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Polyisobutylene-Based Thermoplastic Elastomers. II. Synthesis and Characterization of Poly(*p*-Methylstyrene-*block*-isobutylene-*block*-*p*-Methylstyrene) Triblock Copolymers

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POLYISOBUTYLENE-BASED THERMOPLASTIC ELASTOMERS. II. SYNTHESIS AND CHARACTERIZATION OF POLY(*p*-METHYLSTYRENE-*block*-ISOBUTYLENE-*block*-*p*-METHYLSTYRENE) TRIBLOCK COPOLYMERS

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ABSTRACT

The synthesis of poly(*p*-methylstyrene)–polyisobutylene–poly(*p*-methylstyrene) triblock copolymer was accomplished by sequential monomer addition. The synthesis involves the living polymerization of isobutylene by the TiCl₄/methylchloride:hexanes, 40:60 v/v/ – 80°C system in the presence of di-*tert*-butylpyridine using di- or trifunctional initiator. When the polymerization of isobutylene is complete, the living polyisobutylene chain end is converted to the corresponding diphenyl alkyl end by capping with 1,1-diphenyl ethylene. Subsequently, titanium(IV)-isopropoxide is added to decrease the Lewis acidity and *p*-methylstyrene is introduced. The best triblocks exhibited ~ 22 MPa tensile strength.

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INTRODUCTION

Utilization of thermoplastic elastomers (TPEs) as replacements for natural or synthetic rubbers is steadily increasing. The primary reasons are the ease of processing using regular extrusion or injection molding equipments, and fewer waste disposal problems. The majority of TPEs are block or graft copolymers. Styrenic block copolymers made by anionic living polymerization based on isoprene or butadiene or their hydrogenated version are the most widely used TPEs. Polyisobutylene-based block copolymer TPEs, predicted to have superior properties, have been in the center of activity in living carbocationic polymerization research [1]. The reported mechanical properties, however, were lower than expected. In a previous publication [2] we reported on the synthesis and characterization of polystyrene-polyisobutylene-polystyrene (PSt-PIB-PSt) triblock copolymers. These TPEs exhibited mechanical properties similar to that of styrenic TPEs obtained by anionic polymerization. TPEs comprising of endblocks with higher T_g s have been the focus of recent interest [3]. Although the T_g of PSt is 100°C, PSt-based TPEs lose their integrity well below that temperature, therefore a plastic endblock having a $T_g > 100^\circ\text{C}$ is desired for applications involving hot water. *para*-Methylstyrene (*p*MeSt) may be a candidate for these applications ($T_g = 113^\circ\text{C}$).

The synthesis of *Pp*MeSt-PIB-*Pp*MeSt triblock copolymers via living cationic sequential block copolymerization has recently been published [4, 5] using essentially the same synthetic scheme. The mechanical properties, however, were rather poor, suggesting diblock contamination [4] or not reported [5]. In a preceding publication [6] we communicated the living polymerization of *p*MeSt but concluded that the polymerization of *p*MeSt by 2,4,4-trimethyl pentyl chloride (TMPCl) or by the living PIB end cannot be initiated efficiently.

For the synthesis of pure block copolymers, 100% crossover efficiency is necessary. Less than 100% crossover efficiency in triblock copolymer synthesis results in diblock copolymer contamination that is detrimental to the mechanical properties of TPEs. It is important to clarify that homopolymers may be absent, i.e., the blocking efficiency may still be 100% for both monomers. Therefore the assumption that 100% blocking efficiency is equivalent to clean triblock copolymer synthesis [3, 4] is unfounded. 100% crossover efficiency may be obtained when the reactivities of the two monomers are similar. It is difficult to attain, however, when the crossover is from the less reactive to the more reactive monomer. Thus the synthesis of PSt-PIB-PSt could be accomplished [1], while the crossover efficiency was found to be low from the PIB living end to *p*MeSt [6], and even lower to isobutyl vinyl ether [7] or α MeSt [8]. To increase the crossover efficiency, the crossover rate relative to the propagation rate of the second monomer should be increased. Lowering the Lewis acid concentration by adding Lewis bases, replacing the Lewis acid with a weaker one, or adding common ion salts lowers the propagation rate but it may also lower the crossover rate, therefore the ratio may not be affected favorably. Attempts using the above methods have failed [7, 8].

