrylate) (PMMA), or poly(isobornyl methacrylate) (PIBMA), have been successfully synthesized by sequential anionic polymerization of butadiene and methacrylates with the diadduct of *tert*-butyllithium to *m*-diisopropenylbenzene as a difunctional initiator. Block copolymers of a narrow molecular weight distribution (1.10) have been analyzed by differential scanning calorimetry, transmission electron microscopy, and dynamic mechanical analysis. These materials are phase-separated and have high mechanical performances. Special attention has been paid to the service temperature of these thermoplastic elastomers in comparison with a styrene−butadiene−styrene (SBS) triblock copolymer. The upper service temperature (UST) has been estimated from the temperature dependence of the tensile properties in the 25−150 °C range and found to change with the outer blocks. Polystyrene (T_g = 100°C) is at the origin of the lower UST, which is however comparable to PEMA (T_g = 90 °C) and P-t-BMA (T_g = 116 °C) containing triblock copolymers of similar molecular weight and composition. PMMA (T_g = 132 °C) outer blocks increase the UST of the triblocks, which is further increased by hydrogenation of the PBD midblock. The higher UST has been found for a PIBMA (T_g = 202 °C)-containing triblock copolymer that shows an ultimate tensile strength higher than 2 MPa at 150 °C.

Introduction

Thermoplastic elastomers (TPE) of the styrene-*b*-butadiene-*b*-styrene type (SBS) are well-known for unique thermomechanical properties associated with a phase morphology of polystyrene (PS) domains dispersed in the continuous rubbery polybutadiene (PBD) phase. This physical network of flexible chains combines the mechanical performances of vulcanized rubbers and the straightforward processing of thermoplastics. As the glass transition temperature of the PS hard phase (T_g = 100 °C) is approached, the physical cross-links start to be deformed and significant creep can occur even for low applied stresses. Accordingly, the practical usefulness of SBS is restricted to an upper temperature dictated by the T_g of the outer blocks. Furthermore, the PS hard phase is poorly resistant to hydrocarbons and oils, which is an additional limitation to practical applications. It is thus a valuable target in this area to widen the service range as much as possible.[1−9] Among several known examples, poly(α-methylstyrene),[1] polyethylene sulfide,[2] poly(*p*-methylstyrene)[9] have been considered as substitutes for the polystyrene blocks.

Recently, special attention has been paid to poly(alkyl methacrylate)s (PAMA) as candidates for the outer blocks.[3−7,10] Indeed, T_g strongly depends on the alkyl substituent, e.g. 90 °C for poly(ethyl methacrylate) and 199 °C for poly(bornyl methacrylate).[11] Furthermore, these polar polymers are more resistant to hydrocarbon solvents than PS. However, synthesis of triblock copolymers containing PAMA outer blocks was a challenge for a long time because of problems of monomer purification and troubles arising from sensitivity of the carbonyl group and of the α-hydrogen atom of acrylates toward nucleophilic attack.[12,13] Furthermore, PAMA anions are unable to initiate the polymerization of dienes, which requires the availability of a difunctional initiator soluble in apolar solvents for the living diene polymerization with a cis-1,4 microstructure. Very recently, poly[methyl methacrylate (MMA)-*b*-butadiene-(BD)-*b*-MMA] (MBM) have been successfully synthesized with syndiotactic poly(methyl methacrylate) (PMMA) blocks and characterized[15] in our laboratory. This paper deals with synthesis and characterization of poly(alkyl methacrylate (AMA)-*b*-BD-*b*-AMA) copolymers in which the T_g of the hard block is in the range from 90 to 202 °C. Special attention will be paid to the effect of the outer block on the temperature dependence of the mechanical properties of these materials.

Experimental Section

Materials. Ethyl methacrylate (EMA), MMA (Aldrich), *tert*-butyl methacrylate (t-BMA) (BASF), and isobutyl methacrylate (IBMA) (Acros Chimica) were first refluxed over CaH_2 under a nitrogen atmosphere. They were then distilled under reduced pressure and stored under nitrogen at −20 °C. Just before polymerization, t-BMA and IBMA were added at −78 °C to a mixture of diisobutyl aluminum hydride (DIBAH, 0.1 N in toluene) and triethylaluminum (TEA, 0.1 N in toluene) (50/50, v/v) until a persistent yellowish green color was observed, whereas EMA and MMA were added to a TEA solution at room temperature. These monomers were then distilled under reduced pressure and polymerized.

LiCl (99.99% purity, Aldrich) was dried overnight at 130 °C and dissolved in dry THF (0.2 N solution). Cyclohexane and diethyl ether were dried over CaH_2 for 24 h, and THF was refluxed over the deep-purple sodium−benzophenone complex. After distillation, all these solvents were further distilled from polystyryllithium under reduced pressure just prior to use. *tert*-Butyllithium (t-BuLi) (Aldrich, 1.3 M in cyclohexane) was diluted with cyclohexane into a 0.2 N solution and the final concentration was measured by double titration.[14] *m*-Diisopropenylbenzene (m-DIB, Aldrich) was first dried over CaH_2 for 24 h and then over fluorenyllithium before use. 1,1-Diphenylethylene (DPE, Aldrich) was dried over

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s-BuLi and distilled from diphenylmethyllithium before use. Butadiene was dried over n-BuLi.

Polymerization. Block copolymerization of butadiene and AMA was carried out in a previously flammed glass reactor equipped with a magnetic stirrer under an dry nitrogen atmosphere. Solvent, initiator, and monomers were transferred into the reactor with syringes and/or stainless steel capillaries. Detailed experimental techniques and conditions for the difunctional lithium initiator (DLI) system used in the synthesis of triblock copolymers were reported elsewhere.[10,15] The synthetic pathway is shown in Scheme 1. The DLI (deep red color) was prepared by addition of 2 equiv of t-BuLi to m-DIB in cyclohexane at 50 °C for 2 h. It was then used to initiate the polymerization of butadiene in a cyclohexane/diethyl ether mixture (100/6, v/v) at room temperature for one night. The initiating efficiency of the DLI used in this study has been ascertained in a previous paper.[15] When the polymerization of butadiene was complete, an aliquot of the solution was picked out and PBD was precipitated into acidified methanol for characterization. Styrene was added and allowed to polymerize for 3 h at room temperature in order to produce SBS triblock copolymers. In case of methacrylate-containing triblock coplymers, the PBD dianions were end-capped with 1,1-diphenylethylene (DPE) at room temperature for 1 h. LiCl containing THF ([LiC]/[living sites] = 5) was then added to the reactor at 0 °C, with formation of a cyclohexane/THF (35/65, v/v) mixture (deep red color), to which AMA was finally added and polymerized at −78 °C. Block copolymers were recovered by precipitation in methanol/H_2O (50/50) for t-BMA-containing triblock copolymers and in methanol for other methacrylates containing copolymers. They were dried at room temperature for 2 days in vacuum.

