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POLYISOBUTYLENE-BASED THERMOPLASTIC ELASTOMERS. I. SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE–POLYISOBUTYLENE–POLYSTYRENE TRIBLOCK COPOLYMERS

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ABSTRACT

Polystyrene–polyisobutylene–polystyrene triblock copolymer thermoplastic elastomers have been synthesized by living carbocationic sequential copolymerization using the *tert*-butyl dicumyl chloride/$TiCl_4$/ methylcyclohexane:methyl chloride (60:40 v:v)/−80°C system in the presence of the proton trap 2,6-di-*tert*-butylpyridine. Structure–property relationships have been examined by varying the M_n of the PIB middle block (39,000 to 156,000) and that of the PSt end-segment (1,000 to 19,000). The tensile strength is controlled by the molecular weight of the PSt segment and independent of the PIB middle block length in the studied range. Phase separation starts when the M_n of the PSt segment reaches ~5,000, and it is complete when the M_n reaches ~15,000. These triblocks exhibited 23–25 MPa tensile strength, similar to that of styrenic thermoplastic elastomers obtained by anionic polymerization.

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INTRODUCTION

The synthesis of polystyrene-polyisobutylene-polystyrene (PSt-PIB-PSt) linear and radial triblock copolymer thermoplastic elastomers (TPEs) through the use of a living carbocationic polymerization with sequential monomer addition was recently reported [1]. The synthesis involved the polymerization of isobutylene (IB) by the dicumyl or tricumyl methyl ether/$TiCl_4$ initiating system followed by the addition of styrene (St) together with an electron donor (ED) and/or a proton trap. The block copolymers exhibited tensile strengths of about 15 MPa. Comparable polystyrene-polyisoprene-polystyrene (PSt-PIP-PSt) or polystyrene-polybutadiene-polystyrene (PSt-PBd-PSt) TPEs made by anionic polymerization, however, typically have tensile strengths of about 26–28 MPa when the PSt domains are well separated [2]. The much lower tensile strength of the PIB-based TPEs could be explained by a different failure mechanism, i.e., failure in the elastomer phase, or it could be due to some phase mixing as a result of diblock contamination. It has been reported [3] for PSt-PBd-PSt triblock copolymers that 5% diblock contamination decreases the tensile strength by ~30%.

Recently we reported [4, 5] that living polymerization of IB and St coinitiated with $TiCl_4$ can be achieved in the presence of the proton trap 2,6-di-*tert*-butylpyridine (DTBP) in concentrations comparable to the concentration of protic impurities in the system. We concluded that the polymerization of IB coinitiated with $TiCl_4$ in the presence of a proton trap is living due to the absence of chain transfer and reversible termination. We have confirmed that the living nature of the polymerizations is not due to carbocation stabilization. Comparison of the results with externally added EDs and/or DTBP suggested that the main function of the EDs is to trap protic impurities in the polymerization system [6]. In the absence of a proton trap, chain transfer to monomer is operational in the polymerization of IB

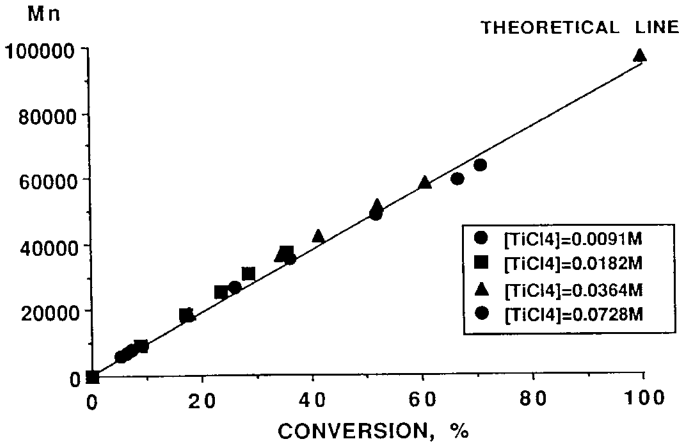


FIG. 1. Molecular weight-conversion plot for the polymerization of IB with the *t*-BudiCUCl/$TiCl_4$/CH_3Cl:MeChx, 40:60 v:v/ −80°C system in the presence of a proton trap (DTBP). $[IB]_0$ = 1.54 M; [*t*-BudiCUCl] = 9.15×10^{-4} M; [$TiCl_4$] = 3.6×10^{-2} M; V_0 = 25 mL; [DTBP] = 2×10^{-3} M.