We invented a novel strategy for the synthesis of block copolymers using sequential monomer addition by first capping PIB with a reactive but nonpolymerizable monomer such as 1,1-diphenylethylene (DPE). Since the diphenyl alkyl cation is more stable than the *p*-methylstyryl cation, the Lewis acidity (or concentration) can be decreased to decrease the rate of *p*MeSt homopolymerization and still main-

tain satisfactory crossover rates. The success of the method was demonstrated by *p*MeSt homopolymerization experiments initiated by TMPCl that resulted in ~100% initiator efficiencies, as well as by the synthesis of PIB-*Pp*MeSt diblock copolymers without homopolymer contaminants [6]. In the present publication the synthesis and characterization of *Pp*MeSt-PIB-*Pp*MeSt triblocks copolymers are reported.

EXPERIMENTAL

Materials

5-*tert*-Butyl-1,3-bis(1-chloro-1-methyl ethyl)-benzene (5-*tert*-butyl-dicumylchloride, DiCumCl) was prepared as described [9]. For the preparation of 1,3,5-tris(1-chloro-1-methyl ethyl)-benzene (tricumylchloride, TriCumCl) 1,3,5-tris(1-methoxy-1-methyl ethyl)-benzene was synthesized according to Reference 10 except that the solution of the trimethyl-1,3,5-benzene-tricarboxylate was added dropwise to the CH₃MgBr solution during the Grignard reaction. TriCumCl was obtained from tricumyl methylether by a reaction with dry HCl gas at 0°C in a dichloromethane solution. The product was recrystallized from hexanes (Hex).

All other materials have been described [5, 9].

Procedures

Polymerizations were carried out in a stainless steel glove box [9] at -80°C, using MeCl/Hex 40/60 v/v solvent mixture.

The copolymerization of IB and DPE were conducted under the following conditions: [IB]₀ + [DPE]₀ = 0.6 M, [TMPCl]₀ = 0.001 M, [TiCl₄] = 0.0364 M, [DTBP] = 0.004 M, reaction volume 50 mL, reaction time 3 minutes. The volume of DPE and that of IB were deducted from the volume of Hex. The charges were quenched with prechilled methanol (MeOH), and the mixture was poured into MeOH containing 10 v% concentrated aqueous NH₄OH. The polymer precipitate was separated and dried. It was redissolved in THF, the solution was filtered, and the polymer was precipitated into MeOH containing 5% water. The precipitates were washed several times and dried.

The triblock copolymer synthesis was carried out in a three-neck flask equipped with a mechanical stirrer. DTBP, the initiator, and the first increment of IB were dissolved in MeCl/Hex 40/60 v/v solvent mixture. The polymerization was started by adding TiCl₄ dissolved in 10 mL MeCl/Hex 40/60 v/v solvent mixture at -80°C. After the TiCl₄ addition the concentrations were: [TiCl₄] = 0.0364 M, [DTBP] = 0.004 M, functional group of initiator = 0.002 M. The volume of the IB was deducted from that of Hex. After the TiCl₄ addition, two additional IB increments were added at the times specified in Table 1. When the conversion of the IB was complete, DPE was introduced. After 1 hour, a 1 mL sample was taken and additional TiCl₄ and Ti(IpO)₄ (in 10 mL MeCl/Hex 40/60 v/v) were added to reach [TiCl₄]:[Ti(IpO)₄] 3:1. Ten minutes later the solution of *p*MeSt (0.225 g/mL) in MeCl/Hex 40/60 v/v containing DTBP to maintain the proton trap concentration at constant 0.004 M was introduced in one or several increments. The polymerizations were quenched with prechilled MeOH and the charge was poured into MeOH. The precipitate was washed with MeOH and dried. The amount or concentration of the reactants and the reaction times are given in Table 1.

TABLE 1. The Conditions of the Triblock Preparation. First Line: The Amount or Concentration of the Reactant, Second (and Third) Line(s): Time (t) Coordinates of the Addition in Minutes. The Times of MeOH Addition Are Given in Parenthesis. The $\text{Ti}(\text{IpO})_4$ Was Added 10 Minutes Prior to the $p\text{MeSt}$ Solution. V_0 is the Volume of the Reaction Mixture before DPE Addition. DPE Excess Refers to the Excess over the Stoichiometric Amount. $[\text{TiCl}_4]$ is Given for the Polymerization of $p\text{MeSt}$. $[\text{TiCl}_4]$ Was 0.0364 M during the IB Period