Film Preparation. Block copolymers were added with 1 wt % Irganox 1010 (Ciba-Geigy Corp.), i.e. hindered phenol antioxidant, and dissolved in toluene. This solution (8 wt %) was poured into a Petri dish and the solvent was allowed to evaporate slowly over 3 to 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 HP GPC 1090 apparatus equipped with linear styragel columns. THF was the eluent (flow rate of 1 mL/min), and polystyrene standards were used for calibration. The method by Benoit et al.[16] for the universal calibration was used with the following viscosimetric relationships:

$$[\eta] = 1.36 \times 10^{-4}\, M^{0.714} \quad \text{(PS in THF)}^{17}$$

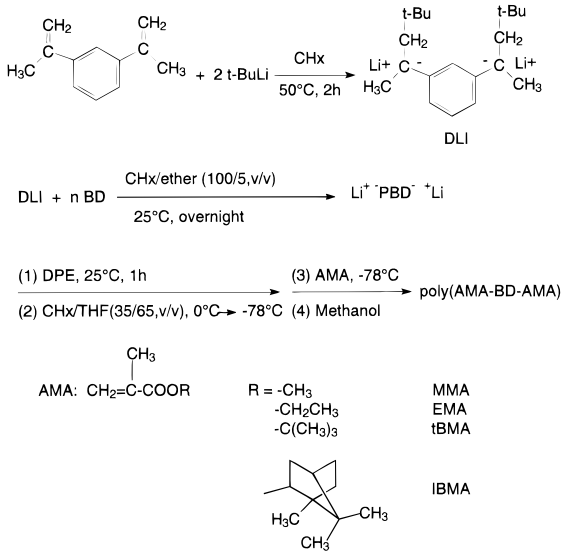
$$[\eta] = 4.57 \times 10^{-4}\, M^{0.693} \quad \text{(PBD in THF)}^{18}$$

^{1}H NMR spectra were recorded with a Brucker AN-400 spectrometer, by using $CDCl_3$ as a solvent. Content of the PBD 1,2-units was calculated by ^{1}H NMR from the relative intensity of the signals at 4.9 ppm (CH_2═, 1,2-double bond) and at 5.4 ppm (CH═, 1,2-plus 1,4-double bond). Composition of the copolymers was calculated by ^{1}H NMR from the integration of the signal for the 1,2-units of PBD and the signal for the OCH_3 group of the MMA units at 3.6 ppm, for the $-OCH_2-$ group of the EMA units at 4.0 ppm, and for the −OCH< group of the IBMA units at 4.4 ppm. Composition of poly(t-BMA-*b*-BD-*b*-t-BMA) was estimated from the initial t-BMA amount and the copolymerization yield, since the pertinent ^{1}H NMR signals were overlapping.

Differential scanning calorimetry (DSC) was carried out with a DuPont 910 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.

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

Scheme 1. Synthesis of Poly(AMA-BD-AMA) Triblock Copolymers



Tensile measurements were conducted with an Instron 1122 tensile tester equipped with a heating chamber. Testing samples (microdumbells) of 1 mm thickness were cut from solution cast films and kept for 3 min at the desired temperature before being extended at 200 mm/min. Strains were measured from the displacement of the crosshead. Reported data are the average of three measurements.

Results and Discussion

Synthesis of Triblock Copolymers. Synthesis of well-defined 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 1 shows that this technique is also successful for the preparation of triblock copolymers in which PEMA, P-t-BMA, and PIBMA are substituted for PMMA. At a comparable monomer concentration (∼2 vol %) and the same reaction temperature, the polymerization rate of EMA, IBMA, and MMA appears to be comparable, since a conversion of ca. 90 wt % is observed in 1 h, in contrast to the polymerization of t-BMA, which takes 3 h to reach the same conversion. Narrow molecular weight distribution is observed for both the PBD midblock (1.10) and the triblock copolymers (1.10), which indicates that the polybutadienyl dianions end-capped by DPE initiate quantitatively and rapidly each of the methacrylates under consideration. A SBS triblock copolymer (sample A, Table 1) has also been prepared for the sake of comparison.

Unsaturated thermoplastic elastomers are known for limited thermo-oxidation resistance compared to saturated rubbers, such as EPR and EPDM, that resist degradation upon exposure to high temperature (in air) and UV radiation. Hydrogenation of the traditional SBS triblock copolymers into saturated counterparts (SEBS) has expectedly improved their thermal resistance,[19] with the additional advantage of improved phase separation and higher tensile properties. In order to check whether this general behavior holds for other thermoplastic elastomers of the ABA type, the PBD midblock of the MBM triblock copolymer D (Table 1) has been hydrogenated into a poly(ethylene-*co*-1,2-butene) (PEB) block (sample HD) by a Co/Al catalyst.[15] FTIR and ^{1}H NMR analysis (not shown here) confirm the quantitative conversion of the PBD block to the saturated counterpart

Table 1. Block Copolymers with a Central PBD Block and Alkyl Methacrylate Outer Blocks

			PBD				PAMA[d]			
sample	hard block	reaction time[a] (h)	M_n^{cal} [b] ($\times 10^{-3}$)	M_n^{SEC} [c] ($\times 10^{-3}$)	M_w/M_n[c]	1,2[d] (%)	M_n ($\times 10^{-3}$)	content (%)	syndio (%)	copolymer M_w/M_n[c]
A	PS	3	72	80	1.10	40	2 × 21	34 (35)	–	1.10
B1	PEMA	1	50	59	1.10	42	2 × 13	31 (35)	75	1.10
B2	PEMA	1	48	52	1.10	42	2 × 7	21 (24)	77	1.10
C	P-t-BMA	3	62	70	1.10	44	2 × 14	29 (31)	nd[e]	1.10
D	PMMA	1	70	80	1.10	41	2 × 25	38 (40)	80	1.10
HD	PMMA		hydrogenated D							1.15
E	PIBMA	1	50	55	1.10	45	2 × 20	42 (44)	nd	1.10

[a] Reaction time for the hard block. [b] From the amount of monomer and initiator used. [c] SEC based on the universal calibration method. [d] ^{1}H NMR, the value in parenthesis is the theoretical composition. [e] Not determined.