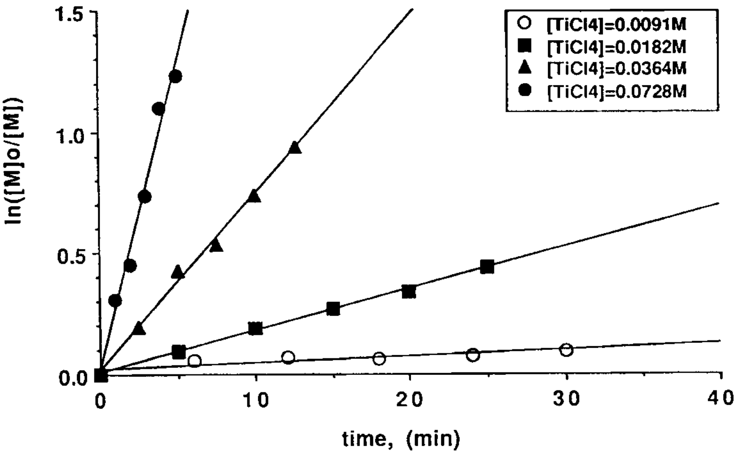


FIG. 2. First-order plots for the polymerization of IB with the *t*-BudiCUCl/$TiCl_4$/ CH_3Cl:MeChx, 40:60 v:v/ −80°C system in the presence of a proton trap (DTBP).

with the dicumyl methylether, 5-*tert*-butyl-1,3-dicumyl-methyl ether, and 5-*tert*-butyl-1,3-dicumyl-chloride/$TiCl_4$/methyl chloride-*n*-hexane (40/60 v/v)/DTBP/ −80°C systems, thus the polymerization is not living. Using methylcyclohexane (MeChx) instead of *n*-hexane with the 5-*tert*-butyl-1,3-dicumyl-methyl ether/$TiCl_4$ initiating system, similar to what was used by Kaszas et al. [1], resulted in a large amount of chain transfer to monomer. Reassuringly, when we carried out the polymerizations in the presence of a proton trap (DTBP), deviations from the theoretical line decreased with increasing DTBP concentration, and at [DTBP] $\geq 2 \times 10^{-3}$ mol/L close to theoretical molecular weights were obtained with narrow molecular weight distributions.

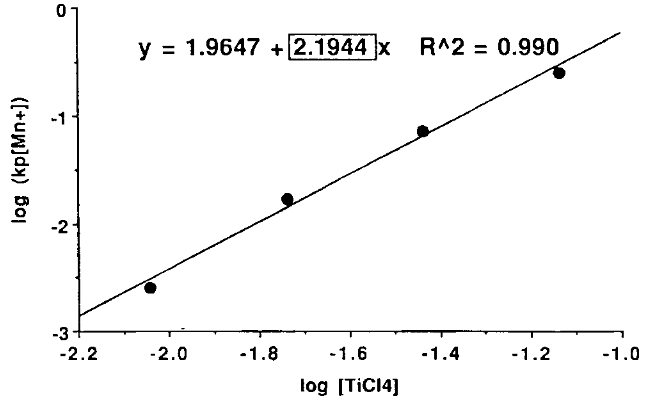


FIG. 3. Reaction order of $TiCl_4$ in the polymerization of IB with the *t*-BudiCUCl/ $TiCl_4$/CH_3Cl:MeChx, 40:60 v:v/ −80°C system in the presence of a proton trap (DTBP).

TABLE 1. Molecular Weights and Molecular Weight Distributions of the PIB Middle Segments and Those of the Triblocks[a]

