Polyisobutylene-Based Thermoplastic Elastomers. 3. Synthesis, Characterization, and Properties of Poly(α-methylstyrene-*b*-isobutylene-*b*-α-methylstyrene) Triblock Copolymers

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ABSTRACT: The first efficient synthesis of poly(α-methylstyrene-*b*-isobutylene-*b*-α-methylstyrene) (PαMeSt–PIB–PαMeSt) triblock copolymer thermoplastic elastomers (TPEs) has been accomplished by living cationic polymerization using sequential monomer additions. Living PIB was prepared by the 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (tBuDiCumCl)/$TiCl_4$/Hex:MeCl 60:40 v:v/−80 °C polymerization system. The living ends were capped by 1,1-diphenylethylene (DPE). $TiCl_4$ was replaced by $SnBr_4$, followed by the addition of αMeSt. Triblock copolymers with close to theoretical molecular weights and narrow molecular weight distributions ($M_w/M_n \sim 1.1$) were obtained. Homopolymer and diblock contamination have been found to be negligible. The thermal stability of the triblock copolymer was characterized by thermogravimetric analysis. Microphase separation was evidenced by the two glass transitions (at −65 and +180 °C) observed by differential scanning calorimetry and in dynamic mechanical analysis. Triblock morphology was examined by transmission electron microscopy. Compression-molded samples with 16–45 wt % PαMeSt exhibited ~12–24.5 MPa tensile strength, apparently directly related to the PαMeSt content and independent of the PIB molecular weight.

Introduction

Recently, a new type of triblock copolymer TPEs with polyisobutylene (PIB) middle segments became available[1–4] based on living cationic polymerization of isobutylene,[5,6] styrene,[7] or styrene derivatives.[8,9] The PIB middle segment greatly improves the thermal and oxidative stability compared with the conventional poly(styrene-*b*-butadiene-*b*-styrene) (PSt–PBd–PSt) or poly(styrene-*b*-isoprene-*b*-styrene) (PSt-PIp-PSt) TPEs.

The main limitation of PSt-based TPEs prepared by anionic or cationic living polymerizations is their low softening temperature due to the low glass transition temperature of PSt ($T_g \sim 100$ °C). Therefore, styrene-based TPEs are not recommended for continuous use above 65 °C, as they retain little strength above this temperature.[10]

A PIB-based TPE with high-T_g plastic segments based on indene (T_g of polyindene is about 200 °C) has recently been reported.[11] Attempts to substitute indene with the much more economical α-methylstyrene ($T_g \sim 175$ °C) were unsuccessful. Low tensile strength and low elongation (4.6 MPa at 260% elongation) were obtained due to a large amount of homoPIB and diblock contamination in the crude triblock copolymer.[12] Even the purified product obtained after selective solvent extraction exhibited rather low 10.6 MPa tensile strength.

For the synthesis of pure block copolymers by living sequential block copolymerization, 100% crossover efficiency is required. That is difficult to achieve when the crossover is from the less reactive to the more reactive monomer. While PSt–PIB–PSt with excellent mechanical properties was obtained using sequential monomer addition,[1] the crossover efficiency was found to be low from the PIB living end to *p*-methylstyrene (pMeSt),[8] and even lower to αMeSt[12] or isobutyl vinyl ether.[13] We invented a novel strategy for the synthesis of block copolymers by sequential monomer addition when the second monomer is more reactive than the first one. The strategy was used for the synthesis of PIB–PpMeSt diblock or PpMeSt–PIB–PpMeSt triblock copolymers. The synthesis involved the living polymerization of IB by the $TiCl_4$/Hex:MeCl 60:40 v:v/−80 °C system in the presence of the proton trap di-*tert*-butylpyridine (DTBP). The living PIB chain ends were converted to the diphenylalkylcarbenium ion by capping with 1,1-diphenylethylene (DPE). Subsequently, titanium(IV) isopropoxide was added to decrease the Lewis acidity of $TiCl_4$ before addition of pMeSt. A crossover efficiency of 100% was verified by the excellent mechanical properties of the PpMeSt–PIB–PpMeSt triblock copolymer.

A somewhat different procedure was found to be successful for the synthesis of PIB–PαMeSt diblock copolymer. After DPE capping, a slight excess of $Ti(OR)_4$ was added to deactivate $TiCl_4$. Then $SnBr_4$, a mild Lewis acid, reportedly inducing living αMeSt polymerization,[9] was added to regenerate the cations. αMeSt was introduced last. The success of the method was demonstrated by αMeSt homopolymerization experiments using 2-chloro-2,4,4-trimethylpentane (TMPCl), resulting in ~100% initiator efficiencies (I_{eff}s), and the ~100% crossover efficiencies obtained in the PIB–PαMeSt diblock copolymer synthesis.[14]

This paper concerns the synthesis of PαMeSt–PIB–PαMeSt triblock copolymer TPEs using the synthetic strategy and polymerization conditions established in the PIB–PαMeSt diblock copolymerization.[14] Characterization and physical properties of this triblock copolymer will be discussed in detail.