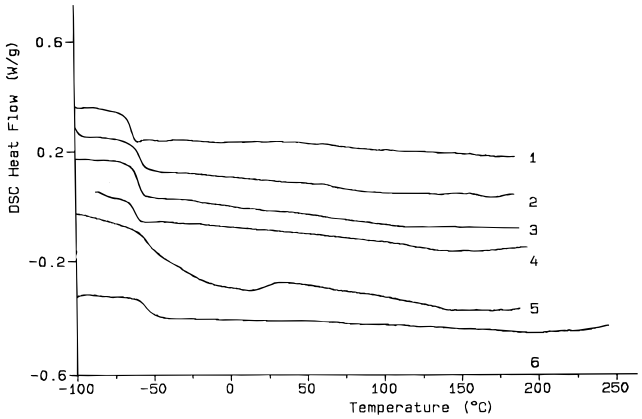


Figure 1. DSC traces of the triblock copolymers: A (1), B1 (2), C (3), D (4), HD (5), and E (6); heating rate, 20 °C/min.

Table 2. Thermal Properties of Poly(alkyl methacrylate)-Based Triblock Copolymers

	DSC (°C)[a]		DMA (°C)[b]	
sample	T_{g1}	T_{g2}	T_{g1}	T_{g2}
A	−62	c	−58	100
B1	−60	66	−58	90
B2	−60	c	−57	84
C	−59	c	−50	116
D	−62	125	−57	132
HD	−54	135	−50	137
E	−56	184	−55	202

[a] Heating rate: 20 °C/min. [b] Heating rate: 5 °C/min, 1 Hz. [c] T_g is too diffuse to be accurately measured.

Differential Scanning Calorimetry. DSC is a very useful technique to detect phase separation in binary blends and block copolymers of two immiscible components, provided that the individual glass transition temperatures (T_g) are sufficiently different from each other and the weight composition is far from the extreme values. Figure 1 shows DSC curves for samples A, B1, C, D, HD, and E (Table 1). A transition at low temperature which is assigned to the glass transition (T_{g1}) of the soft PBD or PEB phase is clearly observed for all the samples. This transition temperature is actually the low service temperature of the triblock copolymer. T_{g1} varies from −56 to −63 °C for the PBD-containing triblock copolymers (Table 2), in a possible relationship with the content of 1,2-units in the PBD midblock (Table 1). The higher T_{g1} is observed for the hydrogenated sample HD (54 °C), the midblock of which is a poly(ethylene-*co*-1,2-butene). The second transition temperature (T_{g2}) characteristic of the hard phase is very faint and observed for samples B1, D, HD, and E (Figure 1, Table 1). Observation of two glass transitions indicates that these materials are phase-separated. It would also be so for samples A, B2, and C, although T_{g2} is too diffuse to be observed. Indeed, T_{g1} is not increased as would be expected in case of miscibility of the hard and the soft blocks.

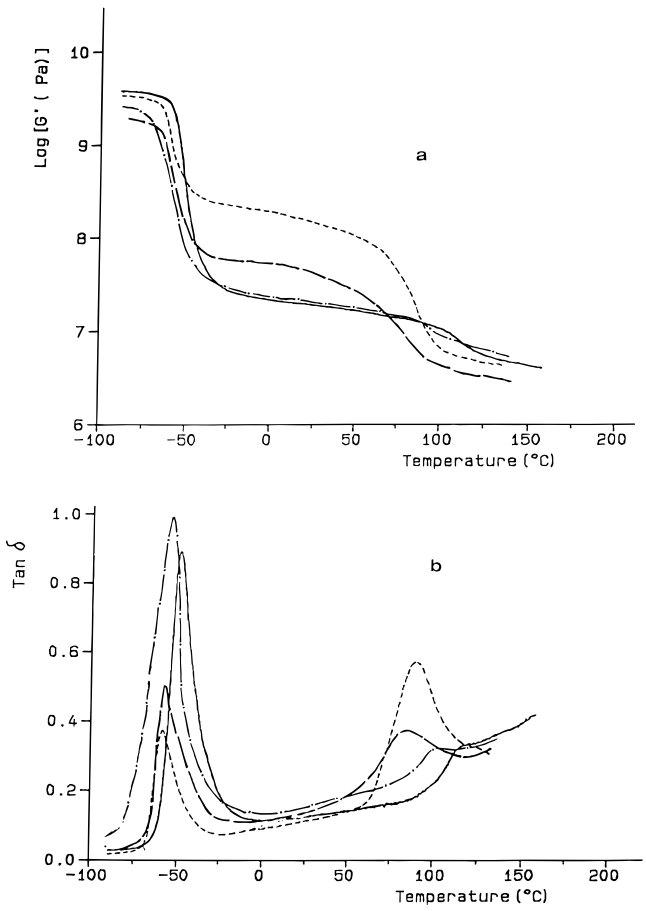


Figure 2. Shear storage modulus (G') (a) and loss tan δ ($=G''/G'$) (b) at 1 Hz for the SBS sample A (— • —), poly(EMA-*b*-BD-*b*-EMA) samples B1 (- - -) and B2 (— —), and poly(t-BMA-*b*-BD-*b*-t-BMA) sample C (—).

In case of sample HD, a broad, ill-defined melting endotherm is observed above T_{g1}, with a diffuse maximum close to −7 °C, which indicates a small number of poorly defined crystalline domains in the PEB matrix. Crystallization originates from short polyethylene blocks delimited by butylene units.[26] Hydrogenation of the MBM copolymer D results in a 10 °C increase in T_{g2} (Table 2), which indicates that the phase separation becomes sharper upon hydrogenation.

DMA Analysis. Figure 2 shows the temperature dependence of the dynamic shear storage modulus (G') and loss tan δ ($=G''/G'$) from −100 to 200 °C for the A, B1, B2, and C copolymers (Table 1). In contrast to DSC analysis, the glass transition of the hard phase is now clearly observed in addition to T_{g1}, which confirms the two-phase morphology of all these copolymers. From

Figure 2a, it appears that G' in the glassy plateau depends on the hard block and particularly on its molecular weight, since G' decreases with this molecular characteristic. Compared to triblocks containing PS (copolymer A) and P-t-BMA (copolymer C) hard blocks, G' in the rubbery plateau increases when PEMA is the outer block as rapidly as when the molecular weight is high (from B2 to B1). This increase is reported for sample B2 although the hard phase content (21 wt %) is much smaller than for samples A and C. It is also noteworthy that the damping associated with the soft phase is significantly smaller for samples B1 and B2 compared to samples A and C, in contrast to what happens when damping at T_{g2} is concerned. This general observation can only be accounted for by a deep difference in the phase morphology of samples A and C compared to samples B1 and B2. As will be discussed hereafter, samples A and C have a cylindrical phase morphology, whereas samples B1 and B2 show a lamellar morphology, which can result in the main observations in Figure 2. Actually, the effect of phase morphology on dynamic mechanical properties has been reported for SBS block copolymers.[24,25] It has been shown that the storage modulus G' of a SBS copolymer may be significantly changed when the casting solvent and thus the phase morphology are changed.[24] As a rule, a sample with a lamellar phase morphology has a higher modulus compared to the morphology with a cylindrical hard phase due to a higher phase connectivity in the former case.[24] In parallel, relaxation of the soft phase in a lamellar organization is only partial at T_{g1} due to restrictions by the alternate hard block layers, in contrast to what happens when the soft phase is continuous. Accordingly, the damping of the soft phase must be comparatively more important at T_{g1} when the hard phase forms cylinders rather than lamellae (independently of the phase content). The main DMA characteristics for samples A and C (cylindrical morphology) and samples B1 and B2 (lamellae) are thus in line with their phase morphology.