Sample	M_{nPIB}	$M_{\text{nPIB*}}$	MWD_{PIB}	$M_{\text{nPSt*}}$	M_{nPSt}	$\text{MWD}_{\text{block}}$
091290-2	83	82	1.09	8	8	1.11
092790-1	84	83	1.09	10	10	1.19
092790-2	80		1.18	6		1.19
092790-3	89	81	1.08	13	12	1.13
092790-4	87	82	1.08	12	11	1.12
011891-2	99	117	1.08	3	3	1.09
011891-3	98	111	1.08	3	3	1.11
011891-4	122	141	1.09	2	3	1.13
012491-1	121	142	1.11	4	5	1.10
012491-2	124	136	1.11	7	6	1.13
012491-3	138	164	1.11	1	1	1.12
012491-4	149	170	1.07	5	5	1.10
030891	96	94		19	16	
040391-1	64	71	1.09	14	15	1.17
040391-2	97	101	1.10	15	16	1.15
040391-3	92	102	1.11	17	19	1.17
040991-1	119	120	1.10	7	6	1.19
040991-2	120	120	1.13	13	13	1.19
041591-1	156	154	1.14	10	10	1.18
041591-2	155	153	1.12	14	14	1.17
041591-3	147	155	1.09	13	13	1.13
042591-1	155	163	1.08	6	6	1.06
042591-2	149	150	1.13	8	6	1.06
042591-3	146	142	1.07	5	5	1.05
071591	48	61	1.19	10	11	1.33
082391-2	39	41	1.19	9	9	1.46

[a] $M_{\text{nPIB*}}$ and $M_{\text{nPSt*}}$ were calculated from the composition and molecular weight of the triblocks determined by the $M_{\text{nblock}} = \text{XPSt} \cdot M_{\text{nPSt}} + \text{XPIB} \cdot M_{\text{nPIB}}$ equation, where XPSt and XPIB are the weight ratios of PSt and PIB in the triblock, respectively, M_{nPSt} and M_{nPIB} are the GPC molecular weights of the triblocks based on PSt and PIB calibration, respectively.

The living polymerization of St was achieved with the 2,4-4-trimethyl-2-pentyl chloride (TMPCl)/$TiCl_4$/DTBP/MeCl:MeChx 40:60 v:v/ − 80 or − 90°C polymerization system. Contrary to results reported by Kaszas et al. for the same system [7], close to 100% initiating efficiencies were obtained, indicating that an efficient crossover from the PIB chain end to St is possible in the sole presence of DTBP.

In the present publication we report on the synthesis, structure, and properties of PSt-PIB-PSt triblock copolymers [8] in comparison with the data already reported [1].

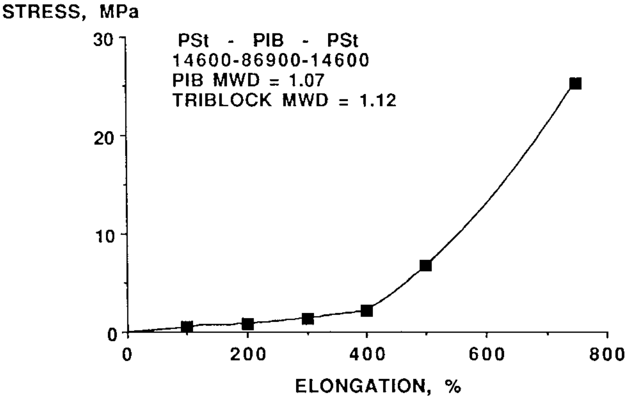


FIG. 4. Stress–strain curve for a PSt–PIB–PSt triblock copolymer.

EXPERIMENTAL

Materials

The synthesis of 5-*tert*-butyl-1,3-dicumyl-chloride (*t*-BudiCUCl) has been described [4]. Styrene (Aldrich) was purified by washing it with 10% aqueous sodium hydroxide solution, followed by distilled water until it was neutral, and then dried over $MgSO_4$. Any traces of water remaining after treatment with $MgSO_4$ were removed by dibutylmagnesium (14 wt% heptane solution, Lithco). This was followed by vacuum distillation in which the first fraction containing the heptane solvent was discarded. Isobutylene and methyl chloride (MeCl, Linde) were dried by passing the gases through in-line gas-purifier columns packed with BaO/Drierite and condensed in the cold bath of the glove box prior to polymerization. Methylcyclohexane (Aldrich) was refluxed for 2 days with concentrated sulfuric acid followed by distilled water washings until it was neutral, dried over molecular sieves, refluxed, and distilled from CaH_2 under a nitrogen atmosphere. Titanium tetrachloride (Aldrich) and the proton trap DTBP (99.1% by GC, Aldrich) were used as received.

