Triblock Thermoplastic Elastomers with Poly(lauryl methacrylate) as the Center Block and Poly(methyl methacrylate) or Poly(*tert*-butyl methacrylate) as End Blocks. Morphology and Thermomechanical Properties

Dhruba P. Chatterjee and Broja M. Mandal*

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

Received June 21, 2006; Revised Manuscript Received October 23, 2006

ABSTRACT: The morphology, dynamic mechanical, and tensile properties of poly(methyl methacrylate)-*b*-poly(lauryl methacrylate)-*b*-poly(methyl methacrylate) triblock copolymers have been studied. Atomic force microscopy reveals that the polymer phase-separates with the PMMA phase appearing as microdomains in a continuous rubbery PLMA matrix for PMMA concentrations ranging between 16.6 and 45% by weight. The domains are spheres for 16.6% PMMA and cylinders, some lying flat on the surface and others buried in the sample with their apexes on the surface, for PMMA concentrations between 26 and 45% PMMA. As the PMMA concentration is increased to 52%, a short lameller morphology is seen. The dynamic mechanical measurements reveal two glass transitions and a rubbery plateau between them. The T_g values indicate some degree of mixing between phases. The tensile properties are poor. For example, for the copolymer with 26% PMMA the elongation at break is 80% and the ultimate tensile strength is 3 MPa. The M_e of PLMA has been measured to be 225000 which confirms the absence of entanglements in the PLMA blocks. Accordingly, the initial tensile behavior fits into the simple elastomer model which gives a surprisingly low value of 3600 for M_c. In the absence of entanglements the expected value of M_c is equal to the M_n of PLMA. The low M_c value has been attributed to shear induced side chain crystallization of PLMA which is not known to crystallize. Evidence of crystallization in the stretched sample has been obtained from X-ray diffraction studies. A poly(*tert*-butyl methacrylate-*b*-LMA-*b*-*tert*-butyl methacrylate)(tBLtB) copolymer prepared in one pot gives a substantially greater elongation at break. The PtBMA block, however, exhibits greater mixing with PLMA presumably due to its being a copolymer containing a small percentage of LMA residues. The initial tensile behavior of this triblock copolymer fitted into the simple elastomer model gives $M_c = 29\,000$ which is still lower than the M_n of the PLMA center block. No crystallization of PLMA in a stretched (200%) sample of this triblock copolymer is evident from XRD studies. Apparently, the higher degree of mixing of PLMA with PtBMA prevents crystallization of the former. The lack of crystallization also helps to get larger elongation of this block copolymer.

Introduction

Triblock copolymers with an elastomeric center block and glassy end blocks exhibit the properties of thermoplastic elastomers (TPE), the well-known examples being the commercially successful SBS or SIS triblock copolymers (S = styrene, B = butadiene, and I = isoprene). They have a multiphase morphology of glassy PS domains dispersed in a continuous elastomeric matrix. The glassy microdomains act as physical cross-links as well as reinforcing fillers so that attractive thermo mechanical properties are obtained without vulcanization and extraneously added fillers.[1−3] However, they have the drawback that the diene center blocks are susceptible to atmospheric oxidation and UV degradation which are overcome by the hydrogenation of the center blocks.[4,5] But this adds to the cost.

Saturated TPEs with poly(alkyl acrylate) center blocks and poly(methyl methacrylate) (PMMA) end blocks (MAM) attracted interest in this regard but unfortunately they were found to be inferior to the diene based TPEs as regards mechanical properties.[6−12] The cause of this deficiency was traced to the high molecular weight between entanglements (M_e) of the polyacrylates compared to the polydienes.[8−10]

Recently, we developed a facile process for the atom transfer radical polymerization[13,14] (ATRP) of higher alkyl methacrylates, e.g., lauryl methacrylate (LMA), at ambient temperature using which the synthesis of the triblock copolymer PMMA-*b*-PLMA-*b*-PMMA (further abbreviated as MLM) could be conveniently done.[15,16] The T_g of PLMA being ca. −65 °C[17] and that of PMMA ca. 109 °C[17] these triblock copolymers should have the properties of a TPE. Accordingly, we present in this paper the characterization, morphology, dynamic mechanical and tensile properties of MLM triblock copolymers of varied compositions.

With the expectation of improving the tensile properties the PMMA end blocks of the MLM copolymers were changed with poly(*tert*-butyl methacrylate) (PtBMA) which has some 30 °C higher T_g than PMMA. These tBLtB block copolymers exhibit higher elongation at break with no improvement in ultimate tensile strengths.

Experimental Section

Materials. LMA (Aldrich, 96%), tBMA (Aldrich, 98%) and MMA (BDH) were washed with 5% aqueous NaOH solution, dried over anhydrous $CaCl_2$, vacuum distilled and stored under argon at −15 °C. Pentamethyldiethylenetriamine (PMDETA) (99%), tricaprylylmethylammonium chloride (Aliquat336, AQCl) all Aldrich products were used as received. CuCl (98%, BDH) was purified by washing with 10% HCl in water followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. The difunctional initiator 1,2-bis(bromoisobutyryloxy)ethane (BiBE) was prepared according to a literature method.[18]

Synthesis of a α,ω-Dichloro-PLMA (Cl—PLMA—Cl). A representative example is given here.

10.1021/ma061391q CCC: $33.50

Table 1. Characterization Details of the Block Copolymers

entry	LMA mole % (NMR)	PLMA		blockwise M_n of copolymers		
		($M_n \times 10^{-3}$)	PDI[c]	($M_n \times 10^{-3}$)[a]	PDI[c]	hard block (wt %)
			MLM Copolymer			
1	66.7	48	1.23	4.8−48−4.8	1.25	16.6
2[b]	51	48	1.23	9.5−48−9.5	1.17	28
3	49.3	48	1.23	10−48−10	1.17	29
4	37	48	1.23	15.5−48−15.5	1.15	39
5	32.8	48	1.23	19.5−48−19.5	1.14	45
6[b]	54	82	1.22	13.5−82−13.5	1.14	25
7	52.6	82	1.22	14.5−82−14.5	1.15	26
8	35	82	1.22	29−82−29	1.13	41.4
9	27	26	1.32	14.5−26−14.5	1.13	52
			tBLtB Copolymer			
10[b]	60.1	88	1.2	16−88−16	1.11	26.5

[a] Determined using data in columns 2 and 3. [b] One pot. [c] Gpc determined.

In a nitrogen purged test tube (8 × 2.5 cm) provided with a B-19 standard joint and a stir bar were added AQCl (0.016 g, 0.019 mmol) and CuCl (0.0019 g, 0.019 mmol). Nitrogen purging was continued for 10 min following which LMA (1.736 g, 6.84 mmol) previously purged with nitrogen was introduced into the tube. The mixture was stirred magnetically under nitrogen for 30 min to prepare a homogeneous solution. PMDETA (0.003 g, 0.019 mmol) and BiBE (0.007 g, 0.019 mmol) were next added under nitrogen. The tube was then closed with a rubber septum which was secured by a copper wire. The polymerization was conducted at 35 °C with stirring. After 24 h, the content of the tube was diluted with 1 mL of THF and poured into 300 mL of methanol. The separated polymer was isolated, redissolved in THF, and reprecipitated into excess methanol. The polymer was white in color, the cupric complex being insoluble in it. It was dried in a vacuum oven at 45 °C for 48 h, and weighed. The conversion was 92% and the M_n and PDI of the polymer were 82000 and 1.22 respectively.