Consistently with T_g of the homopolymers, T_{g2} is lower for PEMA-containing triblock copolymers B1 (90 °C) and B2 (84 °C). It is comparatively higher for the SBS sample (100 °C). The higher T_{g2} in this series is observed in the case of P-t-BMA hard blocks (C), as shown in Figure 2b. The soft phase transition is observed at the same temperature (T_{g1}) for samples A, B1, and B2 as result of a comparable microstructure of the PBD block. Poly(t-BMA-*b*-BD-*b*-t-BMA) sample C has a higher T_{g1}, more likely as result of a more diffuse interphase with PBD.

Figure 3 shows the dynamic mechanical properties for the triblock copolymer D, the hydrogenated counterpart HD, and the PIBMA-containing copolymer E. Two transitions confirm the two-phase morphology that was suspected after DSC. Hydrogenation of sample D decreases G' in the glassy plateau, although G' is increased in the rubbery plateau, in agreement with a change in the chemical structure of the midblock. Samples E and HD have a comparable G' up to ca. 90 °C. At higher temperatures, G' of sample HD starts to decrease rapidly, whereas it persists up to 160 °C for sample E. That phase separation in PMMA-containing copolymers becomes sharper upon hydrogenation is confirmed by an increase in T_{g2} and the associated damping of sample D (Figure 3b). It is worth recalling that hydrogenation of SBS copolymers has been reported to increase the upper service temperature by ca.

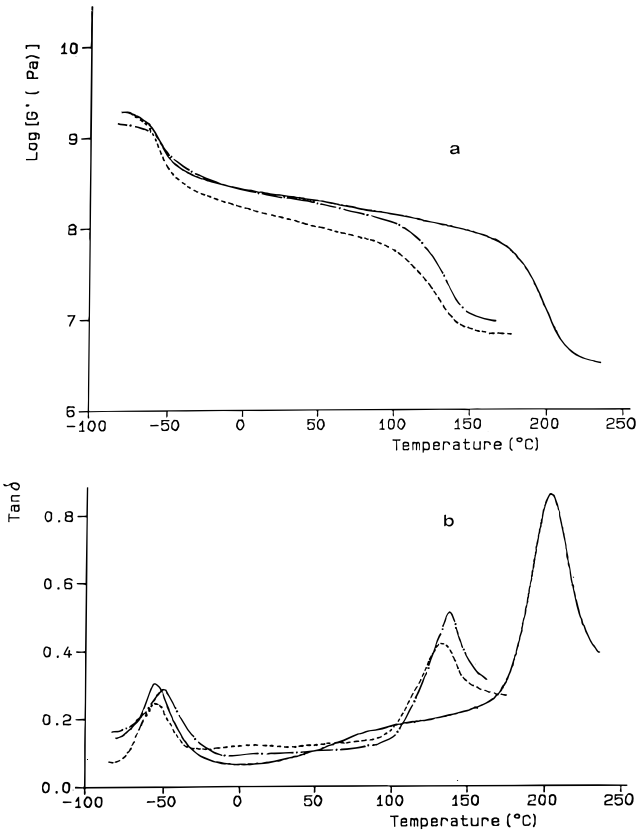


Figure 3. Shear storage modulus (G') (a) and loss tan δ ($=G''/G'$) (b) at 1 Hz for the MBM sample D (- - -), hydrogenated MBM sample HD (— · —), and poly(IBMA-*b*-BD-*b*-IBMA) sample E (—).

20 °C as a result of a better phase separation.[19] This effect is comparatively less important in the case of the MBM copolymers (<10 °C) under consideration. Substitution of PIBMA for PMMA outer blocks results in a substantial increase in the upper service temperature, in agreement with a much higher T_g for PIBMA (190 °C, by DSC) compared to that of PMMA.[15]

Morphological Observations. The phase morphology has been analyzed by transmission electron microscopy (TEM), which confirms the phase separation shown by DSC and DMA analysis. Figures 4 and 5 show transmission electron micrographs of toluene cast films annealed at 140 °C for 3 days under vacuum. PBD is observed as the dark phase as a result of selective staining by OsO_4. The equilibrium phase morphology of multicomponent materials is known to be dictated by their composition, as reported for SB and SBS triblock copolymers.[20,21] As a rule, a spherical morphology is observed for a PBD content in the 0−18 wt % range. When the PBD content is as high as 18−38 wt %, a cylindrical morphology is observed, whereas a lamellar morphology is reported for 36−60 wt % PBD.[20] Figure 4 compares the phase morphology for the two PEMA-containing samples B1 (Figure 4a) and B2 (Figure 4b). A lamellar morphology is clearly observed in Figure 4a with ca. 15 nm thick PBD lamellae. The PEMA layers are comparatively much thinner due to a lower polymer content. The phase morphology observed in Figure 4b is more complex, although reminiscent of a modified lamellar morphology and particularly of a lamellar-catenoid morphology,[22] with ca. 17 nm thick PBD lamellae. It is clear that associated with PBD, PEMA is prone to form two-dimensional continuous phases even at contents as low as 31 wt % (B1 sample) and 21