No.	IB, mL	V_0 , mL	DPE excess, %	$[\text{TiCl}_4] \times 10^2 \text{M}$	$p\text{MeSt}$ solution, mL	
1 ^a	17.4 + 17.4 + 5	335	4.10	3.12	51.8	
t	0, 12, 17		58		107	(142)
2	17.4 + 17.4 + 5	335	3.9	5.56	86.0	
t	0, 15, 25		90		168	(296)
3	17.4 + 17.4 + 5	335	17.8	5.63	84.5	
t	0, 15, 25		85		162	(290)
4	17.4 + 17.4 + 5	335	29.4	5.67	84.5	
t	0, 15, 25		93		171	(476)
5	17.4 + 17.4 + 5	330	32.9	5.73	84.5	
t	0, 15, 27		95		170	(475)
6	17.4 + 17.4 + 5	335	99.2	3.67	169	
t	0, 15, 30		90		160	(1260)
7	17.4 + 17.4 + 5	330	99.5	5.21	105	
t	0, 15, 25		85		178	(586)
8	17.4 + 17.4 + 5	330	200	5.21	105	
t	0, 15, 25		85		174	(583)
9	17.4 + 17.4 + 5	335	100	4.65 to 3.82	$5 \times 28 + 29$	
t	0, 15, 25		85		160, 180, 200, 220 240, 280	(1029)
10	17.5 + 17.5 + 5	335	100	6.18 to 5.12	$5 \times 28 + 29$	
t	0, 15, 25		85		172, 192, 212, 232 252, 272	(1097)
11	17.4 + 17.4 + 5	330	104	8.18 to 6.32	$5 \times 26.5 + 17.6$	
t	0, 15, 25		105		180, 214, 248, 282 316, 350	(1131)

TABLE 1. Continued

No.	IB, mL	V_0 , mL	DPE excess, %	$[\text{TiCl}_4] \times 10^2 \text{M}$	<i>p</i> MeSt solution, mL	
12	17.4 + 17.4 + 5	335	98.9	12.1 to 9.28	5 × 26 + 1.6	
<i>t</i>	0, 15, 25		95		170, 204, 238, 272	
					306, 340	(1090)
13	14.8 + 14.5 + 4.8	290	100	6.44	46.6	
<i>t</i>	0, 16, 26		86		156	(456)
14	14.9 + 14.9 + 4.3	290	100	5.93	46.6	
<i>t</i>	0, 15, 25		91		162	(462)
15	14.6 + 15.1 + 4.4	290	100	6.44	46.6	
<i>t</i>	0, 16, 26		88		160	(462)

^a $[\text{TiCl}_4]:[\text{Ti}(\text{IpO})_4] = 25:7$ in *p*MeSt period.

The polymer was dissolved in benzene (~10% w/v), mixed and stirred vigorously with 10 mL concentrated aqueous NH_4OH solution. The organic phase was filtered, and the solvent was evaporated. The polymer was redissolved in benzene and precipitated into MeOH. This procedure was repeated until the benzene solution was clear.

The molecular weights of the PIB middle segments were measured by GPC as described [9]. The molecular weights of the copolymers were measured with the same GPC system, using a miniDAWN multiangle laser light-scattering detector (MALLS, Wyatt Technology Inc.). As the refractive index increments (dn/dc) of the copolymers were unknown, 100% recovery of the injected mass was assumed in the calculations. The absolute molecular weights, molecular weight distributions (MWDs), and the average dn/dc values were calculated with the ASTRette software.

NMR spectra were recorded on a Bruker 270 MHz multinuclear spectroscope equipped with a temperature controller.

Extraction studies were carried out using a Soxhlet extractor, methyl-ethylketone (MEK) and *n*-pentane as solvents. The extraction was carried out for a minimum of 60 hours or until the solvent around the thimble turned clear and remained clear on cooling.

The mechanical properties were determined on compression-molded samples according to ASTM D412.

RESULTS AND DISCUSSION

Scheme 1 describes the synthetic route.

The success of *Pp*MeSt-PIB-*Pp*MeSt triblock copolymer synthesis depends upon the crossover efficiency from PIB end to *p*MeSt. To achieve 100% crossover

TABLE 3. The Average dn/dc Values, the p MeSt Contents, the Tensile Strengths (σ), and the Elongations at Break (λ) of the Triblocks in Table 2

No.	dn/dc , mL/g	Arms	p MeSt content				σ , MPa	λ , %
			From NMR		From conversion			
			mol%	wt%	mol%	wt%		
1		2	22.7	31.9	18.2	31.9	12.3	400
2	0.124	2	30.8	48.4	24.0	39.9	4.46	221
3	0.121	2	25.2	41.5	24.2	40.2	10.7	438
4	0.120	2	23.2	38.8	22.9	38.5	12.1	452
5	0.115	2	17.3	30.6	16.1	28.8	15.0	654

(Fig. 5) were quite narrow; however, the mechanical properties indicate the presence of diblock copolymers. Evidently GPC is not as sensitive as the mechanical properties for the presence of small amount of diblock copolymers.