Procedures

Polymerizations were carried out in a MBraun 150M stainless steel glove box (Innovative Technology Inc.) equipped with a gas purification system (15 lb molecular sieves and 11 lb copper catalyst) under dry nitrogen atmosphere (H_2O and O_2 less than 1 ppm). The moisture content in the glove box was monitored by an MBraun moisture analyzer. Round-bottom flasks (250–500 mL) or 1000 mL glass reactors were used for all block copolymerization experiments to obtain 10–30 g triblock copolymer. The concentration of initiator (1×10^{-3} M), coinitiator (3.64×10^{-2} M), and DTBP (2×10^{-3} M) were kept constant. Large (75 mL) test tubes were used as polymerization reactors in the IB homopolymerization experiments. The reagents were added in the following sequence: 1) solvents (MeChx/MeCl, 60 v/40 v); 2) initiator; 3) proton trap (DTBP); 4) isobutylene; 5) titanium

TABLE 2. Stress (MPa)-Strain Data of the PSt-PIB-PSt Triblock Copolymers

Sample	100%	200%	300%	400%	500%	Tensile strength, MPa	Elongation, %
091290-2	0.43	0.57	0.79	1.12	1.64	13.10	865.00
092790-1	0.59	0.88	1.52	2.49	6.53	18.63	650.00
092790-2	0.30		0.24		0.36	0.52	850.00
092790-3	0.61	0.86	1.38	2.17	6.14	20.65	685.00
092790-4	0.59	0.84	1.36	2.21	6.67	25.32	750.00
110891-2	0.21	0.21	0.19	0.19	0.19	0.23	935.00
110891-3	0.23	0.23	0.21	0.20	0.20	0.26	965.00
110891-4	0.14	0.14	0.11			0.08	385.00
120491-1	0.35	0.39	0.41	0.41	0.44	5.66	1200.00
120491-2	0.39	0.49	0.63	0.74	0.90	10.72	1015.00
120491-3	0.17	0.17	0.13	0.11		0.10	410.00
120491-4	0.35	0.39	0.40	0.40	0.40	5.02	1275.00
030891	0.81	1.19	2.70	7.21	17.03	22.71	590.00
040391-1	0.82	1.28	2.90	7.45	16.77	19.11	565.00
040391-2	0.55	0.83	1.36	2.57	8.11	22.00	700.00
040391-3	0.71	1.04	1.85	4.37	12.49	22.48	665.00
040991-1	0.38	0.51	0.57	0.75	0.93	13.68	900.00
040991-2	0.52	0.64	0.90	1.21	1.97	19.86	800.00
041591-1	0.45	0.55	0.79	0.96	1.20	14.90	900.00
041591-2	0.50	0.62	0.88	1.26	2.31	20.89	810.00
041591-3	0.46	0.57	0.70	0.86	1.19	18.06	850.00
042591-1	0.35	0.40	0.41	0.41	0.43	5.18	1215.00
042591-2	0.39	0.46	0.50	0.55	0.63	7.98	1025.00
042591-3	0.32	0.35	0.34	0.33	0.33	1.80	1350.00
071591	0.62	0.88	1.43	2.53	8.83	14.54	640.00
082391-2	0.88	1.47	3.15	6.62		10.98	510.00

tetrachloride. IB was allowed to polymerize for 30 minutes which was necessary to reach ~100% conversion at the initiator and coinitiator concentrations used for blocking. At the end of 30 minutes a 1-mL sample was withdrawn by syringe and injected into cold methanol. This sample was used for the determination of the molecular weight and the molecular weight distribution of the PIB middle segment. Immediately after sampling, St diluted with MeChx (1:4) was added to the living polymerization system. After 20 minutes the polymerization was quenched by the addition of prechilled methanol. The polymers were purified by precipitation in methanol and then dried in vacuum.

Molecular weights were measured using a Waters HPLC system equipped with a Model 510 HPLC pump, a Model 410 differential refractometer, a Model 486 tunable UV/Vis detector (set to 254 nm), a Model 712 sample processor, and five μ-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5,