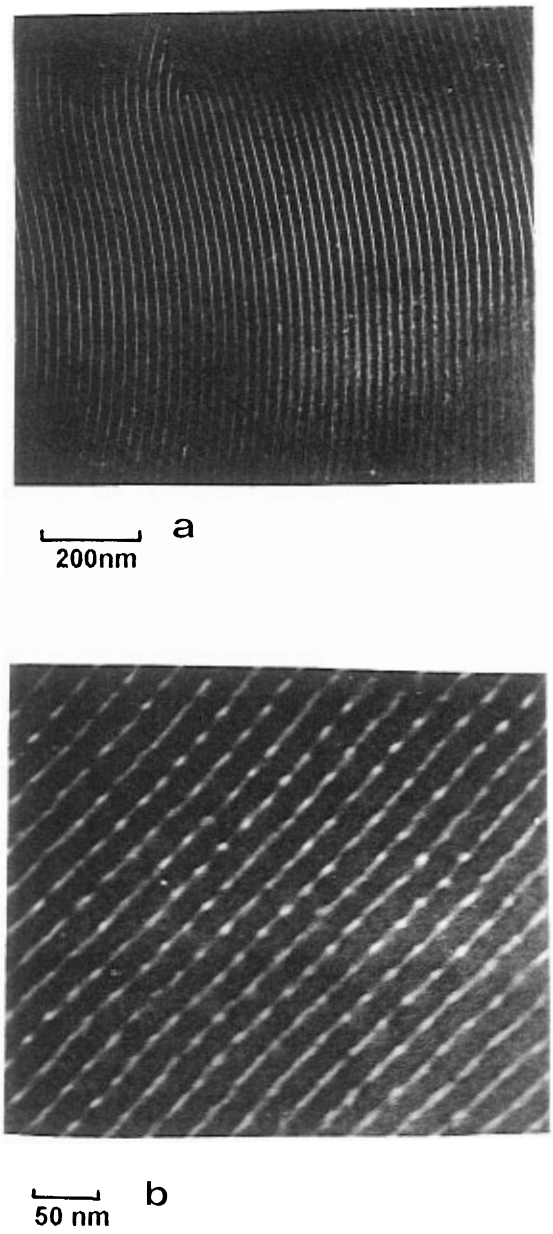


Figure 4. Transmission electron micrographs for the block copolymers B1 (a) and B2 (b). PBD is the black phase stained with OsO_4.

wt % (B2 sample), respectively, which is quite surprising. Indeed, in this composition range, the PS blocks of SBS copolymers typically form cylinders.[20] This unusual observation has already been reported by McGrath et al., who observed a lamellar structure for poly(t-BMA-*b*-BD-*b*-t-BMA) containing 16 vol % hard block.[23] The reason for this apparently surprising observation might be found in the different chemical structure of the hard block. Indeed, composition of block copolymers is not the only variable which determines the equilibrium morphology ; other parameters, such as the Flory−Huggins interaction parameter of the two blocks and the polymerization degree of each of them, affect the phase morphology.[27] The lamellar morphology for samples B1 and B2 is responsible for the higher storage modulus in the rubbery plateau and the low damping observed at T_{g1} (Figure 2).

TEM of samples C, D, and E are shown in Figure 5 and confirm a two-phase morphology. Cylinders of P-t-BMA are observed to be dispersed in a continuous PBD matrix in the case of sample C (Figure 5a), which has

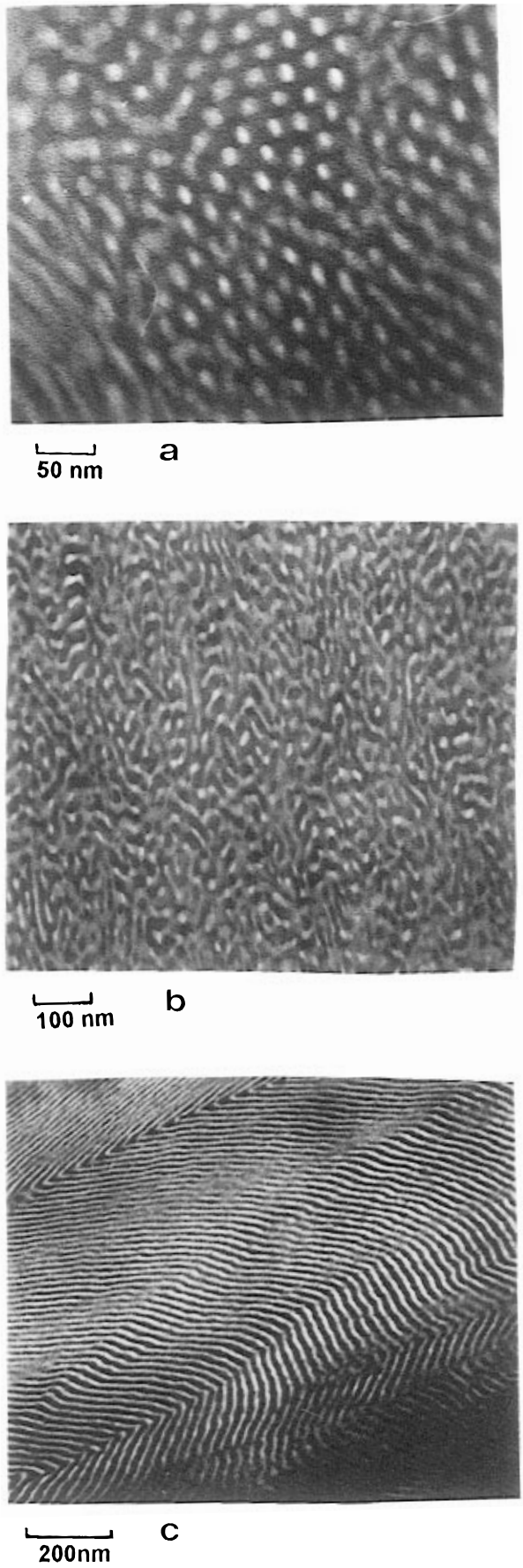


Figure 5. Transmission electron micrographs for the block copolymers C (a), D (b), and E (c). PBD is the black phase stained with OsO_4.

molecular characteristics comparable to sample B1. The PMMA phase in sample D is intermediate between

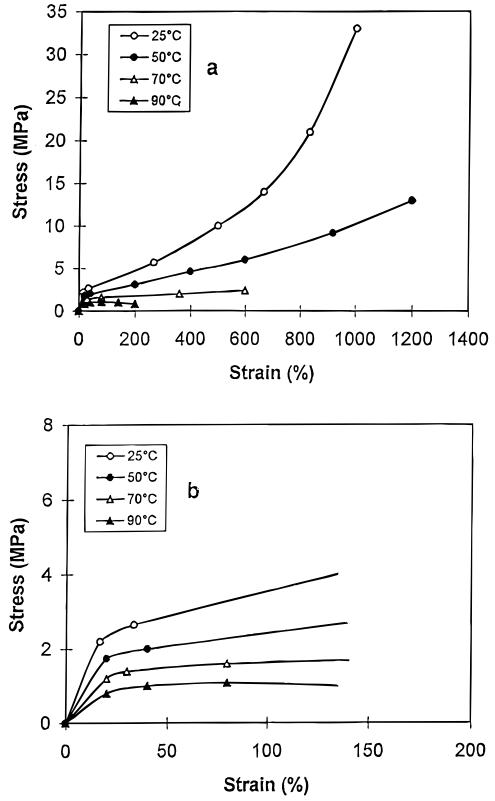


Figure 6. Stress−strain curves at different temperatures for the SBS triblock copolymer A: (a) full curves and (b) curves in the small strain region.

cylinders and lamellae, but without long range order (Figure 5b). Finally, although the solubility parameter of PIBMA [8.1 (cal/cm^3)$^{1/2}$] is quite close to PBD [8.4 (cal/cm^3)$^{1/2}$],[28] which would suggest a poor phase separation, alternate PBD and PIBMA lamellae are clearly observed for the poly(IBMA-*b*-BD-*b*-IBMA) sample E (Figure 5c) with 8−10 mm thick PIBMA layers.