It has been found that traces of moisture improves the rate of the polymerization. The present results were obtained by handling AQCl, which is hygroscopic, in a room with a relative humidity 65% at 28 °C.

Synthesis of MLM Triblock Copolymers. A two pot procedure has been used except for two samples. One example is given below.

A purified Cl−PLMA−Cl macroinitiator (0.89 g, 0.011 mmol, $M_n = 82\,000$, PDI = 1.22) prepared as described in the previous example was taken in the reaction tube provided with a stir bar along with AQCl (0.018 g, 0.043 mmol). The tube was purged with nitrogen for 10 min, following which CuCl (0.0011 g, 0.011 mmol) was added into it, and nitrogen purging continued for another 25 min. The tube was then closed with a rubber septum, which was secured with Cu wire. MMA (0.47 g, 4.7 mmol) previously purged with nitrogen was next injected into the tube using a gastight syringe. The macroinitiator was dissolved completely in MMA for 24 h. PMDETA (0.0019 g, 0.011 mmol) was then injected into the tube and mixed with the solution using a vortex mixer. The polymerization was conducted at 35 °C unstirred. After 48 h the polymer was isolated, purified and dried as described in the case of PLMA. Conversion was 70%. The M_n and PDI values were 111 000 and 1.15 respectively.

Extraction of Dead PLMA and Diblock Copolymer from the Triblock Copolymer. The triblock copolymers prepared as above are expectedly contaminated with dead PLMA (carried with the macroinitiator) and also diblock copolymer (formed from any monofunctional contaminant in the difunctional macroinitiator). These contaminants lower the mechanical properties. In order to examine the extent of such lowering, the contaminants were removed in one of the samples (sample 7, Table 1) by selective extraction with appropriate solvents. PLMA was extracted using petroleum ether (boiling range 60−80 °C) for 72 h. A further extraction was then done with the solvent mixture benzene/cyclohexane (25/75 v/v) for 1 week to extract the diblock copolymer. In this solvent mixture, the triblock copolymer was highly swollen.

Synthesis of tBLtB Triblock Copolymers. A one pot procedure was followed. In a nitrogen purged test tube (8 × 2.5 cm) provided with a B-19 standard joint and a stir bar were added AQCl (0.031 g, 0.076 mmol) and CuCl (0.0038 g, 0.038 mmol). Nitrogen purging was continued for 10 min following which LMA (1.736 g, 6.84 mmol) previously purged with nitrogen was introduced into the tube. The mixture was stirred magnetically under nitrogen for 30 min to prepare a homogeneous solution. PMDETA (0.007 g, 0.038 mmol) and BiBE (0.007 g, 0.019 mmol) were next added under nitrogen. The tube was then closed with a rubber septum which was secured by a copper wire. The polymerization was conducted at 35 °C with stirring. After 24 h, a small sample was withdrawn for gpc analysis under positive N_2 pressure (the system reaches 98% conversion with M_n and PDI of PLMA being 88000 and 1.2 respectively). tBMA (0.875 g, 6.16 mmol) previously purged with N_2 was then injected into the reaction tube and stirred vigorously using a vortex mixer for 30 min until all of the PLMA becomes soluble in the added tBMA. Polymerization was allowed to continue at 35 °C for 48 h. The content of the tube was then diluted with 2 mL of THF and poured into 300 mL of methanol. The separated polymer was isolated, redissolved in THF, and reprecipitated into excess methanol. The polymer was white in color, the cupric complex being insoluble in it. It was dried in a vacuum oven at 45 °C for 48 h, and weighed. The conversion of tBMA to its polymer was 70%. The M_n and PDI of the copolymer were 120000 and 1.11 respectively.

Characterization. Molecular Weight and Molecular Weight Distribution. The molecular weights of PLMA were determined by θ solvent viscometry using *n*-amyl alcohol as the solvent (θ = 29.5 °C), for which the intrinsic viscosity was determined by the single point method using eq 1.[19]

$$[\eta] = \frac{\sqrt{2\eta_{sp} - 2(\ln \eta_{rel})}}{c} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, η_{rel} is the relative viscosity at concentration C in g/dL and η_{sp} is the specific viscosity. The weight-average molecular weight (M_w) was calculated using the following Mark−Houwink relation.[20]

$$[\eta] = 3.48 \times 10^{-4}\overline{M_w}^{0.5} \tag{2}$$

As the polymers are of low polydispersity, $M_v \approx M_w$. The number-average molecular weight M_n was therefore calculated from M_w using the PDI values of the samples which were determined by gpc.

The gpc was performed at room-temperature using a Waters model 510 HPLC pump, a Waters series R-400 differential refractometer and Waters UltraStyragel columns of 10000, 1000, 500 Å pore size which were preceded by a prefilter. HPLC grade THF (Spectrochem, India) was used as the eluent at a flow rate of 1 mL/min. Before injection into the gpc system the polymer solutions were treated with cation exchange resin Dowex 50 W (Fluka) to free them from Cu salts. They were then filtered through a prefilter−filter combination system compatible with organic solvents. PMMA standards were used for calibration.

The M_ns of the PMMA or the PtBMA blocks were estimated from the knowledge of the mole ratios of the LMA to MMA residues in the block copolymer as determined by ^{1}H NMR and the M_n of PLMA with the assumption that the blocks are symmetrical.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR spectra of the samples were recorded at 25 °C with a Bruker 300 MHz spectrometer using $CDCl_3$ as the solvent and TMS as internal reference.

Thermomechanical Property Measurements. Sample Preparation. Films were cast from a solution of the MLM copolymer (12.5% w/v, 6 mL) in chloroform onto a polyethylene petri dish

(60 mm diameter) which was previously treated with chloroform for 24 h to leach out the compounding agents and any other leachable material. The solvent was let to evaporate for 24 h at room temperature. The films were dried at 160 °C for 3 days in a vacuum oven in order to remove the last traces of solvent and then quenched to room temperature.

Dynamic Mechanical Analysis. Dynamic mechanical properties were measured using a dynamic mechanical analyzer (DMA Q800, TA Instruments). The temperature sweep experiments were carried out at 1 Hz (ramp mode, heating rate of 2 °C/min) holding the film with a film tension clamp.

Differential Scanning Calorimetry. Differential scanning calorimetry measurements were performed in a Perkin-Elmer Diamond DSC fitted with an Intra-cooler-IIP for low temperature measurements. The temperature scale was calibrated with cyclohexane and indium. Samples (~20 mg) were first scanned from −100 to +180 °C at 10 °C/min. The sample was then quenched to −100 °C after holding it for 5 min at +180 °C and then the second scan was performed. Analysis of the results was done with Pyris software version 7.0.0.0110.