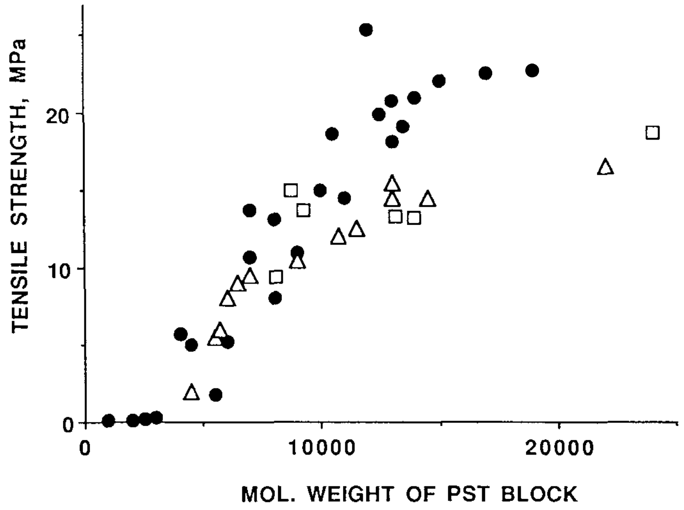


FIG. 5. The effect of the PSt segment size on the tensile strength of PSt-PIB-PSt triblock copolymers with a PIB middle segment with M_ns from 39,000 to 156,000 (●) in comparison with data from References 1 (□) and 9 (△).

and 100 Å. The flow rate (THF) was 1.0 mL/min. Narrow MWD PIB and PSt (Polysciences Inc.) samples were used as calibration standards. For data acquisition and computing, a Waters Baseline chromatography workstation was used. The compositions of the copolymers were determined by ^{1}H-NMR measurements using a Bruker 270 MHz instrument.

Stress-strain measurements were obtained according to ASTM D412. The test samples were compression molded for 15 minutes at 160°C.

For transmission electron microscopy (TEM), films were cast from toluene solution at room temperature and annealed for 3 days at 70°C. The PSt domains were stained with 0.5% aqueous RuO_4 for 3 days and then cryo-microtomed at −130°C. Imaging was with 100 kV electrons.

RESULTS AND DISCUSSION

The synthesis of PSt-PIB-PSt triblock copolymer requires the use of MeChx for PSt segment solubility. It was therefore necessary to carry out IB homopolymerization experiments with the *t*-BudiCUCl/$TiCl_4$/MeCHx/MeCl (60/40 v/v)/DTBP/−80°C polymerization system in the presence of DTBP to confirm the living nature of the polymerization. Theoretical molecular weights were obtained in the presence of DTBP, verifying the absence of chain transfer (Fig. 1). Similar results were obtained with the methylether initiator [4]. In addition, the linear $\ln([M]_0/[M])$-time plots (Fig. 2) indicate the absence of termination. Polymerization rates measured at different $TiCl_4$ concentrations are plotted as $\ln(k_p[M_n^+])$ vs $\ln[TiCl_4]$ (Fig. 3). The slope (2.19) of the linear plot confirms that the polymerization is second order in $TiCl_4$ [4, 5]. After establishing the living polymerization of IB with the *t*-BudiCuCl/$TiCl_4$/MeCHx/MeCl (60/40 v/v)/DTBP/−80°C system,