Stress−Strain Behavior. The network structure of the triblock copolymers under consideration results from immiscibility and phase separation on a microscopic scale of the constitutive blocks. Although the minor rigid blocks prevent viscous flow from occurring and provide these block copolymers with rubber-like properties at room temperature (well below the T_g of the hard block), these characteristic features are lost upon heating in the vicinity of and above the T_g of the hard block. Since triblock copolymers containing hard blocks of different T_g's have been synthesized, it is worth investigating how effective the physical cross-linking is in stabilizing the network structure and thus in preventing the viscous flow at high temperatures. This information has been collected from the temperature dependence of the stress−strain curves and the ultimate mechanical properties.

For the sake of comparison, a SBS triblock copolymer has been analyzed first. Figure 6 shows the stress−strain curves for the SBS sample A in a temperature range from 25 to 90 °C, whereas the typical ultimate mechanical properties are reported in Table 3. A high ultimate tensile strength (σ_b) is observed at 25 °C, which rapidly decreases as the temperature is increased. More than 90% of the strength at 25 °C is lost at 70 °C and, in parallel, the modulus in the small strain region decreases upon increasing temperature (Figure 6b). Typical stress−strain curves for the poly(EMA-*b*-BD-*b*-EMA) triblock copolymer B1 from 25 to 90 °C are

Table 3. Mechanical Properties of Poly(alkyl methacrylate)-Based Triblock Copolymers

sample	tensile properties[a]	*T* (°C) 25	50	70	90	110	125	140	150
A	σ_y (MPa)	−	−	−	−				
	σ_b (MPa)	33.0	13.0	2.4	0.8				
	ϵ_b (%)	1100	1200	600	200				
B1	σ_y (MPa)	4.0	3.2	2.3	−				
	σ_b (MPa)	18.7	14.0	4.0	1.4				
	ϵ_b (%)	1120	1280	850	530				
B2	σ_y (MPa)	2.3							
	σ_b (MPa)	19.0							
	ϵ_b (%)	1200							
C	σ_y (MPa)	−	−	−	−				
	σ_b (MPa)	24.0	16.1	4.8	1.8				
	ϵ_b (%)	1080	1270	910	570				
D	σ_y (MPa)	4.6	nd	3.8	3.2	2.4	1.7		
	σ_b (MPa)	32.0	nd	20.0	14.3	5.5	2.2		
	ϵ_b (%)	835	nd	1200	1240	970	1086		
HD	σ_y (MPa)	6.3	nd	4.9	3.6	3.4	2.8		
	σ_b (MPa)	38.0	nd	24.0	18.2	8.4	3.8		
	ϵ_b (%)	700	nd	1150	1400	1100	970		
E	σ_y (MPa)	9.6	nd	nd	3.5	2.9	2.6	2.5	1.9
	σ_b (MPa)	35.0	nd	nd	16.5	11.5	8.4	5.6	2.2
	ϵ_b (%)	650	nd	nd	1040	1050	1080	920	600

[a] σ_y = yield stress, σ_b = ultimate tensile strength, ϵ_b = elongation at break.

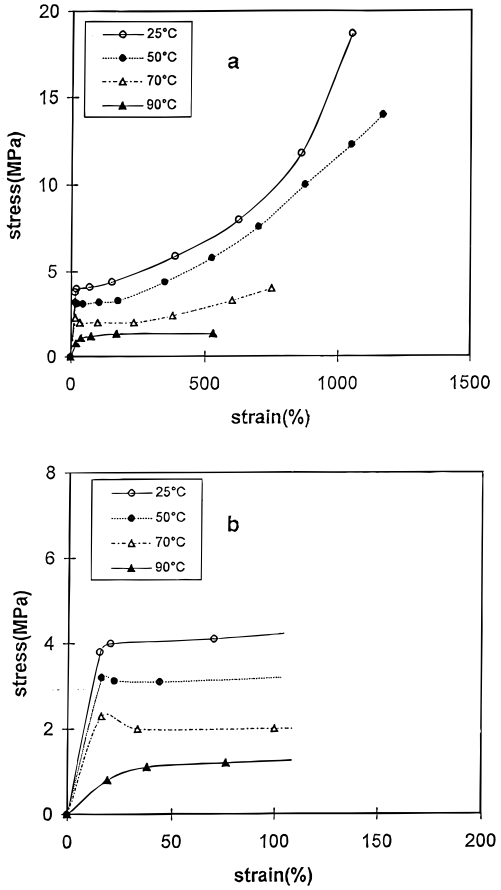


Figure 7. Stress−strain curves at different temperatures for the poly(EMA-*b*-BD-*b*-EMA) triblock copolymer B1: (a) full curves and (b) curves in the small strain region.

shown in Figure 7. At room temperature, this material shows a stress−strain behavior typical of a cross-linked rubber, i.e. high elongation at break (ϵ_b) and high ultimate tensile strength (Table 3). This observation is indicative of sharp phase separation and efficiency of the PEMA microdomains in restricting the flow of the soft polybutadiene segments. A yield point is observed in spite of the relatively low hard block content (31%),