Experimental Section

Materials. All materials have already been described.[7,8]

Polymerization. The triblock synthesis was carried out in a three neck flask equipped with an overhead stirrer at −80 °C under a dry ([H_2O] < 1.0 ppm) nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technology Inc.). A

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hexane stock solution containing the difunctional initiator tBuDiCumCl and DTBP was prepared and charged to the flask followed by the addition of MeCl to reach the Hex/MeCl = 6:4 v:v ratio at −80 °C. Then $TiCl_4$ (in Hex with $TiCl_4$/Hex = 1:3 v:v) was added. The concentrations were [tBuDiCumCl] = 0.001 M, [DTBP] = 0.004 M, and [$TiCl_4$] = 0.036 M. IB was introduced to the flask 10 min after the addition of $TiCl_4$. After 1 h of polymerization (~100% conversion), 1 mL of the reaction mixture was withdrawn from the flask and quenched with 2 mL of prechilled methanol for molecular weight measurement of the PIB middle segment. Then DPE was added. After 1 h $Ti(OIp)_4$ (in Hex/MeCl 6:4 v:v) was added ([$Ti(OIp)_4$]/[$TiCl_4$] = 1.1) to deactivate $TiCl_4$. $SnBr_4$ was introduced 5 min after the addition of $Ti(OIp)_4$ to regenerate the diphenylcarbenium ions. Finally, αMeSt (a solution in Hex/MeCl 6:4 v:v) was introduced. The polymerization was quenched after 16 h by adding prechilled methanol. The mixture was poured into a large beaker containing excess methanol. The precipitated polymer was separated and dried. The dried polymer was redissolved in toluene, to which concentrated NH_4OH (1/100 of the total volume) was added to help precipitate inorganic salts. The organic phase was filtered, and the polymer was precipitated in methanol. This process was repeated.

Solvent Extraction. Selective solvent extraction was carried out using a Soxhlet extractor. Approximately, 10 g of triblock copolymer was placed in a cellulose thimble and extracted with methyl ethyl ketone (MEK) for 48 h and then with *n*-pentane for another 48 h. The extracts were isolated by evaporation of the solvent, dried under vacuum, weighted, and analyzed by GPC and ^{1}H NMR spectroscopy.

Characterization. Molecular weights were measured using a Waters HPLC system already described.[1] For data acquisition (RI and UV) and computing using a calibration curve obtained by well-characterized PIB (made by living polymerization) with narrow molecular weight distribution (M_w/M_n < 1.1) and PαMeSt standards (Polysciences Inc.), a Waters Baseline chromatography workstation was used. The absolute molecular weights and molecular weight distributions of the triblock copolymers were determined by a GPC on line multiangle laser light scattering detector (miniDawn, Wyatt Technology Inc.) using the ASTrette software (Wyatt Technology Inc.). Refractive index increments (d*n*/d*c*) used for the absolute molecular weight calculation were calculated from the individual d*n*/d*c* values of PIB (0.11 cm^3/g) and PαMeSt (0.225 cm^3/g) based on their relative composition. The d*n*/d*c* of PIB and PαMeSt was determined by a laser interferometer (Optilab, Wyatt Technology Inc.) in THF.

NMR measurements were carried out by a Bruker 270 MHz spectrometer.

The glass transition temperatures of the triblock copolymers were determined by a DuPont 910 differential scanning calorimeter. The samples were heated at 220 °C at 20 °C/min to remove any effects from thermal history and then brought down to −100 °C, and the second thermogram was recorded.

The thermal stability of the triblock copolymer was determined using a DuPont 2950 thermogravimetric analyzer (TGA) under N_2 at a 20 °C/min heating rate.

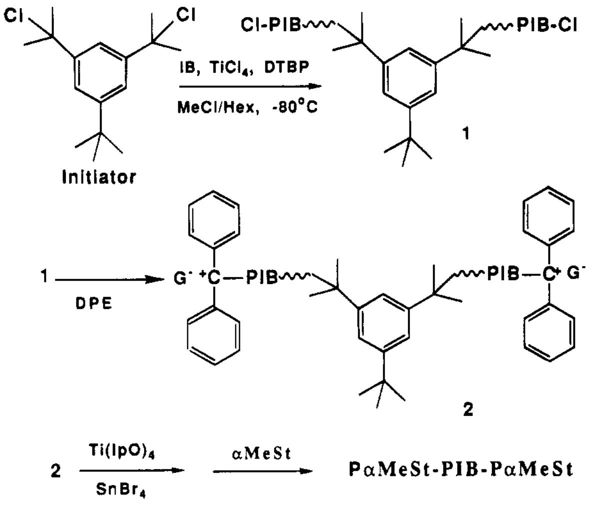
The viscoelastic properties of the triblock copolymers were measured using a DuPont 983 dynamic mechanical analyzer (DMA) with a 1 rad/s fixed frequency.