Samples 1 and 2 were extracted with MEK, a good solvent for Pp MeSt and a nonsolvent for PIB, and with pentane which dissolves PIB but not Pp MeSt. Only 3% of Sample 1 was soluble in MEK, and the MEK insoluble part was completely soluble in pentane. A relatively high percentage, 21 wt% of Sample 2 was MEK soluble. However, the composition and molecular weight of the MEK-soluble part was virtually identical with that of the crude polymer, indicating the absence of homopolymers. Thus the presence of diblock copolymer due to low crossover efficiency accounts for the poor mechanical properties.

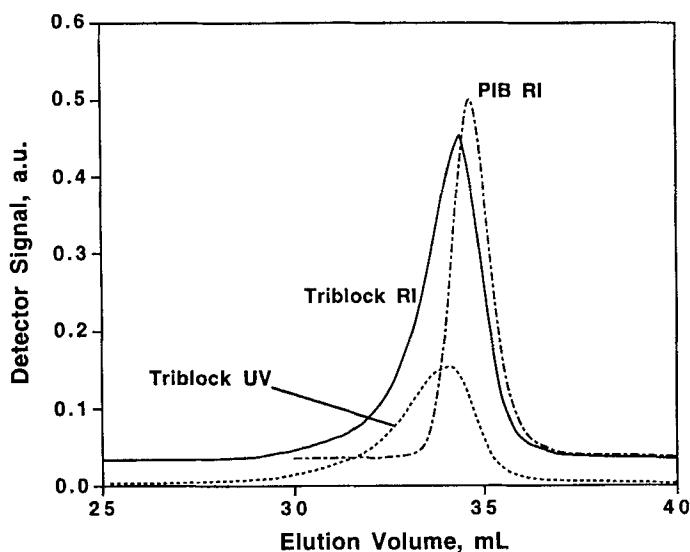


FIG. 1. The GPC traces of the DPE-capped PIB middle segment and those of the triblock in Expt. 1, DPE excess 4.1%, $[TiCl_4]:[Ti(IpO)_4] = 25.7$.

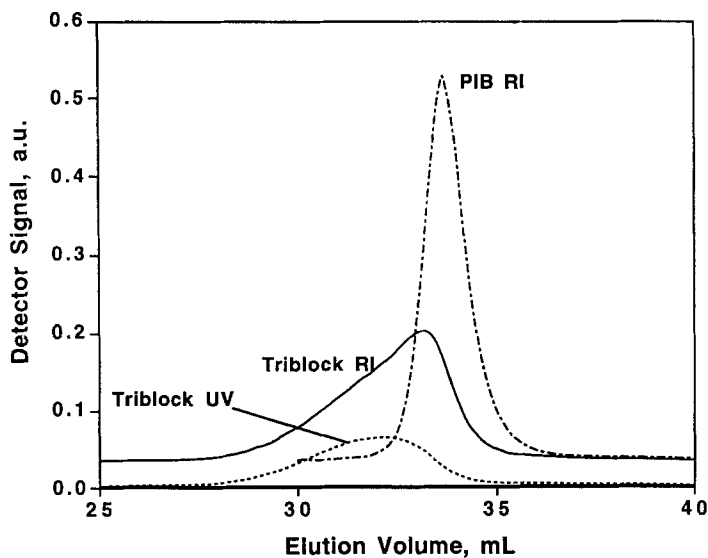


FIG. 2. The GPC traces of the DPE-capped PIB middle segment and those of the triblock in Expt. 2, DPE excess 3.9%.

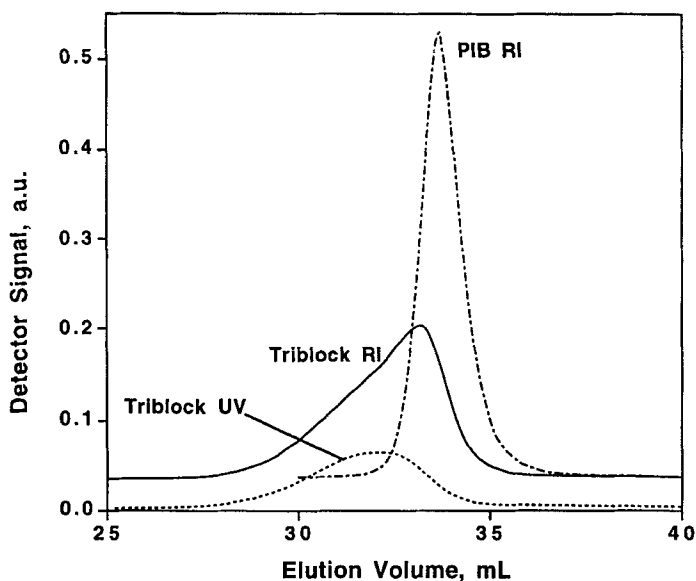


FIG. 3. The GPC traces of the DPE-capped PIB middle segment and those of the triblock in Expt. 3, DPE excess 17.8%.