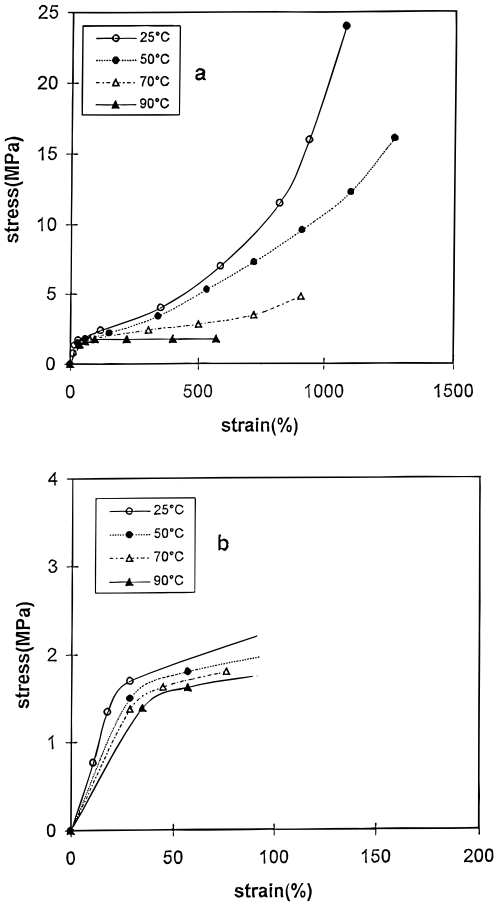


Figure 8. Stress−strain curves at different temperatures for the poly(t-BMA-*b*-BD-*b*-t-BMA) triblock copolymer C: (a) full curves and (b) curves in the small strain region.

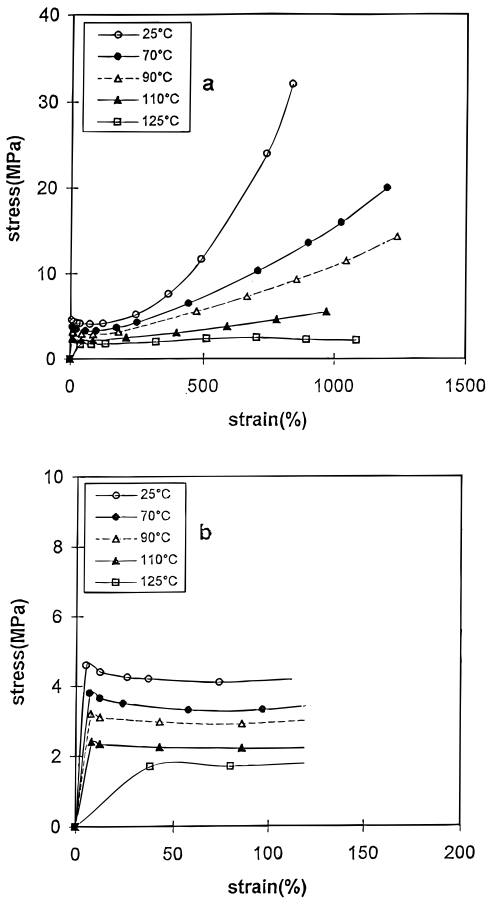


Figure 9. Stress−strain curves at different temperatures for the MBM triblock copolymer D: (a) full curves and (b) curves in the small strain region.

which is indicative of a semicontinuous PEMA phase in the PBD matrix, in agreement with the lamellar morphology observed by TEM (Figure 4a). The ultimate tensile strength, the yield stress and the initial modulus decrease with increasing temperature, as result of the increased mobility of the PEMA microdomains. The yield point persists up to 70 °C, and a necking over a large strain followed by an increasing stress is still observed at 70 °C, close to the glass transition temperature of PEMA (Table 2). Compared to the SBS sample (Figure 6), the initial modulus of B1 decreases more slowly upon heating up to 70 °C (Figure 7b) and the stress−strain curve of B1 at 90 °C is comparable to that of SBS at 70 °C, which indicates a better thermal resistance when PEMA is substituted for PS of a higher T_g (Table 2). It is noteworthy that a yield point is observed at room temperature for the poly(EMA-*b*-BD-*b*-EMA) sample B2 of a lower hard block content (21 wt %) (Table 3), which agrees with the pseudolamellar morphology observed by TEM (Figure 4b).

In the case of poly(t-BMA-*b*-BD-*b*-t-BMA) triblock copolymer (sample C, Table 1), no yield point is observed (Figure 8). σ_b and the initial modulus (Figure 8b) are continuously decreasing with increasing temperature. Although T_g of the P-t-BMA end block (116 °C, DMA) is higher than PEMA (90 °C, DMA), the tensile properties are not maintained at significantly higher temperature compared to the PEMA-based triblock copolymers, since σ_b and ϵ_b for these two copolymers are quite similar at 70 and 90 °C, respectively (Table 3).

Figure 9 shows stress−strain curves at different temperatures (25−125 °C) for the poly(MMA-*b*-BD-*b*-MMA) triblock copolymer D containing 38 wt % hard block. Yielding occurs at room temperature and persists to 110 °C (Figure 9b), which is consistent with the phase morphology reported in Figure 5. σ_b and the initial modulus once again decrease with increasing temperature. The decrease of modulus becomes dramatic above 110 °C, close to the T_g of PMMA. The typical behavior of a thermoplastic elastomer is maintained at 90 °C (σ_b = 14 MPa and ϵ_b = 1240%), which may be compared to the stress−strain curve for the SBS copolymer A at 50 °C, except for the yield point. Thus an increase in T_g of the hard phase from 100 °C (PS) to 132 °C (PMMA) improves by ca. 40 °C the upper service temperature of the otherwise identical thermoplastic elastomers (Table 1).

DSC and DMA analysis have suggested a better phase separation as result of hydrogenation of copolymer D. Figure 10 and Table 3 confirm an improved thermal resistance for the tensile properties. Indeed, σ_b for the hydrogenated copolymer HD is generally higher compared to the original copolymer D. In the temperature range from 110 to 125 °C, the initial modulus of copolymer HD (Figure 10b) is only slightly decreased, in sharp contrast to what happens in case of sample D (Figure 9b).

PIBMA is known for a high T_g (up to 190 °C).[11] Triblock copolymers with PIBMA outer blocks are thus expected to retain their ultimate tensile properties until high temperatures. Figure 11 shows stress−strain curves in the temperature range from 25 to 150 °C for copolymer E (Table 1) containing 42 wt % PIBMA. Only the curves at four temperatures are reported for the

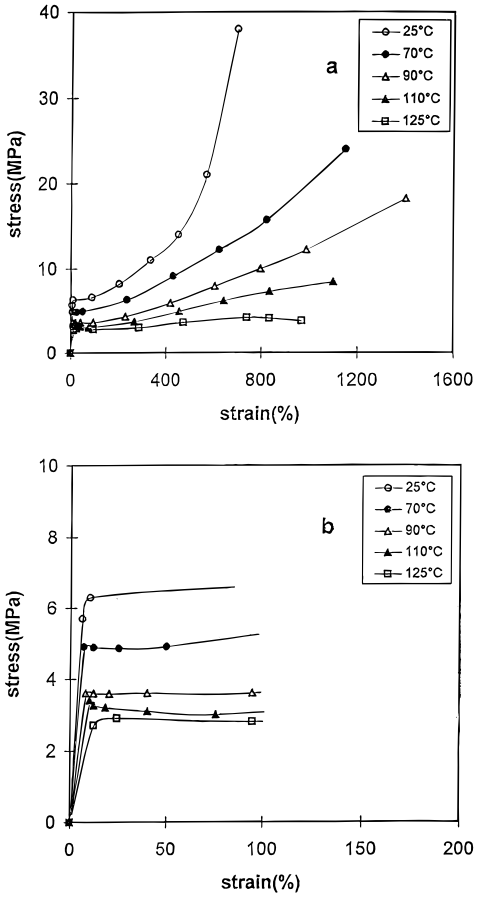


Figure 10. Stress−strain curves at different temperatures for the MEBM triblock copolymer HD: (a) full curves and (b) curves in the small strain region.