For stress−strain measurements sheets were made by compression molding the triblock copolymers at 205 °C for 10 min. Dumbbells were then cut from these sheets using a cutting die. The measurements were carried out on a Universal tension/compression tester Model TCD-500 (John Chatillon & Sons, Inc.) according to ASTM 412. Jaw speeds of 10 in./min at 23 °C were applied. Annealing the samples resulted in negligible changes in the mechanical properties.

Shore A hardness was determined according to ASTM D2240.

The morphology of triblock copolymers was examined by transmission electron microscopy (Philips Electronic Instrument Co.). Thin films (<500 Å) were cast on a water surface and then picked up on the carbon-coated TEM grids. The PαMeSt domains were then stained in the vapor phase of 0.5% RuO_4 aqueous solution for 15 min to improve the phase contrast. Films were imaged with 120 kV electrons.

Scheme 1. Synthesis of PαMeSt−PIB−PαMeSt Triblock Copolymer



Results and Discussion

Synthesis of PαMeSt−PIB−PαMeSt. Scheme 1 describes the synthesis of PαMeSt−PIB−PαMeSt triblock copolymer.

A series of triblock copolymers with different middle and end segment molecular weights were prepared (Table 1).

Figure 1 shows the GPC traces of a representative triblock copolymer and the PIB middle segment. The GPC trace shifts to a lower elution volume without tailing. Figure 2 shows the ^{1}H NMR spectrum of the same sample.

Solvent Extraction. To determine homopolymer and/or diblock contamination in the triblock copolymers, selective solvent extraction was carried out with MEK (good solvent for PαMeSt) and *n*-pentane (good solvent for PIB). Six triblock copolymer samples were examined.

Tables 2 and 3 list the amounts and molecular weights of the extracts of selected triblock samples. The amounts of MEK soluble fractions are negligible (<1%), indicating the absence of homoPαMeSt.

Compared with the MEK soluble fraction, the amounts of pentane soluble fractions are significant and reach as high as 10% in samples no. 8 and no. 9. To determine the composition of the pentane soluble fraction, GPC and ^{1}H NMR measurements were carried out. The GPC RI trace of a pentane soluble fraction (no. 8) is shown in Figure 3, in comparison with the RI traces of the crude triblock and the PIB middle segment. The trace lies between the traces of the crude triblock and the PIB middle segment, suggesting that the pentane soluble fraction is not homoPIB. This is further verified by the fact that the sample shows intense UV absorption. The PαMeSt content determined by ^{1}H NMR spectroscopy is shown in Table 3.

Thermal Stability. Degradation of PIB and PαMeSt have been studied.[15,16] Figure 4 shows the result of TGA for triblock no. 5. It is noted that PαMeSt starts to degrade at 265 °C, and the PIB segment at 350 °C. The copolymer degraded completely at 450 °C. The low stability of PαMeSt compared to PIB is due to the low ceiling temperature of αMeSt, since a high ceiling temperature is usually associated with high thermal

Table 1. Molecular Weight Characterization of Triblock Copolymers

	PIB midsegment		triblock					
			$10^{-3}M_n$					
no.	$10^{-3}M_n$[a]	M_w/M_n[a]	LS-GPC[b]	NMR	M_w/M_n[b]	d*n*/d*c*[c]	$10^{-3}M_n$[d] of PαMeSt	αMeSt conv[e] (%)
1	85.7	1.07	141	142	1.11	0.145	2 × 27.3	91
2	104	1.06	159	169	1.10	0.145	2 × 27.3	91
3	111	1.08	199	199	1.07	0.162	2 × 44.1	98
4	72.0	1.03	123	142	1.05	0.170	2 × 28.5	95
5	81.6	1.08	136	144	1.05	0.150	2 × 27.0	90
6	108	1.09	157	155	1.08	0.140	2 × 24.5	85
7	66.4	1.03	96.0	108	1.04	0.145	2 × 14.8	96
8	63.0	1.02	81.0	87.3	1.03	0.136	2 × 9.0	100
9	107	1.10	136	145	1.07	0.135	2 × 14.7	98
10	82.2	1.09	98.2	113	1.08	0.128	2 × 8.1	90

[a] Determined by GPC MALLS with d*n*/d*c* of PIB 0.11. [b] Determined by GPC MALLS with d*n*/d*c* from *c*. [c] Calculated from the individual d*n*/d*c* of PIB and PαMeSt and the composition of the triblock copolymer. [d] $M_{n\text{triblock}} - M_{n\text{PIB}}$. [e] Based on the weight of the triblock obtained and 100% IB conversion.