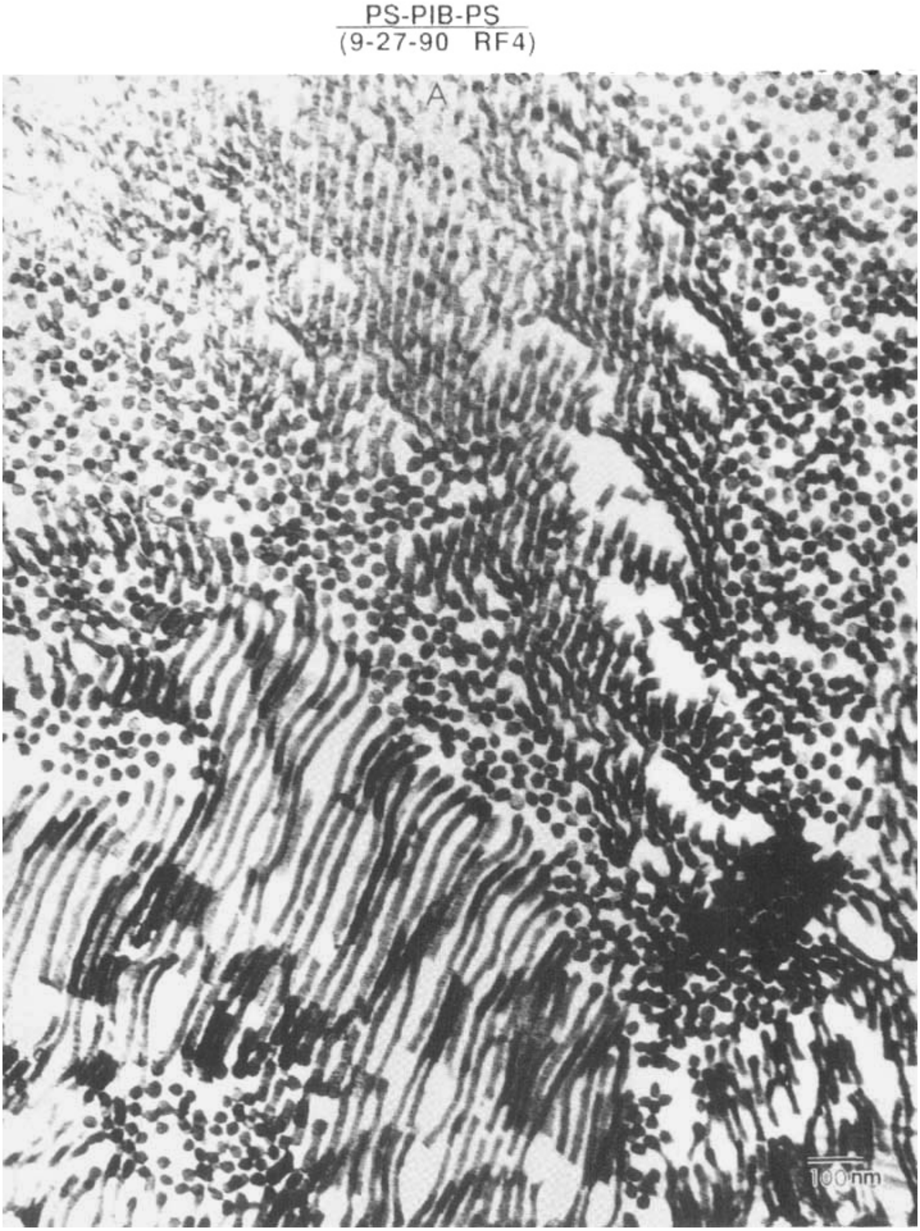
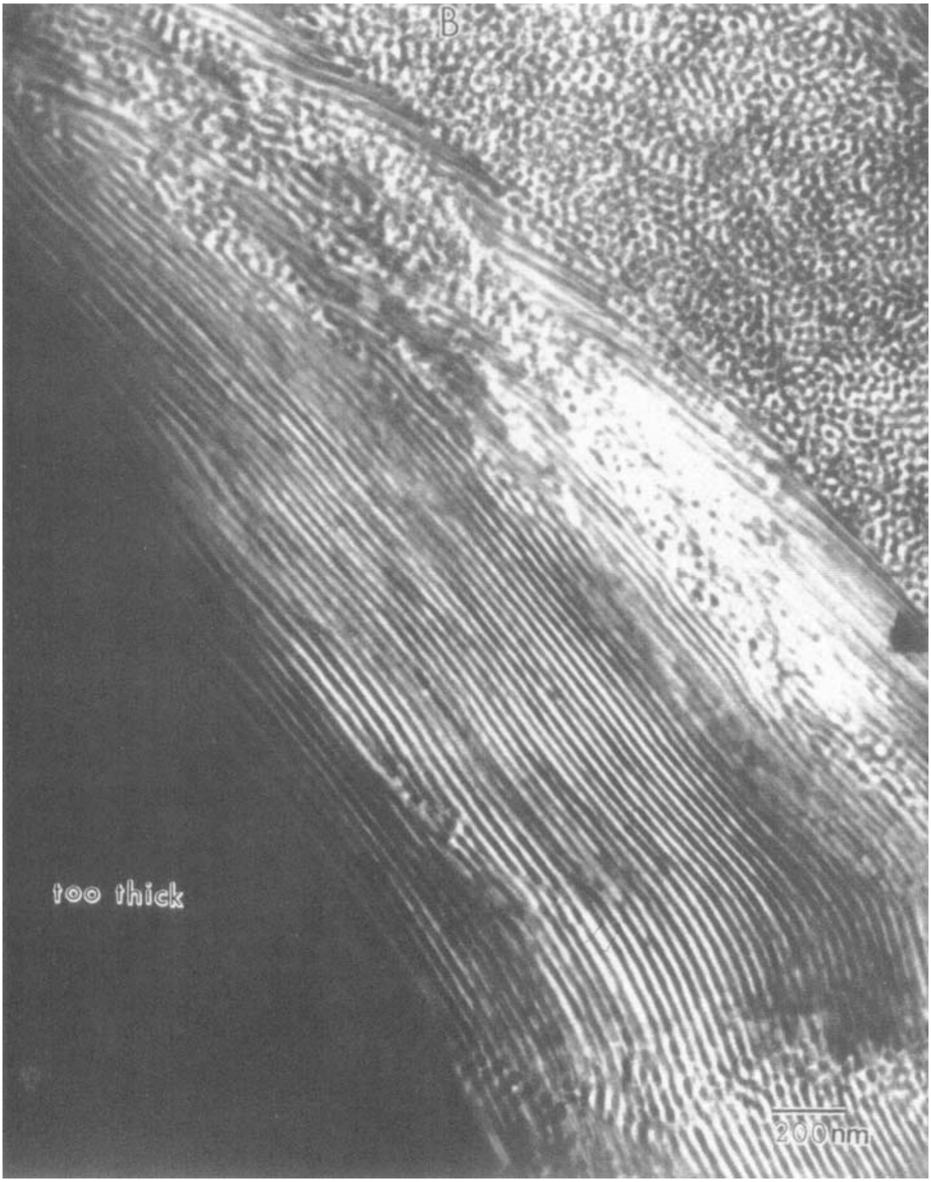