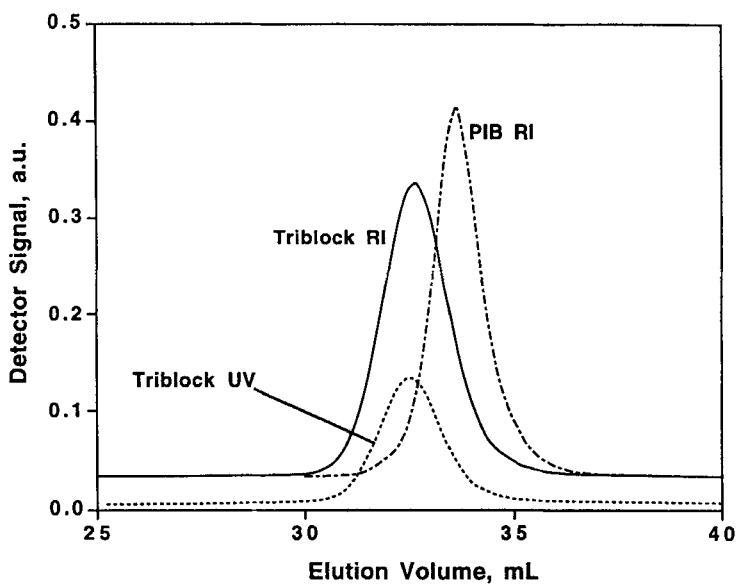


FIG. 4. The GPC traces of the DPE-capped PIB middle segment and those of the triblock in Expt. 4, DPE excess 29.4%.

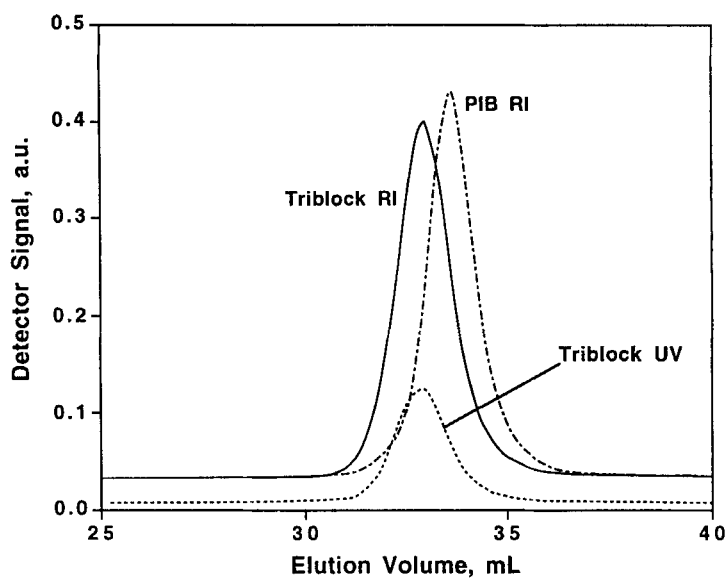


FIG. 5. The GPC traces of the DPE-capped PIB middle segment and those of the triblock in Expt. 5, DPE excess 32.9%.

Examining the differences between the synthesis of homoP*p*MeSt, diblock, and triblock copolymers, we recognized that in addition to the 100% capping the conversion of IB must be 100% when DPE is added. If the polymerization system contains unreacted IB when the DPE is added, the DPE-capped PIB may react with IB, regenerating the PIB-Cl ends. Subsequent addition of titaniumalkoxide results in the formation of TiCl₃(OR), a weak Lewis acid that is unable to ionize the PIB-Cl ends. Complete IB conversion is especially important when low initiator and consequently low [DPE] is used, i.e., when high M_n PIB is desired. With [DPE] = 0.002 M and [IB]₀ = 2 M, at 99.9% IB conversion, the concentration of unreacted IB equals that of DPE. To confirm our hypothesis, experiments were carried out polymerizing IB by the incremental monomer addition technique using two increments (Expt. 1 in Table 4), followed by DPE capping and the addition of *p*MeSt (Expt. 2 in Table 4). In another experiment, DPE was reacted before the second IB increment, which was followed by the addition of *p*MeSt (Expt. 3 in Table 4).

The observed molecular weights are close to the theoretical value calculated for the measured conversions. The conversion of the second IB increment was, however, only 48% and that of *p*MeSt was only 25% when IB was added after DPE capping (Expt. 3). This indicates that IB is able to react with the diphenyl alkyl chain ends and the reformed PIBCl ends do not participate in the initiation of *p*MeSt, confirming our hypothesis.