Rheological Measurements. The AR 2000 rheometer equipped with a force balance transducer was used, with the cone−plate geometry (plate 40 mm diameter; 2^0 angle; gap 56 μm between the cone tip and the plate). The dynamic storage and loss moduli, G' and G'', were measured as a function of angular frequency at various temperatures. The temperature control was better than 1 °C. The applied strain was kept within the linear viscoelastic regime, whatever the temperature is.

Tensile Testing. Tensile properties were measured using a Hounsfield H10K-S universal testing machine at the Indian Institute of Technology, Kharagpur, India. Polymer strips were cut out from the solution cast films and mounted in a standardized die of paper. The gauge-length was kept at 25 mm and width at 4 mm. The thickness of the specimens ranged from 0.2 to 0.3 mm and was measured using a Fowler Premium Line electronic digital caliper. All the copolymer specimens were drawn at a crosshead speed of 10 mm/min at room temperature. At least three independent measurements were recorded for each sample, and the best of the three results was taken.

Atomic Force Microscopy. Sample Preparation. Thin MLM films (~500 nm thick) were cast following Jerome et al. on freshly cleaved mica foil from a dilute solution of the polymer in THF (2 mg/mL) by slow evaporation of THF.[10,12] This was done inside a desiccator saturated with THF vapor and provided with an outlet fitted with a stopcock. The films were then dried at 160 °C in a vacuum oven for 72 h after which the vacuum was broken by letting in air through a sintered glass filter and the films were immediately taken out of the oven. Two films of one sample (no. 7, Table 1) were also cast from chloroform and dried as above. One of these films was cooled slowly after drying by turning the oven heater off.

Measurements. The AFM measurements were performed in the “soft tapping mode” at the Indian Institute of Technology, Kharagpur, India using a Nanonics SPM 100, (made by Nanonics Imaging Ltd., Israel) instrument at room temperature in air. Images were recorded from different area of each sample, and the time for scanning was ca. 5 min. The images were gathered at 300 dpi. The software used for image analysis was “Quartz”.

X-ray Diffraction. Solvent cast films under stretched and unstretched conditions were used. X-ray diffraction patterns of the samples were recorded with Philips X’Pert−PRO high-resolution X-ray generator operating at 45 kV and 40 mA with Cu_α radiation having a wavelength of 1.54178 Å. Data were collected in a step scan mode having a step size of 0.02°, 2θ in a scan range of 1.5−80° with a programmable automatic slit system to give a constant illuminated area during the whole scan. X’Pert−Plus software was used for analysis of the results.

Results and Discussion

Synthesis. The synthesis of the MLM triblock copolymers by bulk ATRP at ambient temperature was described earlier using CuCl/PMDETA/Aliquat as the catalyst.[16] The synthesis was carried out in two steps. In the first step an α,ω-dichloro PLMA was synthesized which was used as the macroinitiator in the second step for the synthesis of the MLM copolymers.[15,16] The macroinitiator was prepared using the halide exchange technique.[21,22] The quaternary ammonium chloride (Aliquat) used with the catalyst also brings about halide exchange.[23] The chloride-based catalyst was shown to give much better control than the bromide based one in the ATRP of MMA[23] or LMA.[15] Three macroinitiators of M_ns 26 000, 48 000, and 82 000 with PDI values of 1.32, 1.23, and 1.25, respectively, were used to prepare a series of the MLM copolymers varying in the lengths of the middle and the end blocks (Table 1). The extent of dead PLMA and diblock copolymers contamination was determined by selective solvent extraction for one sample (sample 7, Table 1) which uses the highest molecular weight PLMA macroinitiator. The dead PLMA amounted 3.8% and the diblock copolymer 2.75%. The PDI of the sample decreases from 1.15 to 1.12 on the removal of PLMA and to 1.09 on the removal of the diblock copolymer as well. The change in MWD is shown in Figure 1. The removal of the contaminants gives a symmetrical gpc trace. Two triblock copolymers were also prepared by the sequential polymerization procedure (one pot). In one of them the first stage LMA polymerization was carried to 98% conversion in 11 h, ($M_{n,PLMA} = 48\,000$), while in the other the conversion was 92% in 24 h ($M_{n,PLMA} = 82\,000$).

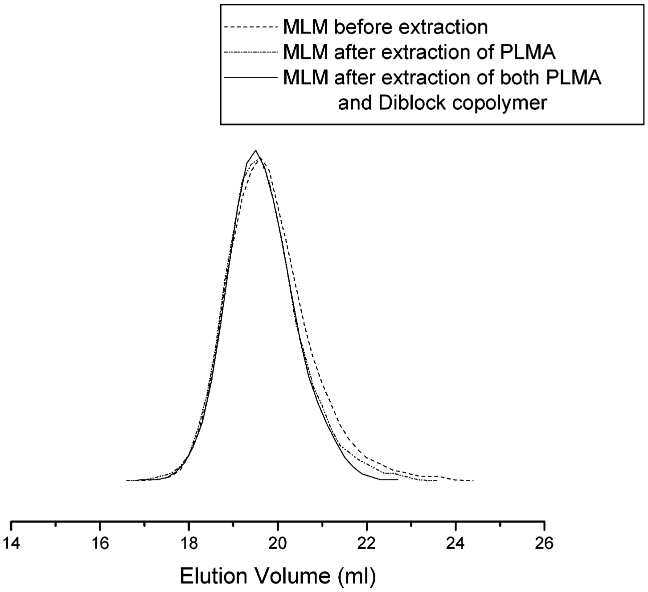

Figure 1. GPC traces of sample 7 (Table 1) before and after extraction of contaminant polymers.

The tBLtB block copolymers were prepared by the sequential polymerization (one pot) method. The conversion in the LMA polymerization done in the first stage was 98%.

The composition of the block copolymers was determined by NMR (Figure 2) from the normalized relative intensities of the $-COOCH_3$ proton in the PMMA blocks or the $-COOC(CH_3)_3$ protons in the PtBMA blocks and the $-COOCH_2-$ proton in the PLMA block. The composition so determined agrees well with that calculated from the amount of PLMA used and MMA or tBMA consumed in the syntheses. The details of the copolymers and their characterization data are given in Table 1.