FIG. 6. Transmission electron micrograph of Sample 092790-4.



PS-PIB-PS
(9-27-90-RF4)

FIG. 7. Transmission electron micrograph of Sample 092790-4.

a series of triblock copolymers was prepared by sequential monomer addition, varying the PSt content and the molecular weight of the PIB center block. Table 1 summarizes the molecular weights and molecular weight distributions of the middle block and that of the triblock copolymer. The M_n of the PIB middle block ranged from 39,000 to 156,000 with MWDs around 1.1. The PSt segment M_ns varied from 1,000 to 19,000. The MWDs of the triblock copolymers were typically around 1.1–1.2 (based on PIB calibration), much narrower than reported in Reference 1.

The best triblocks exhibited 23–25 MPa (3300–3700 psi) tensile strengths. A typical stress-strain curve can be seen in Fig. 4. The tensile strength (Table 2) appears to increase with increasing PSt content at constant PIB block length or with increasing PIB block length at constant PSt content and then levels off. The main factor, however, appears to be the molecular weight of the PSt segment, since increasing the PIB M_n at a constant PSt content also increases the M_n of the PSt segment. A clear relationship can be established by plotting the tensile strength against the M_n of the PSt segment for all triblocks independently of the M_n (39,000–156,000) of the PIB middle block (Fig. 5). Phase separation starts when the M_n of the PSt segment reaches ~5,000, and it is complete when the M_n reaches ~15,000. Data from a similar plot reported by Kaszas [9], and published by Kaszas et al [1], are also plotted for comparison. Although the general shape of the plots are similar, the ultimate tensile properties of our triblock copolymer TPEs are superior. In agreement with the results of Kaszas [9], according to Fig. 5, the tensile strength is independent of the M_n of the middle block in the molecular weight range (39,000–156,000) studied. This is not surprising in light of an identical conclusion reached with PSt–PIP–PSt triblock copolymers [2].

The microstructures of the triblock copolymers were studied by TEM. Figures 6 and 7 show transmission electron micrographs of Sample 092790-4 at two different magnifications. This sample exhibited the highest tensile strength. The PSt domains are 20–30 nm in diameter. Interestingly, this sample contains spherical as well as cylindrical domains. Other samples with essentially the same composition and molecular weight but with lower tensile strength (for instance, Sample 092790-3) contained only spherical PSt domains.

CONCLUSIONS

Living carbocationic sequential block copolymerizations of IB and St can be achieved in the presence of a proton trap in concentrations slightly higher than the concentrations of protic impurities in the system. The resulting PSt–PIB–PSt triblock copolymer TPEs exhibit mechanical properties similar to those of styrenic TPEs obtained by anionic polymerization with comparable hard–soft segment compositions.

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