The low IB conversion and the 25% *p*MeSt conversion (that could have been initiated only from the diphenylalkyl chain ends) in Expt. 3 suggests that the crossover from the diphenylalkyl chain end to IB is slow. This is also suggested by the results of copolymerization experiments carried out at very low DPE concentration (Table 5). Although the molecular weights are similar, the molecular weight distributions broaden substantially with the increase of [DPE].

Results of copolymerizations at higher DPE concentrations are shown in Table 6.

The purified copolymer was a white powder, soluble in THF and CDCl₃. However, the solutions became hazy a few hours after preparation. Oligomers that were also formed were soluble in 95% methanol aq and were removed with the unreacted DPE. According to the molecular weights determined by GPC, the oligomer is possibly a DPE dimer. The copolymerizations were quenched after 3 minutes to obtain low conversion. Experiments carried out for 127 minutes, however, also resulted in very low (~5%) conversions.

Since the conventional copolymerization equation is not valid (DPE does not homopolymerize but may dimerize), the copolymer composition equation was obtained by the following mathematical treatment;

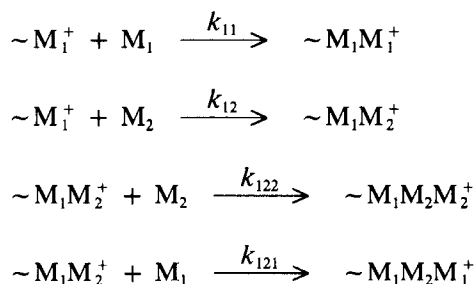


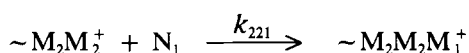
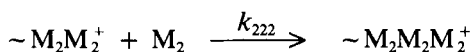
TABLE 4. The Reactants, Their Addition Sequence, *p*MeSt Conversions, and Molecular Weight Data^a

No.	Reactants	Conversion		M_n	
		IB, %	<i>p</i> MeSt, %	Theoretical	Observed
1	IB IB	100 + 100		5,100	5,200
2	IB IB DPE	100 + 100	100	16,400	15,400
3	IB DPE IB	100 + 48	25	6,300	6,200

^aMeCl/Hex 40/60 v/v, -80°C, TMPCl = 1×10^{-4} mol, TiCl₄ = 9.098×10^{-4} mol, 4MeDTBP = 1×10^{-4} mol, DPE = 1.03×10^{-4} mol (dissolved in 1 mL MeCl/Hex 40/60 v/v solvent mixture), Ti(BuO)₄ = 3.033×10^{-4} mol (dissolved in 1 mL Hex) *p*MeSt = 0.00875 mol (dissolved in MeCl/Hex 40/60 v/v solvent). Reaction times: DPE 30 minutes, IB 10 minutes, Ti(BuO)₄ 10 minutes, *p*MeSt 10 minutes, total volume 25 mL.

TABLE 5. Copolymerization of IB and DPE at Low DPE Concentrations

Conversion, %		[DPE] × 10 ³	<i>M_n</i>	<i>M_w/M_n</i>
IB	DPE			
100		0	2100	1.20
100	100	2.06	2500	1.36
100	62	4.12	1800	1.69



where $M_1 = \text{IB}$ and $M_2 = \text{DPE}$.

With the reactivity ratios $r_1 = k_{11}/k_{12}$, $r_2 = k_{122}/k_{121}$, and $r_2' = k_{222}/k_{221} = 0$, the following instantaneous composition equation can be obtained:

$$d[\text{IB}]/d[\text{DPE}] = (1 + r_1X)(r_2 + X)/(2r_2 + X) \quad (1)$$

where $X = [\text{IB}]/[\text{DPE}]$.

The reactivity ratios $r_1 = 0.5$ and $r_2 = 7$ were obtained from Eq. (1) using the simplex method. Due to experimental errors in the determination of the copolymer composition, especially at low X , r_2 is less accurate than r_1 . (Interestingly, similar values, $r_1 = 0.5$ and $r_2 = 6$, were obtained by assuming that the conventional copolymer equation is valid.) The reactivity ratios indicate that PIB^+ prefers to add DPE and that PIBDPE^+ preferentially adds DPE. DPE, however, cannot homopolymerize; therefore the copolymerization is extremely slow and stops short of completion.