Morphology. Parts a−g of Figure 3 show the PDI images obtained for the surface of thin films (~500 nm) of block copolymers which vary in PMMA concentrations from 16 to

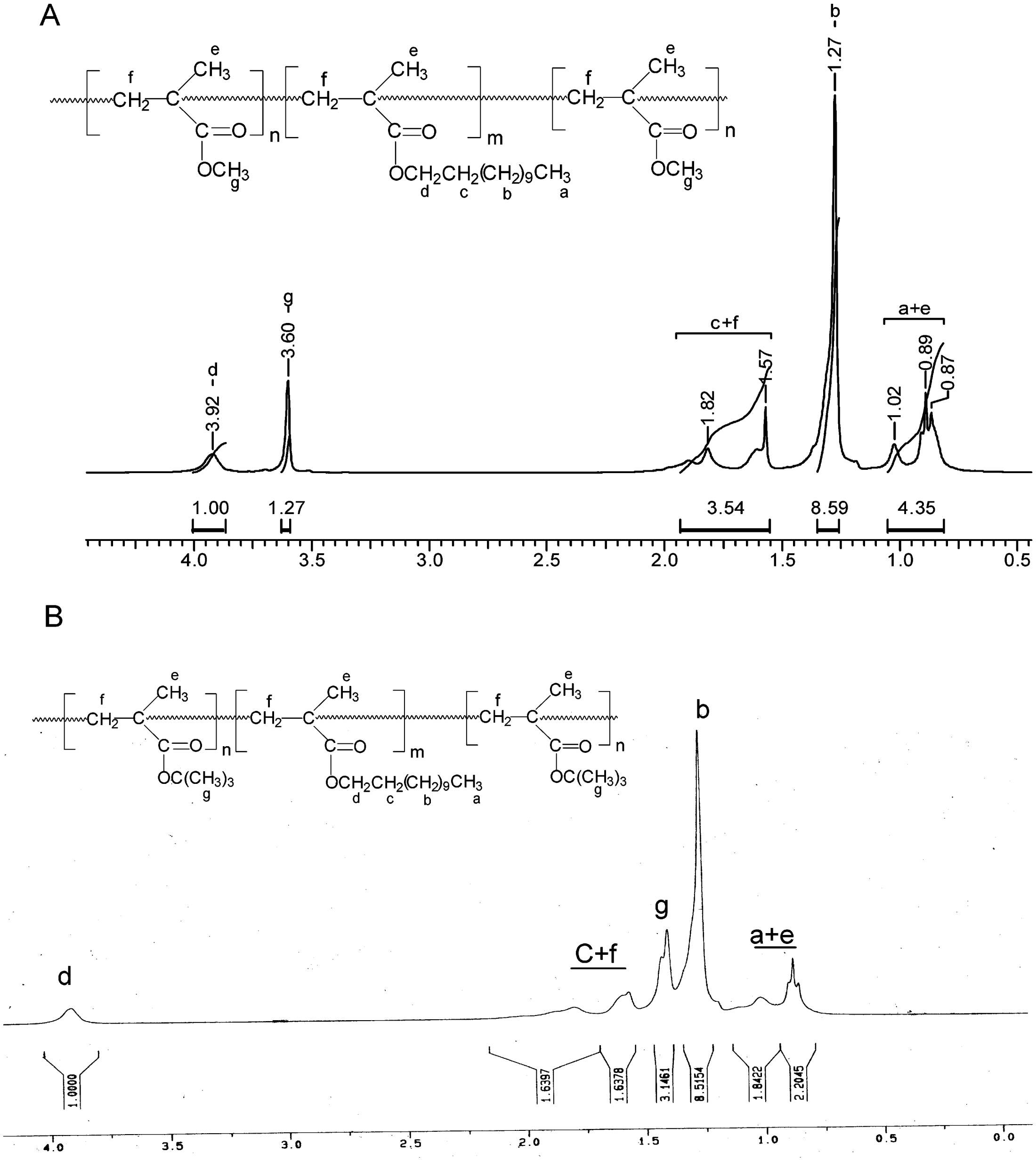

Figure 2. (A) ^{1}H NMR spectrum of the MLM block copolymer and (B) ^{1}H NMR spectrum of the tBLtB block copolymer

52% (by weight). A representative height image on the same area of the film for the 40% PMMA sample is shown also (Figure 3c′). The height image is feature less. The root-mean-square (rms) roughness for a 350 × 350 nm^2 area is 1.45 nm. The film surface is therefore smooth enough not to influence the PDI image contrast owing to the difference in the surface topography.[10,12,24] The surface roughness is of this order for all the films except for the one containing 16% PMMA. Although this film was similarly cast as others were, the rms surface roughness was 52 nm on a 350 × 350 nm^2 area. The fluidity of the polymer which is a thick viscous liquid is probably responsible for this uneven surface topography. Nevertheless, the PDI image of this sample (Figure 3a) shows the presence of white spherical objects in a black matrix. On average, the spheres are of 15 nm diameter with a center to center spacing of 23 nm between them. In previous studies of AFM images for MAM copolymers by Jerome et al. the bright areas were assigned to the hard PMMA-phase inasmuch as in “soft tapping” operation the magnitude of the phase shift is directly related to the elastic modulus of the sample.[10,12,24] The same assignment holds here.

The three PDI images (b−d) corresponding to 26, 40, and 45% PMMA content respectively show a simultaneous presence of elongated bright objects alongwith some bright dots interspaced with dark areas. All these films were cast from THF. Similar morphology was reported with MAM copolymers at PMMA concentrations ranging from 20 to 30% (MAM = MBM for A = *n*-butyl acrylate and MIM for A = isooctyl acrylate). The elongated bright objects have been identified by Jerome et al. as PMMA cylinders lying flat on the surface while the bright dots as PMMA cylinders standing vertically inside the rubbery matrix so that only their end surface can be seen.[10,12,24]

On increasing the PMMA content still further to 52% a short lamellar morphology (Figure 3e) is seen with isolated bright dots. In the literature the lamellar morphology in MIM copolymers was reported to be found at lower PMMA concentration (ca. 36%) while in the styrene-diene block copolymers at 36−62 wt % PS.[25,26]

The effect of the film casting solvent on surface morphology was also examined. Figure 3f shows that the film (26% PMMA) cast from chloroform has qualitatively the same morphology