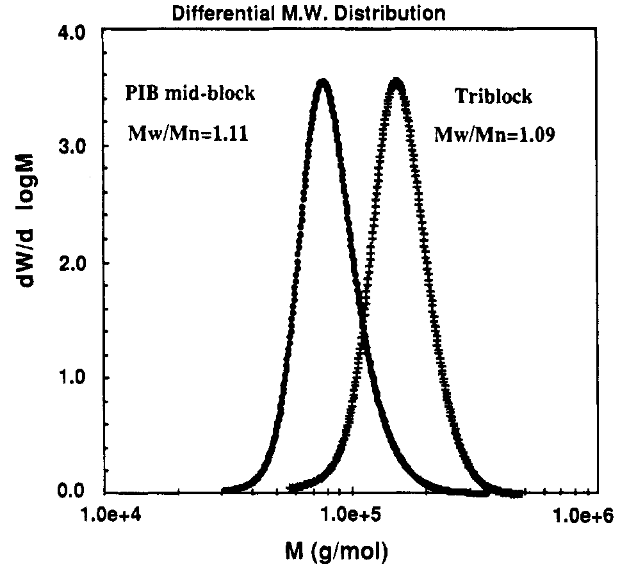


Figure 1. GPC traces of a representative triblock copolymer (no. 9, molecular weight 14 700–107 000–14 700, M_w/M_n = 1.09) and its PIB middle segment (M_w/M_n = 1.11).

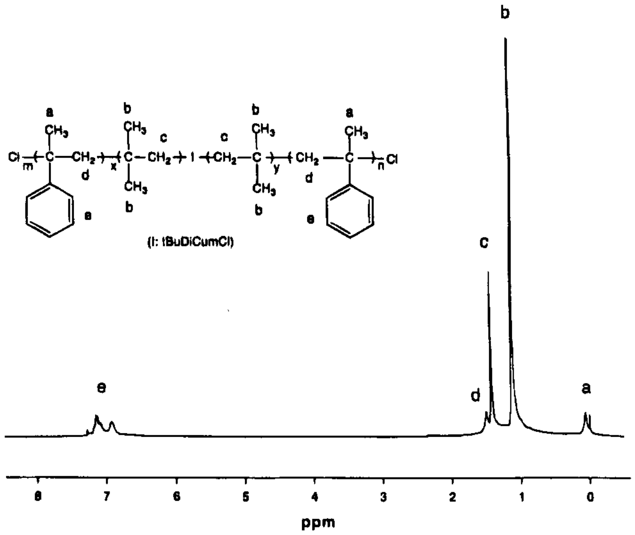


Figure 2. ^{1}H NMR spectroscopy of a representative triblock copolymer (14 700–107 000–14 700 M_w/M_n = 1.09).

Scheme 2. Solvent Extraction

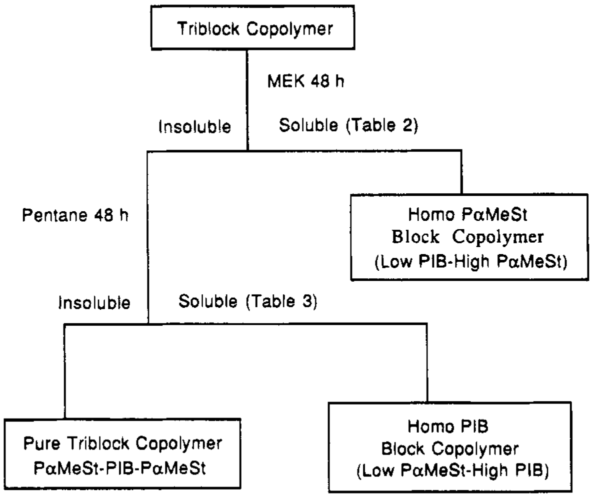


Table 2. MEK Soluble extracts

no.[a]	fraction in MEK (%)	M_n[b]	MWD[b]	M_n[c]
4	0.28	32 900	1.45	39 300
5	0.67	33 400	1.38	32 910
6	0.86	33 600	1.46	34 250
7	0.59	21 900	1.38	25 000
8	0.45	15 200	1.32	15 790
9	0.65	22 500	1.41	20 600

[a] From Table 1. [b] Determined using the PαMeSt calibration curve. [c] Determined by the GPC MALLS using PαMeSt d*n*/d*c* = 0.225 cm^3/g.