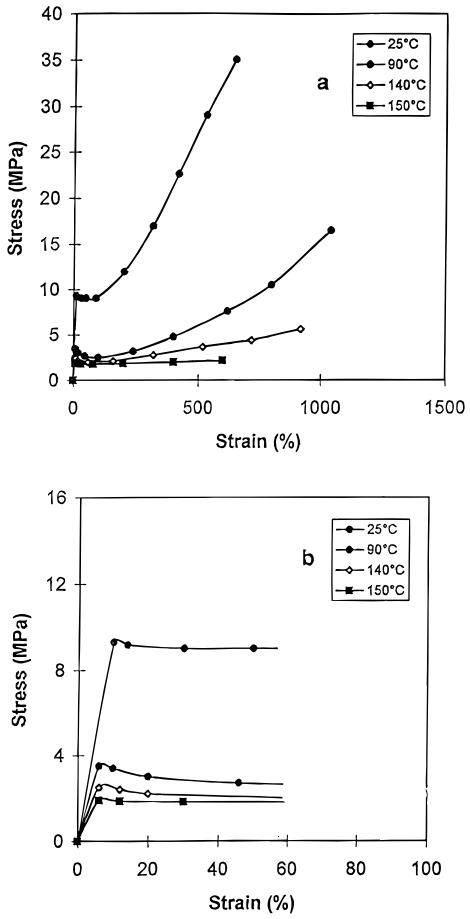


Figure 11. Stress−strain curves at different temperatures for the poly(IBMA-*b*-BD-*b*-IBMA) triblock copolymer sample E: (a) full curves and (b) curves in the small strain region.

sake of clarity, the data at the additional temperatures being listed in Table 3. At room temperature, σ_b (35 MPa) and the yield stress (9 MPa) are high, and ϵ_b is relatively small (650%). The initial modulus steadily decreases with increasing temperature up to 150 °C (Figure 11b). At temperatures as high as 140 °C, the material shows a yield point at 2.5 MPa followed by a necking process over a strain range of ca. 200%. The stress increases again upon increasing strain until the sample breaks down at 5.6 MPa and 920% elongation. Thus the typical features of thermoplastic elastomers persist at this temperature.

The temperature dependence of the ultimate tensile strength (σ_b) is plotted in Figure 12 for all the investigated copolymers. At room temperature, the PEMA-containing copolymers B1 and B2 (Table 3) have the lower σ_b compared to the other copolymers, which cannot be explained by the hard block content, particularly for sample B1. In this respect, Morton et al.[8] have reported that triblock copolymers with hard blocks of a lower T_g usually have a lower ultimate tensile strength. The degradation of the ultimate mechanical properties above 25 °C is by far more drastic in the case of the SBS sample A. Clearly, the triblocks containing PMMA and PIBMA hard blocks (samples D, HD, and E) have an improved upper service temperature. The decrease in σ_b upon heating is quite comparable up to 90 °C. Beyond that temperature, the σ_b of PMMA-containing samples D and HD decreases rapidly upon further heating, in contrast to the steadily linear decrease in σ_b observed for the PIBMA-containing sample E up to 150 °C.

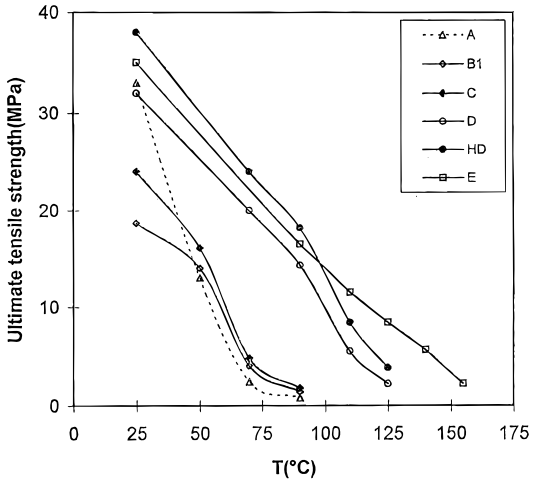


Figure 12. Ultimate tensile strength as a function of temperature for different triblock copolymers.

As a rule, the elongation at break (Table 3) changes with temperature, while passing through a maximum, whatever the sample.

Conclusion

Block copolymers of the ABA type, where B stands for PBD and A for PEMA, P-t-BMA, PMMA, or PIBMA, have been successfully synthesized by sequential anionic polymerization of butadiene and methacrylates with the diadduct of t-BuLi to m-DIB as a difunctional initiator. These triblock copolymers have a narrow molecular

weight distribution and the PBD midblock contains ca. 44% 1,2-units.

DMA is a more sensitive technique compared to DSC for probing phase separation, which is a common feature of all the investigated copolymers. The phase morphology observed by TEM has confirmed the well-known dependence on composition, although a lamellar microstructure has been reported for the triblock copolymer containing 21 wt % PEMA.

The upper service temperature (UST) of the polymethacrylate-containing thermoplastic elastomers has been compared to a traditional SBS triblock copolymer, on the basis of the thermal dependence of the tensile mechanical properties. The PS ($T_g = 100$ °C)-containing triblock copolymer has the lower UST. PEMA ($T_g = 90$ °C)- and P-t-BMA ($T_g = 110$ °C)-containing triblock copolymers show the same UST at least for the investigated composition and molecular weight. The UST of the PMMA ($T_g = 125$ °C)-containing triblock copolymer is significantly higher, and this property is further increased by hydrogenation of the PBD midblock. The higher UST is finally observed for the PIBMA ($T_g = 202$ °C)-containing triblock copolymer, which shows an ultimate tensile strength higher than 2MPa and a elongation at break of 600% at 150 °C.

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