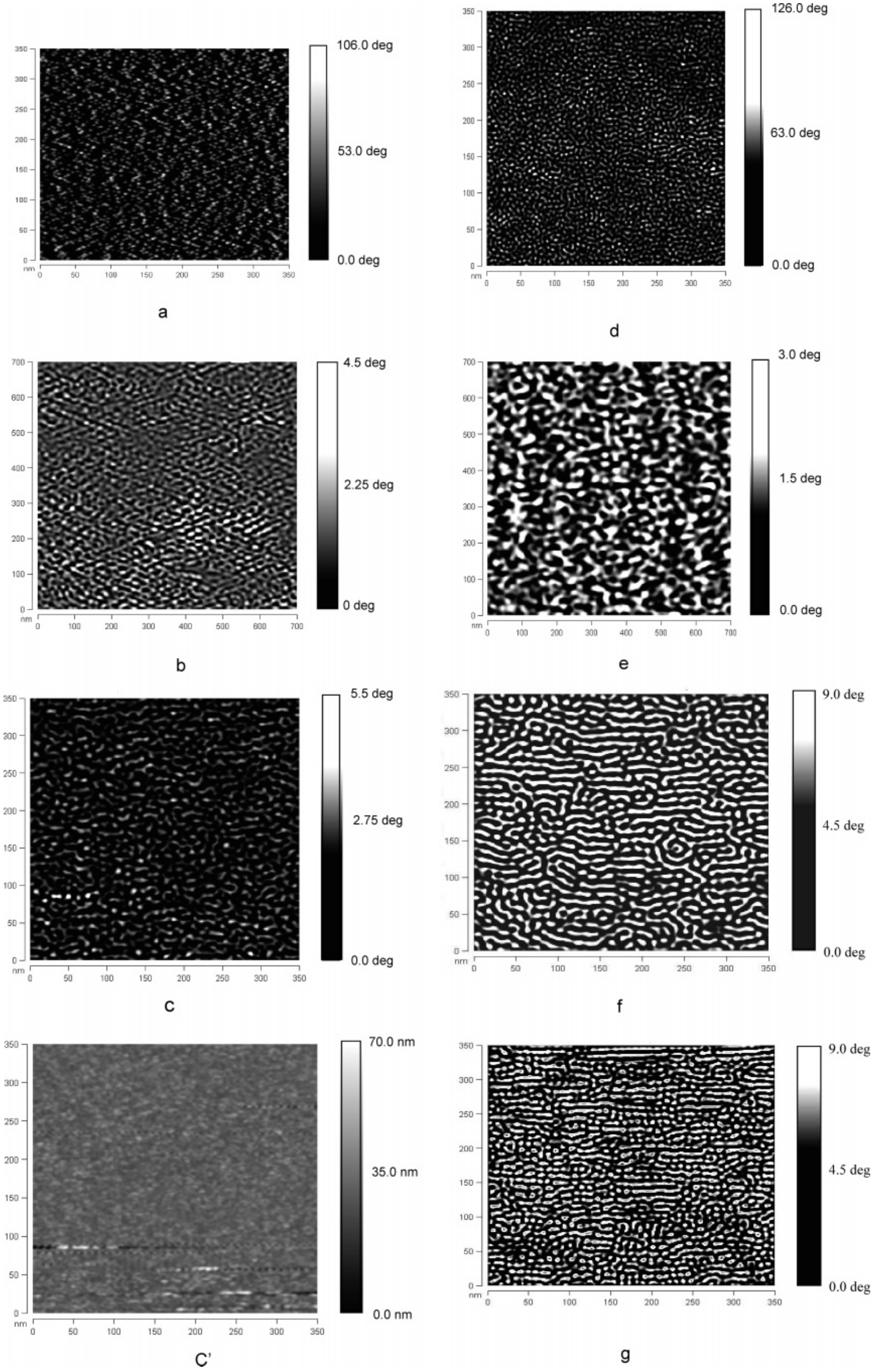

Figure 3. Tapping mode AFM images of the MLM block copolymers. Parts a−e are phase images for THF cast films containing 16.6, 26, 39, 45, and 52% PMMA respectively, parts f and g (annealed) are for chloroform cast films (26% PMMA), while part c′ is the height image corresponding to part c.

as the one cast from THF (Figure 3b) has. The effect of annealing was also studied. Figure 3g is that for a film (26% PMMA) cast from chloroform and annealed (kept at 160 °C for 72 h followed by slow cooling). A comparison of the pictures

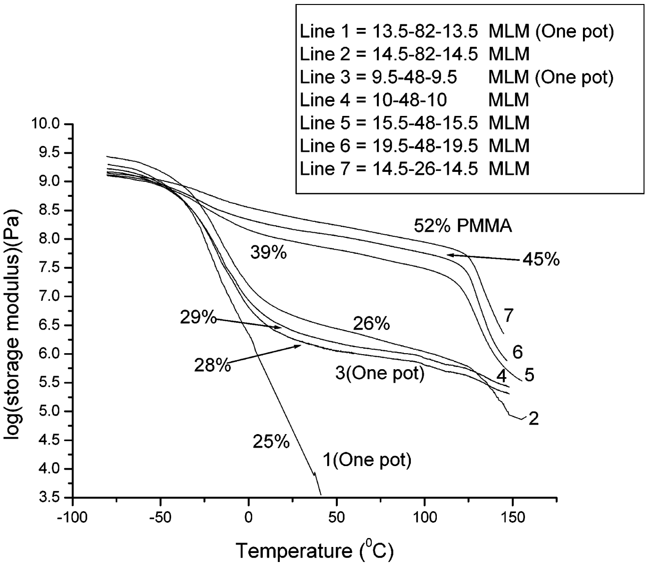

Figure 4. Plot of storage modulus vs temperature at 1 Hz of the MLM samples at a heating rate of 2 °C/min. The first stage conversion for the one pot (curve 1) was 92% and that of curve 3 was 98%.

in parts f and g of Figure 3 shows that on annealing the PMMA phase appears more as dots than cylinders as was reported for MAM copolymers.[12] Quick cooling after drying the samples for 72 h at 160 °C gives predominantly "cylinders-on-surface" morphology (Figure 3f), while slow cooling gives predominantly "cylinder tips-on-surface" morphology. PMMA has a higher surface energy (41.1×10^{-3} N/m at 20 °C)[27] than PLMA (32.8×10^{-3} N/m at 20 °C).[28] This would have required all the PMMA cylinders to stand vertically and appear as dots in order to reduce the surface energy. However, such an ordered morphology would be at the cost of lost entropy. Thus, a mixed morphology is favored.[24] However, the difference in surface energy between the two polymers decreases as their mixing increases with increase in temperature.[29−31] This factor allows more cylinders to lie on the surface at higher temperature which are retained in the rapidly cooled film.

Dynamic Mechanical Properties. Figure 4 shows the temperature dependence of the storage modulus (G') from −80 to 150 °C for the MLM triblock copolymers introduced in Table 1. The dynamic mechanical behavior is typical of the MAM thermoplastic elastomers which shows two glass transitions and a rubbery plateau between them (except for one of the two one pot polymers).[9−12] For the two samples with short PMMA chains ($M_n \approx 10\,000$) the plateau is not distinct. Such behavior in MAM copolymers has been reported earlier and attributed to the failure of the shorter chains (as would be present in a sample with PDI = 1.17) to get involved in the network formation.[11]

When the fall in G' in the transition zone in Figure 4 is compared, it is observed that barring the two samples with PMMA of lower M_n all the samples show a sharp decline followed by an indication of tapering at a temperature somewhat below 150 °C. Unfortunately, the G' measurement could not be extended above 150 °C because the stiffness of the polymers falls below the minimum required by the instrument. The extensive work of Jerome et al. on the MAM triblock copolymers revealed that when the PMMA molecular weight exceeds certain values (e.g., $M_n = 15\,000$ and 7000 when the center blocks are poly(n-butyl acrylate) and poly(isooctyl acrylate) respectively) the G' tends to level off beyond the T_g of PMMA indicating that the polymer does not flow at least up to the investigated temperature of 200 °C.[9,10,12] This has been attributed to the persistence of microdomain structure beyond the T_g of PMMA. In the present case the tapering indication from around 150 °C is suggestive of the existence of microdomains.