Table 3. *n*-Pentane Soluble Extracts

no.[a]	fraction in pentane (%)	M_n[b]	MWD[b]	d*n*/d*c*[c]	amt of PαMeSt (wt %)[d]
4	1.1	62 100	1.04	0.122	10.4
5	4.3	73 900	1.08	0.117	6.0
6	8.0	95 000	1.07	0.118	6.7
7	4.3	43 860	1.22	0.120	7.7
8	1.1	62 400	1.02	0.121	9.7
9	9.0	100 000	1.10	0.115	4.2

[a] From Table 1. [b] Determined by the GPC MALLS with d*n*/d*c* from *c*. [c] Calculated from the individual d*n*/d*c* of PIB and PαMeSt based on their composition in the triblock copolymer. [d] Determined by NMR.

stability. Metals or metal ions contained in the polymer can significantly decrease the polymer thermal stability. In the synthesis of PαMeSt–PIB–PαMeSt copolymer, relatively high concentrations of Lewis acids such as $TiCl_4$ or $SnBr_4$ were used. Traces of these metal ions may remain in the polymer after purification, resulting in a depolymerization temperature of PαMeSt that is 25 deg lower than that reported.[17]

Thermal Transitions. A DSC scan of a representative triblock copolymer (no. 5) is shown in Figure 5. The two glass transitions found at ~−60 °C (T_g of PIB) and

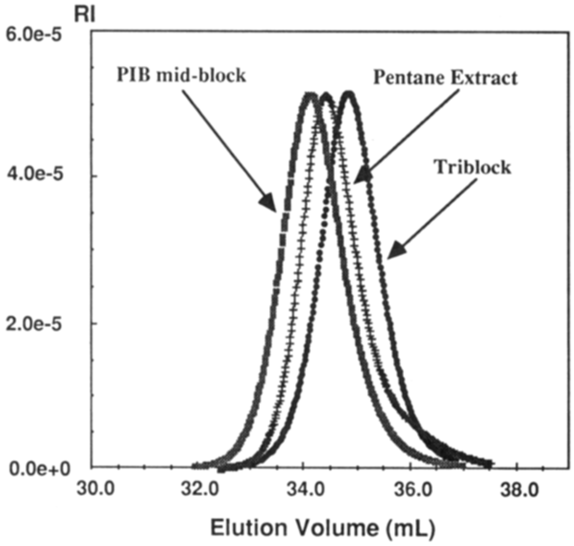


Figure 3. Comparison of the GPC traces of a representative triblock copolymer (No. 8, molecular weight 9000−63 000−9000, $M_w/M_n = 1.03$), its PIB middle segment ($M_w/M_n = 1.02$), and the pentane soluble extract (MW 62 400, $M_w/M_n = 1.02$).

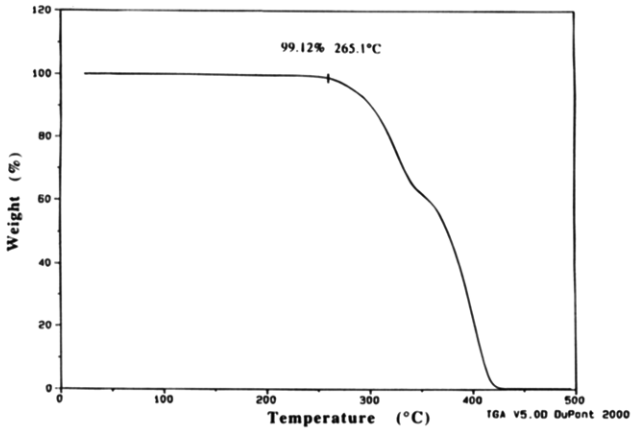


Figure 4. TGA scan of a triblock copolymer (27 000−81 600−27 000).

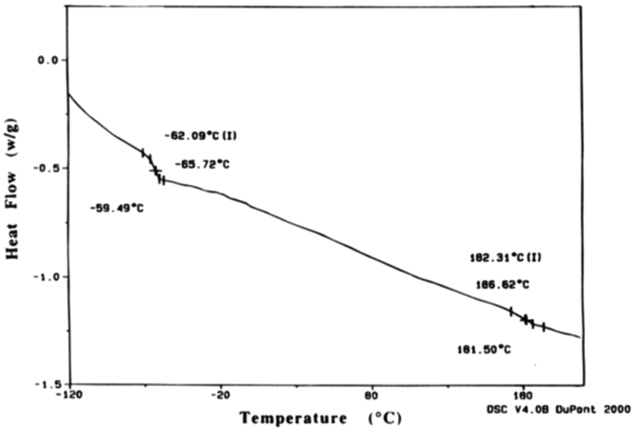


Figure 5. DSC scan of a representative triblock copolymer (molecular weight 27 000−81 600−27 000).

∼180 °C (T_g of PαMeSt) indicate the expected two-phase morphology.

Dynamic Mechanical Analysis (DMA). Thermal transitions in multiphase systems can also be detected by DMA. Figure 6 shows a typical modulus−temperature curve of a representative triblock copolymer (no. 3). The two steps are characteristics of the two-phase microstructure. The two peaks in the damping-temperature curve correspond to the two glass transition temperatures of each component.