According to these results, very small amount of unreacted IB may actually be tolerated in the DPE capping reaction. To obtain very close to 100% conversion, impractically long polymerization times are needed. We decided, therefore, to use higher DPE excess instead of long polymerization times in the triblock copolymer

TABLE 6. The Copolymerization of IB with DPE

No.	IB content, mol%		Conversion, %	<i>M_n</i>	<i>M_w/M_n</i>
	Feed	Copolymer			
1	90.5	81.7	2.13	4620	1.29
2	90	77.8	2.70	4090	1.62
3	80	53.4	2.94	4230	1.46
4	70	40.3	2.09	5120	1.32
5	60	28.6	6.00	5880	1.53

synthesis. With the higher DPE excess, capping reaction times are lowered and, more importantly, PIBCl chain ends generated by the reaction between DPE capped ends and IB may be converted back to diphenylalkyl carbenium ions by the addition of a second DPE.

The triblock copolymer molecular weights, molecular weight distributions, and *p*MeSt conversions are given in Table 7. The compositions and the mechanical properties of the triblocks are listed in Table 8. A typical stress-strain curve is shown in Fig. 6.

The molecular weight distributions of the triblock copolymers are narrow, $M_w/M_n = 1.1$ – 1.2 . GPC traces of two select triblock copolymers with $\sim 100\%$ crossover efficiency are shown in Figs. 7 and 8. As we have concluded however, GPC is not as sensitive as the mechanical properties for the presence of small amount of diblock copolymers. The success of the synthetic strategy, i.e., the absence of diblock contaminants, is evident from the excellent mechanical properties. The best linear and starblock copolymers exhibited ~ 22 MPa tensile strength, close to what we have achieved with PSt-PIB-PSt TPEs.

TABLE 7. Molecular Weights and Molecular Weight Distributions of Triblock Copolymers. First Line: Measured Values; Second Line: Targeted Values^a

No.	PIB		Triblock		<i>Pp</i> MeSt segment M_n	<i>p</i> MeSt conversion, %
	M_n	M_w/M_n	M_n	M_w/M_n		
6	126,300	1.09	336,600	1.20	3 × 70,100	100
	126,900		297,200		3 × 56,800	
7	99,200	1.10	190,100	1.12	2 × 45,500	85.0
	85,600		156,200		2 × 35,300	
8	100,300	1.10	211,600	1.23	2 × 55,700	100
	85,800		156,600		2 × 35,400	
9	124,900	1.10	257,000	1.12	3 × 44,000	55.4
	128,700		299,600		3 × 57,000	
10	127,300	1.07	293,700	1.12	3 × 55,500	70.3
	124,900		295,800		3 × 57,000	
11	100,000	1.09	237,100	1.23	2 × 68,600	100
	84,900		186,600		2 × 50,800	
12	101,100	1.07	233,500	1.26	2 × 66,200	100
	85,300		184,100		2 × 49,400	
13	115,200	1.25	170,400	1.08	2 × 27,600	100
	99,600		142,200		2 × 21,300	
14	102,000	1.12	158,000	1.09	2 × 28,000	100 ^b
	85,000		121,400		2 × 18,200	
15	115,700	1.12	155,700	1.10	2 × 20,000	100 ^b
	139,300		199,100		2 × 29,900	

^aIB conversions are 100%.

^bConversion was $\sim 100\%$ after 2 hours.

TABLE 8. The Average dn/dc Values, the p MeSt Contents, the Tensile Strengths (σ), and the Elongations at Break (λ) of the Triblocks

No.	dn/dc , mL/g	Arms	p MeSt content				σ , MPa	λ , %
			From NMR		From conversion			
			mol%	wt%	mol%	wt%		
6	0.132	3	44.4	62.8	38.9	57.3	18.1	285
7	0.121	2	30.9	48.5	25.0	41.2	14.3	384
8	0.120	2	30.8	48.4	28.1	45.1	19.2	470
9	0.124	3	26.7	43.5	25.7	42.1	21.0	482
10	0.124	3	33.5	51.5	30.5	48.1	21.5	437
11	0.127	2	35.3	53.4	36.1	54.4	20.0	365
12	0.130	2	35.3	53.5	35.4	53.5	22.3	400
13	0.115	2	16.6	29.6	16.9	29.9	17.1	640
14	0.117	2	17.8	31.3	16.9	29.9	19.1	730
15	0.117	2	17.7	31.1	16.9	29.9	17.6	710

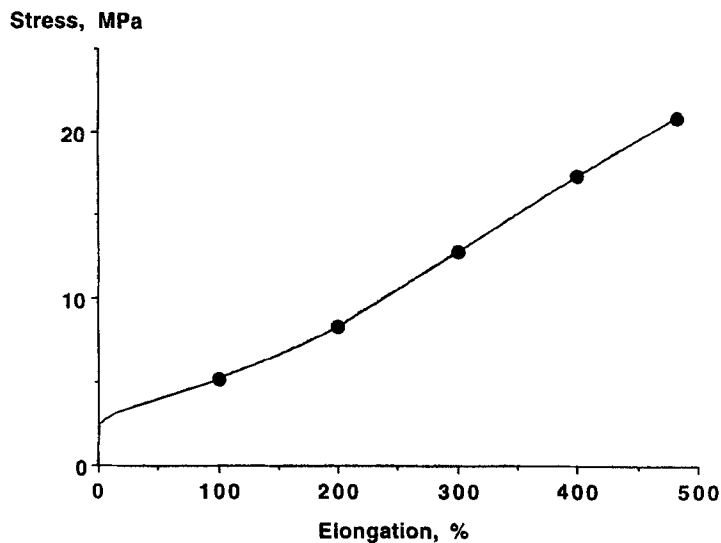


FIG. 6. Stress-strain curve of triblock copolymer No. 9.