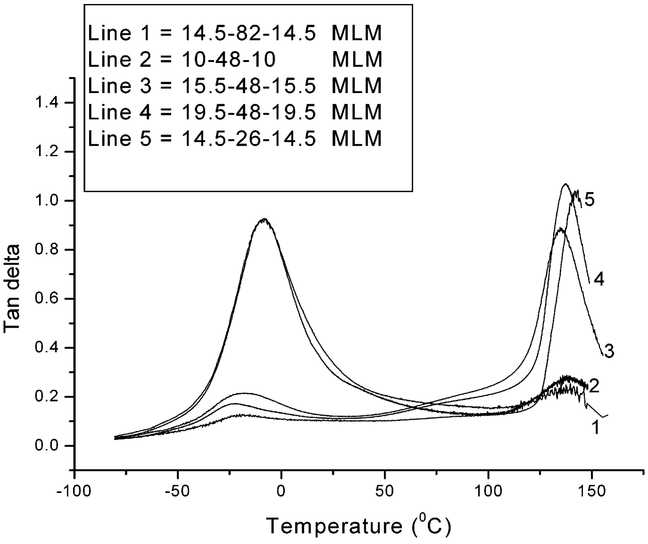

Figure 5. Temperature dependence of tan δ of the MLM samples.

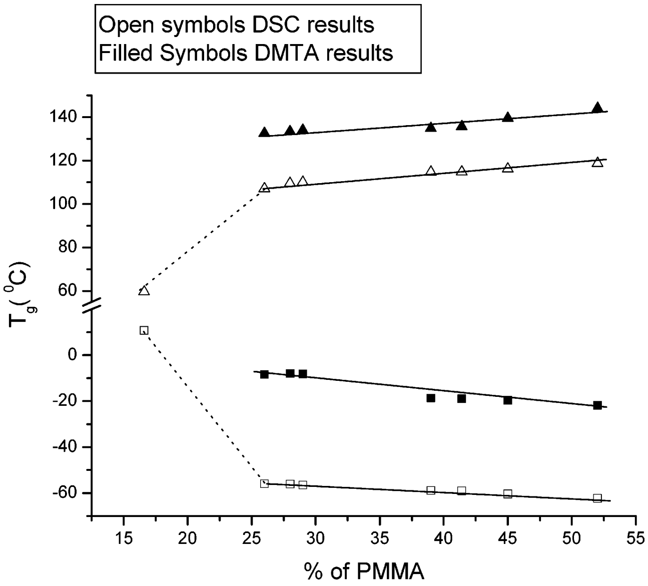

Figure 6. Dependence of T_g of the PLMA and PMMA blocks on the PMMA weight percent for MLM triblocks.

A comparison between the dynamic mechanical behavior between polymers prepared by one pot and two pot methods is also available from Figure 4. The first stage conversions were 98 and 92% for the two one pot samples with PLMA molecular weights of 48000 and 82000 respectively. Accordingly, the latter one gave a less pure PMMA block (being a copolymer containing greater amount of LMA). This is reflected in the poor dynamic mechanical property, the G' falling steeply with increase in temperature (curve 1, Figure 4), while in the other case the PMMA block was not too impure to give a very low property. In fact, this one pot polymer (curve 3) is only little inferior to the two pot polymer (curve 4).

The transition temperatures are recorded from the maxima in the tan δ vs temperature plots (Figure 5). Figure 6 shows how the DMTA measured T_gs of the PMMA and PLMA blocks change with PMMA content. DMTA measurements at low frequency give an overestimate of T_g[32,33]. Hence, the T_g values determined by DSC are also included in the figure. In the present case, DSC determined T_g of PMMA appears about 30^0 and that of PLMA about 40° lower than those determined by DMTA. The transition at the low temperature is due to the soft PLMA block, while that at the high temperature is due to the hard PMMA block. In the figure there are data for two samples for which the PLMA block length ($M_n = 26\,000$ and 82000) was different from the rest ($M_n = 48\,000$). The common phenomenon observed is that the T_g of the PLMA block decreases and that of the PMMA block increases with the increase in PMMA content. For the samples with the same PLMA block length, a longer PMMA block length is commensurate with a greater PMMA content. The results in Figure 6 therefore imply that there exists partial miscibility between the two polymers which decreases with increase in the PMMA content. Partial miscibility between polymethacrylate blocks was also earlier reported in the MAM block copolymer.[9−12] The effect of the PMMA content turns out to be greater than that of the molecular weights as are used here. Thus, the 14.5−26−14.5 polymer (52% PMMA) shows lower miscibility between blocks (as evidenced from a higher T_g of the PMMA block and a lower T_g of the PLMA block) than the 19.5−48−19.5 polymer (45% PMMA) although the latter has both the blocks longer in length than the former. Similarly, the 14.5−82−14.5 polymer (26% PMMA) shows almost similar miscibility between blocks as the 10−49−10 polymer (29% PMMA) although the latter has both the PMMA and PLMA block lengths lower than the former. The greater miscibility with the lower molecular weight polymers is expected from the greater combinatorial entropy of mixing. But, the dominating effect of PMMA content in the above-discussed molecular weight range on the miscibility suggests that the thermodynamic interaction parameter (χ) between PLMA and PMMA increases at a greater rate with PMMA content than the rate at which it decreases with molecular weight. A significant composition dependence of χ is expected in view of the large difference in free volumes that exists between a rubbery (PLMA) and a glassy polymer (PMMA).[29−31] However, when the M_n of the PMMA becomes very low as in the 4.8−48−4.8 polymer the molecular weight effect on miscibility becomes dominant as is seen in Figure 6.

Tensile Properties. a. MLM Copolymers. The tensile properties are shown in Figure 7. The values of the initial modulus, ultimate tensile strength, and percent elongation at break are given in Table 2. It is found that the polymers have poor tensile properties. When the PMMA content is ca. 26−29%, the samples show a small region of low modulus which increases to a higher value over the elongation range of 20−50% before becoming constant. The elongation at break is low, ca. 80% compared to 800% and the ultimate tensile strength is ca. 3.5 MPa compared to 30 MPa for the SBS or SIS block copolymers. The properties are inferior even to those of the lowest performer of the MAM triblock copolymer family viz., MIM which showed an ultimate tensile strength of 6.5 MPa with a 320% elongation at break for a comparable PMMA content of 28.6%.[10] Removal of contaminant polymers, e.g., PLMA homopolymer and the diblock copolymer which do not take part in the network formation does not bring about any significant change in tensile properties. This would be evident from a comparison of the curves 5a and 5b in Figure 7.