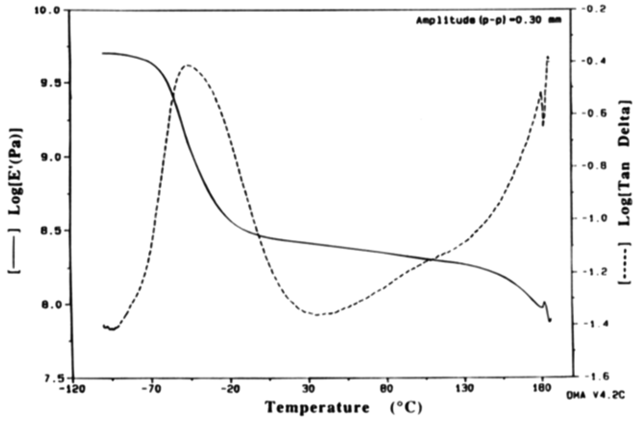


Figure 6. Dynamic mechanical properties of a representative triblock copolymer (molecular weight 44 000−111 000−44 000).

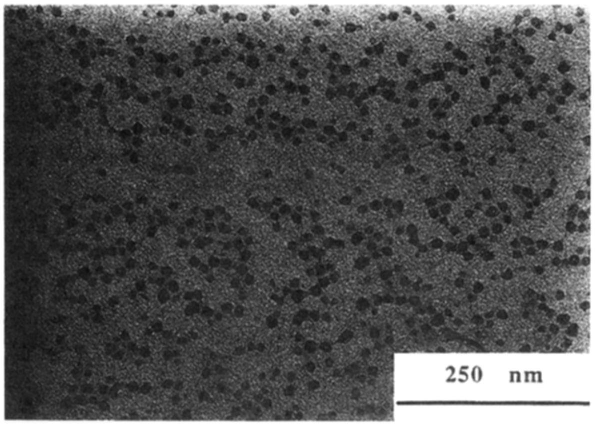


Figure 7. TEM micrograph of a triblock copolymer containing 20% PαMeSt.

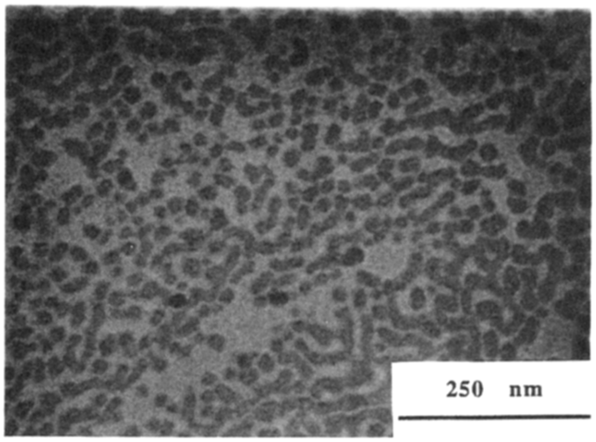


Figure 8. TEM micrograph of a triblock copolymer containing 30% PαMeSt.

Morphology of Triblock Copolymers. The morphology of the triblock copolymers was investigated by transmission electron microscopy. Three triblock copolymers with ∼20, 30, and 40% PαMeSt content were examined, as shown in Figures 7−10. The black areas represent the ruthenium tetraoxide stained PαMeSt phase while the white areas represent the unstained PIB phase. The PαMeSt domains are dispersed in a continuous PIB phase for the copolymer with 20% PαMeSt content (Figure 7). PαMeSt spheric domains with 150−200 Å diameter were observed. The somewhat uneven spacing between domains could be due to

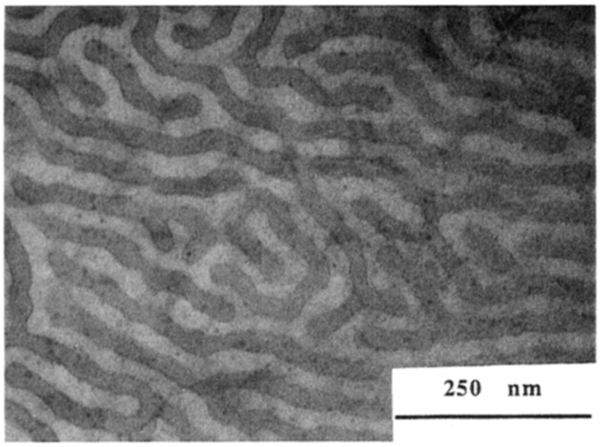


Figure 9. TEM micrograph of a triblock copolymer containing 40% PαMeSt.