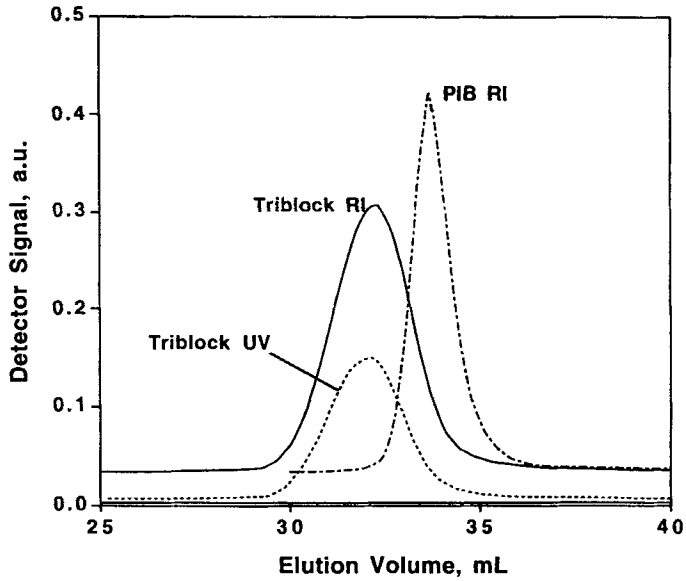


FIG. 7. The GPC traces of the DPE-capped PIB middle segment and those of the triblock in Expt. 11, DPE excess 104%.

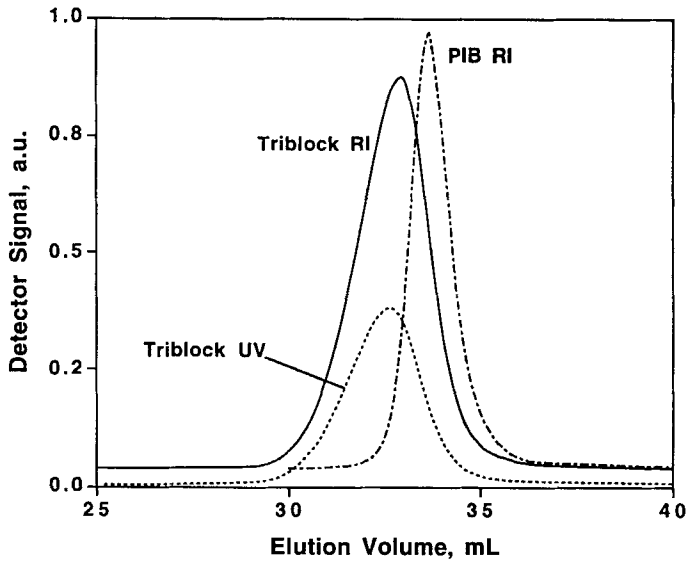


FIG. 8. The GPC traces of the DPE-capped PIB middle segment and those of the triblock in Expt. 8, DPE excess 200%.

TABLE 9. Extraction Results of Select Triblocks

No.	Arms	Block		MEK extract		
		<i>p</i> MeSt, ^a wt%	Extracted, wt%	<i>p</i> MeSt content, ^a wt%	M_n^b	M_w/M_n^b
12	2	53.5	6.6	52.9	231,600	1.29
10	3	51.5	9.6	46.9	158,100	1.99

^aDetermined by NMR.

^bDetermined by GPC MALLS.

As expected, extraction results of select triblock copolymers (Table 9) confirmed the absence of homopolymers. The MEK soluble fraction was under 10%. Moreover, the composition and molecular weight of the MEK extracts were nearly identical to those of the crude product.

CONCLUSION

The synthesis of *Pp*MeSt-PIB-*Pp*MeSt triblock copolymer was accomplished by sequential monomer addition via DPE capping. 100% crossover efficiency was indicated by the excellent mechanical properties. Research is in progress to utilize our novel synthetic strategy for the preparation of a wide variety of block copolymers that cannot be obtained by conventional sequential monomer addition.

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