Jerome et al. also reported that the tensile properties of an MIM (20−140−20) copolymer with 22% PMMA deteriorates heavily on heating for 160 °C for 5 h in a mold. The ultimate tensile stress decreases from 7.1 to 1.9 MPa, the elongation at break reduces from 480 to 130%. Since the MLM samples were routinely dried at 160 °C for 72 h in a vacuum oven in the present work, we checked whether the low property of the MLM samples is due to this stringent drying condition. We, therefore examined one 26% PMMA content sample (entry 3 in Table 2) which was dried in a vacuum oven at 60 °C for 72 h. The tensile properties do not show any significant improvement. Hence, the low tensile properties are intrinsic to the MLM copolymers.

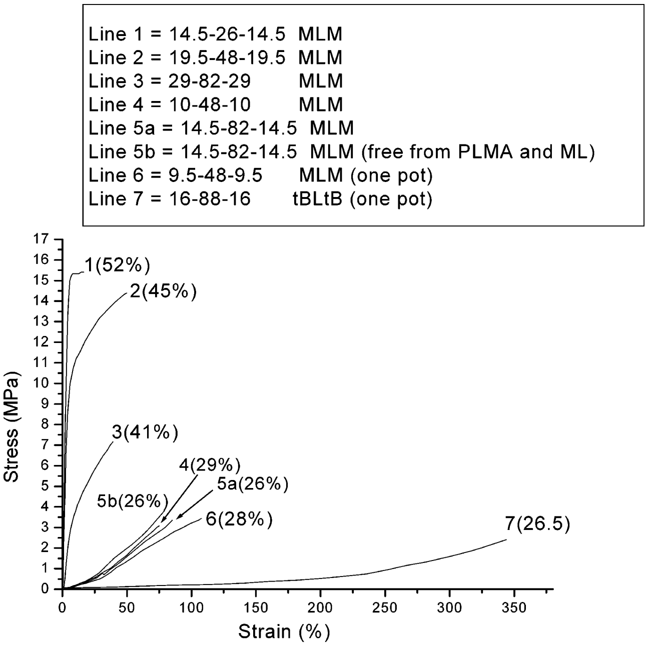

Figure 7. Tensile stress−strain curves for MLM and tBLtB triblock copolymers. The numbers in parentheses refer to the weight percentages of PMMA.

Table 2. Tensile Properties of the Copolymers

entry	polymer designation[a]	hard block (wt %)	initial modulus (MPa)	ultimate tensile stress (MPa)	elongation (%) at break
		MLM Copolymer			
1	4.8−48−4.8	16.6			
2	14.5−82−14.5	26	3.2	3.4	83
3[c]	14.5−82−14.5	26	2.35	3.58	100
4	9.5−48−9.5[b]	28	1.6	3.4	106
5	10−48−10	29	1.6	3	75
6	15.5−48−15.5	39			
7	29−82−29	41.4	64.1	7.1	38
8	19.5−48−19.5	45	257	14.2	49
9	14.5−26−14.5	52	434.6	15.4	11
		tBLtB Copolymer			
10	16−88−16[b]	26.5	0.25	2.41	350

[a] Designated by blockwise molecular weights reduced by the factor 1000. [b] Synthesized in one pot. [c] Sample dried in vacuum at 50 °C for 72 h, other samples dried in vacuum at 160 °C for 72 h.

Figure 7 also shows that as the PMMA content increases to around 40%, the modulus increases as also the ultimate tensile stress but the elongation at break decreases. The sample with 52% PMMA shows an yield followed by a short draw and then break. Drawing has been explained to be the result of a phase change. Before elongation the continuous phase was that of PMMA. On elongation a phase change occurs without however forming a continuous rubbery phase due to its lower content so that the material breaks followed by a short draw.[1] The near continuous PMMA phase discerned from the morphology supports this.

The high performance of the SBS or SIS triblock copolymers has been attributed to the reinforcing filler effect of the polystyrene microdomains and the stress distribution mechanism provided by the slippage of the entangled rubber chains which

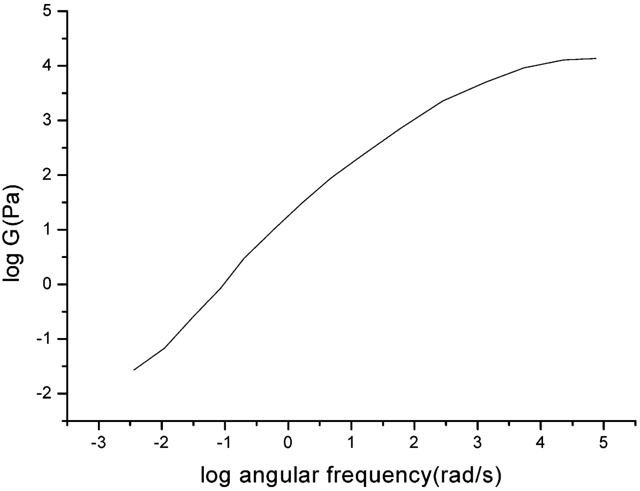

Figure 8. Plot of shear storage modulus vs angular frequency at 25 °C for PLMA of $M_n = 82\,000$.

delays the ductile failure of the PS microdomains.[1−3] From an in-depth study of the MAM triblock copolymers Jerome et al. attributed the poor tensile properties of the MAM triblocks compared to the diene-based TPEs to the much higher M_e's in the former than in the latter.[8−10] The M_e increases with the increase in the length of the alkyl group in poly(alkyl acrylates) so that for the poly(isooctyl acrylate) (PiOA) it has the value 59000. Thus, there is hardly any entanglement in the PiOA block of the MIM triblocks. We have determined the M_e of PLMA to be 225000 from rheological measurements using the constructed master curve shown in Figure 8. The M_e is obtained from eq 3.[34]

$$M_e = \rho RT/G^0_N \tag{3}$$

where G^0_N is the shear modulus in the rubbery plateau region, ρ the polymer density (determined to be 0.92 g/dL at 30 °C), and R the gas constant. The M_e value is way above the M_n of the MLM center blocks in the MLM copolymers. The PLMA in the rubbery matrix is therefore nonentangled. In such situations, the initial tensile behavior of the polymer fits into the simple elastomer model as expressed by eq 4 which does not consider chain entanglements.[35]

$$\sigma = \rho RT/M_c(\lambda - (1/\lambda^2)) \tag{4}$$

where σ is the tensile stress, λ the extension ratio, ρ the density of the polymer, R the gas constant, T the absolute temperature, M_c is the average molecular weight between cross-links of the rubber. Figure 9 shows that eq 4 fits the initial tensile behavior of the present TPE. From the slope of the line in Figure 9 for the MLM copolymer we calculate $M_c \approx 3260$. This came as a surprise since the M_c should have been equal to M_n in the absence of chain entanglements. One reason for the low M_c value could be that of PLMA has undergone side chain crystallization unlike in a neat sample. These crystallites form physical cross-links. The very low elongation is a consequence of the formation of such cross-links which increases in density with stretching.

The X-ray diffraction intensity of a nonstretched and a stretched (30% extension) film of the MLM copolymer (26% PMMA) is shown in Figure 10. The diffractogram for the stretched sample shows some peaks over the amorphous halo indicating some degree of crystallization.