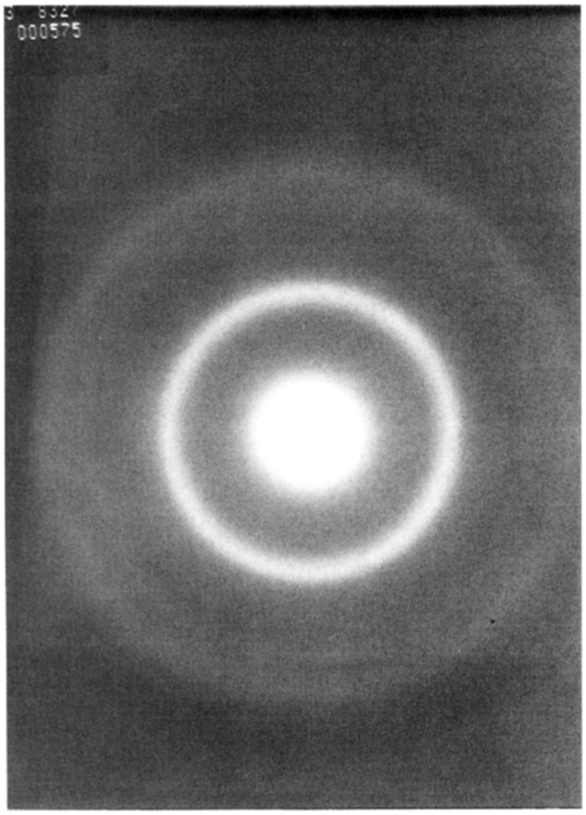


Figure 10. TEM diffraction pattern of a triblock copolymer containing 20% PαMeSt.

the nonequilibrium morphology. TEM of compression-molded and cryo-microtomed samples is in progress and will be reported later. When the PαMeSt content is increased to 30%, a close to cylindrical morphology is observed (Figure 8). Lamellar morphology with uniform ~300 Å thickness is observed for the triblock copolymer with 40% PαMeSt content (Figure 9). The lamellar morphology explains the yielding behavior in the stress–strain curve when PαMeSt is above 40%.

Figure 10 shows the diffraction pattern of a triblock copolymer with 20% PαMeSt. Evidently, the triblock copolymer is amorphous.

Mechanical Properties. The stress–strain properties of six representative PαMeSt–PIB–PαMeSt triblock copolymers with different PαMeSt contents (Table 1) are shown in Figure 11. Samples no. 1 and no. 2, prepared using a [DPE]/[tBuDiCumCl] = 0.95 ratio, exhibit lower than expected tensile strengths (Table 4).

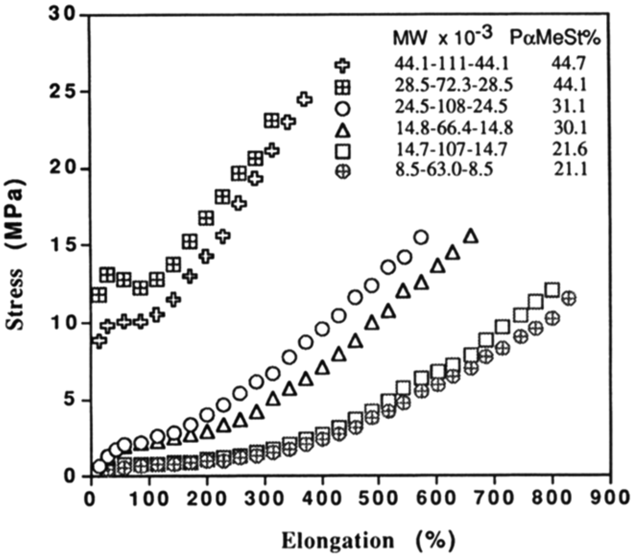


Figure 11. Stress–strain properties of PαMeSt–PIB–PαMeSt triblock copolymers with various molecular weights of PIB and PαMeSt.

A similar observation was reported and rationalized for PpMeSt–PIB–PpMeSt triblock copolymers.[8] Investigation of IB–αMeSt diblock copolymerization also confirmed that at this ratio crossover is somewhat lower than 100%.[14] 100% crossover was found with [DPE]/[tBuDiCumCl] = 2. Therefore, this ratio was used in all other triblock syntheses.

Copolymers with 20% PαMeSt gave a low tensile strength (~11 MPa). The tensile strength increased with increasing PαMeSt content independently of the molecular weight of the rubbery segment. Copolymers containing 44% PαMeSt exhibited a ~24 MPa tensile strength. Such dependence of the tensile strength on the plastic content is contrary to the results obtained with PSt–PIB–PSt TPEs, where the tensile strength was found to be independent of the PSt content when the molecular weight of the PSt segment is above 15 000.[1] A similar phenomenon, i.e., increasing tensile strength with increasing plastic content, has also been reported with PSt–PBd–PSt.[18] It was explained by better phase separation at higher volume fraction since PBd ($\delta = 8.4$) is more compatible with PSt ($\delta = 9.2$) than PIp ($\delta = 8.1$). Since PIB ($\delta = 8.0$) is more compatible with PαMeSt ($\delta = 8.8$) compared to PSt ($\delta = 9.2$), a similar rationalization may hold. Yielding behavior is well-defined in the stress–strain curves when the PαMeSt content is above 40%. Yielding is a polymer "cold-flow" phenomenon under stress. It is usually shown as a discontinuity on the stress–stain curve. For polymers with lamellar morphology, yielding is due to the breakdown of the lamellar structure, which is evidenced by the significant tensile set.

The modulus at different strain, tensile strength, elongation, tensile set, and the Shore A hardness of these copolymers with different PαMeSt wt % are tabulated in Table 4. Copolymers containing more than 40% PαMeSt gave a high tensile set (>100%) due to "cold-flow" of the plastic phase.

For PSt–PBd–PSt or PSt–PIp–PSt TPEs the tensile failure mechanism is a ductile failure in the styrene phase.[19] When the failure is in the plastic domain, the tensile strength increases with the increase of the T_g of the plastic segment. Accordingly, ~50 MPa tensile strength was achieved when the PSt end blocks were replaced by PαMeSt.[20] In contrast, PIB-based TPEs

Table 4. Some Mechanical Properties of Triblock Copolymers with Various Molecular Weights

no.	amt of PαMeSt (wt %)[a]	modulus (MPa) 25%	100%	300%	tensile strength (MPa)[b]	elongation @ break (%)[b]	tensile set @ 200%[b]	yield[c]	Shore A hardness[d]
1	38.8	12.8	4.0	2.1	6.5	350	120	yes	60
2	34.5	7.2	2.5	1.7	7.0	480	80	no	56
3	44.7	38.0	10.0	6.5	24.5	370	150	yes	90
4	44.1	50.0	13.0	7.3	23.0	320	140	yes	85
5	40.0	29.6	8.0	5.3	19.4	370	110	yes	79
6	31.1	4.0	2.5	2.2	15.5	570	15	no	55
7	30.1	4.0	2.5	1.7	15.5	660	18	no	63
8	22.0	2.0	1.0	0.7	11.5	830	12	no	32
9	21.6	2.5	1.1	0.8	12.0	800	12	no	30
10	16.1	3.8	1.3	1.7	11.0	570	11	no	28

[a] Based on MALLS. [b] According to ASTM D412. [c] Indication of cold-drawing in the stress–strain curve. [d] Based on ASTM D2240.

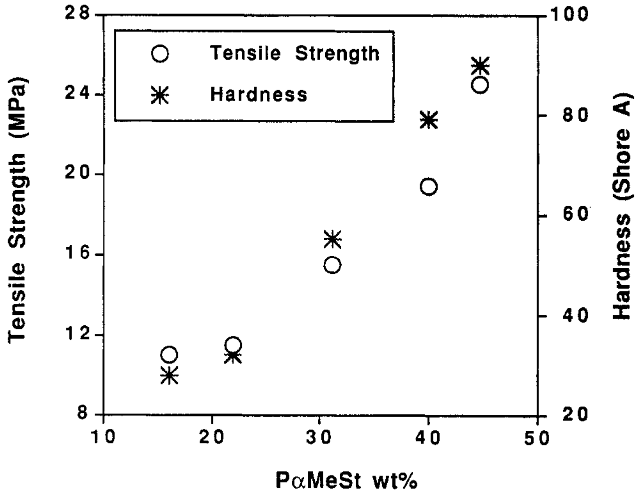


Figure 12. Effects of wt % of PαMeSt on the tensile strength and hardness of PαMeSt–PIB–PαMeSt triblock copolymers.

with different styrene glassy segments exhibit similar tensile strengths (~24 MPa), indicating that the failure is most probably in the elastomeric phase. This conclusion is in line with the reported tensile strength of vulcanized butyl rubber.[21]

The copolymers with different rubber/plastic compositions show different Shore A hardnesses ranging from 28 to 90. The tensile strength and hardness versus wt % of PαMeSt of some selected triblock copolymers are plotted in Figure 12. Both the tensile strength and Shore A hardness increase with increasing PαMeSt content in the copolymer.

Conclusions

The first efficient synthesis of PαMeSt–PIB–PαMeSt triblock copolymer thermoplastic elastomer has been accomplished by living cationic sequential block copolymerization. Microphase separation was evidenced by two glass transitions exhibited in the DSC and DMA scans. Solvent extraction results and the excellent mechanical properties indicate the absence of homopolymer or diblock contamination. Spherical, cylindrical, and lamellar phase morphology was observed by transmission electron microscopy when the plastic content was ~20, ~30, and ~40%, respectively. The tensile strength was found to be independent of PIB molecular weight, but increased almost linearly with increasing PαMeSt content. In addition, this new TPE with different wt % of PαMeSt show a diverse Shore A hardness range from 25 to 90. The proposed tensile failure mechanism in the triblock copolymer is elastic failure of PIB segments.

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