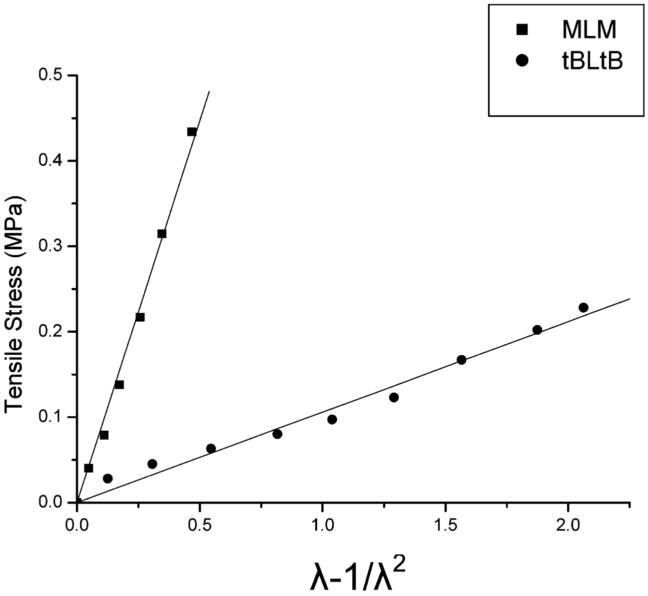

Figure 9. Plot of σ vs $\lambda - 1/\lambda^2$ for the MLM and tBLtB copolymer samples (entry 7 and entry 10 respectively in Table 1).

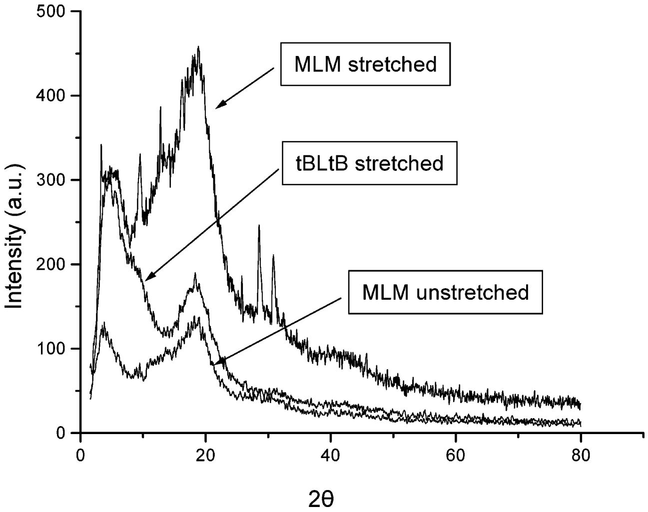

Figure 10. X-ray diffractograms of MLM (entry 7, Table 1) under stretched (30% elongation) and unstretched conditions and tBLtB (entry 10, Table 1) under stretched (200%) condition.

Table 3. *d* Spacings in the MLM Copolymers and Poly(cetyl Methacylate)

polymer		*d* spacings(Å)						
PMA-16[a]	isotactic	27	13.5	9.16			4.19	–
PMA-16[a]	atactic	29	14.7	8.47			4.19	2.41
MLM[b]	stretched (30%)	26.3		9.29	6.28	5.46	3.13	2.9

[a] Reference 36. [b] This work.

PLMA does not crystallize, but the higher homologues of PLMA do. Thus, poly(cetyl methacrylate) (PCMA) spontaneously crystallizes in a hexagonal lattice with a $T_m = 22$ °C.[36] The crystallization of the PLMA block in the MLM copolymers may be related to the glassy domains acting as nuclei and the absence of free tails in the PLMA molecules. However, stretching is required in order to induce crystallization. The *d* spacing of the reflections seen in Figure 10 are given in Table 3 along with those for the PCMA. The wide angle reflections in PCMA and also in other spontaneously crystallizing higher alkyl polyacrylates.[36] e.g. poly(lauryl acrylate) (PLA) and poly(cetyl acrylate) (PCA) (not shown here) conform to a hexagonal lattice. The different *d* spacings for the wide angle reflections observed for the PLMA block in the MLM copolymer suggest a type of packing different from that observed in spontaneously crystallizing polyalkyl (meth)-acrylates. In the unstretched sample we could not detect any melting temperature by DSC after annealing the polymer at −30 °C (35° above T_g).

b. tBLtB Copolymers. In order to improve the tensile property, we also studied the effect of changing the PMMA end block with PtBMA which has some 15^0 higher T_g than PMMA. A triblock copolymer was prepared with PLMA (M_n = 88 000) as the center block and PtBMA (M_n = 16 000) as end blocks. The copolymer has the glassy PtBMA content of 26.5%. The characterization data of this copolymer are included in Table 1 and the tensile properties in Table 2 and Figure 7. The copolymer shows much higher elongation at break (350%) than the MLM copolymer for which the value is 80%, but the ultimate tensile property does not improve. The initial tensile behavior fits well with that for the simple elastomer model (eq 4) as shown in Figure 9. The M_c value from the slope of the line in Figure 9 for this copolymer comes out to be 29000, which is about 9 times greater than that found for the MLM copolymer. This value, however, is still much lower than the M_n value of the PLMA center block. The XRD studies of a stretched (200%) film shows no evidence of crystallization unlike in the MLM copolymer as shown in Figure 10. The higher elongation is therefore attributable to some difficulty in crystallization even in the stretched sample. In order to find out a reason for this crystallization difficulty the T_g of the block copolymer was measured by DSC. It gave two T_gs, the one for the glassy PtBMA block appears at 110 °C which is 15° lower than that of pure PtBMA. The T_g for the rubbery block appears at a 13° higher temperature than the T_g of pure PLMA. These T_g changes are much greater than those found for MLM copolymers at comparable PMMA molecular weights and concentrations. This indicates greater miscibility of PLMA with PtBMA than with PMMA. This could be due to the PtBMA block being not pure but a copolymer of LMA and tBMA since this triblock copolymer was prepared in one pot where the conversion in the first step was 98%. This greater miscibility hinders the crystallization of the PLMA block. The nonimprovement of the ultimate tensile strength of the tBLtB copolymer over that of the MLM copolymer is attributable to the T_g lowering due to the PtBMA block being a copolymer containing small percentage of LMA residues.

Conclusion

This study shows that the MLM triblock copolymers show similar morphology as was reported by Jerome et al. for MAM copolymers. But unlike the MAM copolymers they have very low elongation at break and ultimate tensile strength. The analysis of the initial tensile behavior using the simple elastomer model gives M_c = 3600 which is much lower than M_e (M_e = 225000) or the center block molecular weight (M_n = 82 000). The low M_c value has been traced to shear induced side chain crystallization in PLMA. The low elongation has been attributed to the side chain crystallization on stretching.

Acknowledgment. Thanks are due to the Council of Scientific & Industrial Research, Government of India for financial support. Thanks are also due to Mr. Samik Pal of Materials Science Centre (IIT, Kharagpur, India) for the AFM measurements.

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MA061391Q