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Living Carbocationic Polymerization. LII. Living Carbocationic Copolymerization of Indene and *p*-Methylstyrene. 2. Synthesis, Characterization, and Physical Properties of Poly((Indene-*co*-*p*-Methylstyrene)-*b*-Isobutylene-*b*-(Indene-*co*-*p*-Methylstyrene)) Thermoplastic Elastomers

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LIVING CARBOCATIONIC POLYMERIZATION. LII. LIVING CARBOCATIONIC COPOLYMERIZATION OF INDENE AND *p*-METHYLSTYRENE. 2. SYNTHESIS, CHARACTERIZATION, AND PHYSICAL PROPERTIES OF POLY((INDENE-*co*-*p*-METHYLSTYRENE)-*b*-ISOBUTYLENE-*b*-(INDENE-*co*-*p*-METHYLSTYRENE)) THERMOPLASTIC ELASTOMERS†

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ABSTRACT

Novel thermoplastic elastomers (TPEs) consisting of a central rubbery polyisobutylene (PIB) segment flanked by two glassy outer segments comprising indene (Ind)-*co*-*p*-methylstyrene (pMeSt) random copolymers have been prepared. The synthesis was effected by sequential monomer addition in one reactor: The process starts by the biliving homopolymerization of isobutylene (IB) and yields the living dication $^+PIB^+$; the latter, upon the introduction of Ind/pMeSt mixtures, induces the living copolymerization of these monomers and yields the target TPE P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt) triblock. The length of the rubbery midblock and the composition of the Ind-*co*-pMeSt random copolymer outer blocks (i.e., the overall composition of the triblocks) can be readily controlled. The glass transition temperature (T_g)

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of the outer blocks can be fine-tuned by controlling the relative Ind/pMeSt composition. The triblocks are excellent TPEs; for example, a P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt) of $\overline{M}_n \approx 115{,}000$ g/mol containing a PIB midblock of $\overline{M}_n \approx 70{,}200$ g/mol and glassy copolymer outer blocks of P(Ind-*co*-pMeSt) [Ind/pMeSt = 41/59 (w/w)] exhibited 23.4 MPa tensile strength and 460% elongation. Tensile strengths and 300% moduli increase with the relative amount of the glassy segment present. Hardness increases with increasing Ind content.

INTRODUCTION

As described in the preceding publication [1], Ind and pMeSt can be readily copolymerized under living conditions, and the products are most likely random copolymers. The T_gs of these copolymers are a linear function of the relative Ind/pMeSt compositions and they can be fine-tuned between ~115°C (the T_g of PpMeSt) and ~194°C (the T_g of PInd).

Our present challenge is to synthesize thermoplastic elastomeric triblocks consisting of a rubbery PIB midblock flanked by two glassy Ind-*co*-pMeSt random copolymer outer blocks by sequential monomer addition (SMA). By the SMA technique the synthesis starts by preparing a diliving $^+$PIB$^+$ dication of appropriate molecular weight ($\overline{M}_n = 50{,}000$–$70{,}000$) and narrow dispersity ($\overline{M}_w/\overline{M}_n \approx 1.1$), and adding to this intermediate mixtures of Ind plus pMeSt. The second step is the random copolymerization of Ind and pMeSt which continues until a sufficient random block copolymer length is reached so as to attain TPE characteristics.

This paper concerns the synthesis, characterization, and some mechanical properties of P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt) triblocks exhibiting excellent TPE characteristics.

EXPERIMENTAL

Materials

The synthesis of the 1,4-bis(2-chloro-2-propyl)benzene (*p*-dicumyl chloride, DiCumCl) initiator has been described [2]. The purification of Ind, pMeSt, and triethylamine (Et_3N) and the source and purification of IB, $TiCl_4$, CH_3Cl, and nC_6H_{14} have been described [1, 3, 4]. Methanol, toluene, MEK, *n*-pentane (Fisher Scientific Co.), and $CDCl_3$ (Aldrich Chemical) were used as received.

Polymerization

Polymerizations were carried out in a drybox under dry nitrogen using 250 mL three-necked round-bottom flasks equipped with a mechanical stirrer. Into the reactors were placed the $CH_3Cl/nC_6H_{14} = 4/6$ (v/v) solvent mixture, the initiator (DiCumCl), and Et_3N, and the charge was thermostated at −80°C. Then the calculated quantity of precooled IB was added. Polymerizations were started by introducing the coinitiator ($TiCl_4$). After stirring for a designated time, a sample was withdrawn by a cooled pipet for molecular weight and conversion analyses. Conversions were determined gravimetrically.

The blocking of Ind/pMeSt mixtures was induced by pouring prechilled solutions of these monomers to stirred living $^+PIB^+$ dication charges at −80°C. The systems were stirred for specific times and quenched with prechilled methanol. The products were precipitated by pouring the contents of the reactors into a large excess of methanol, filtering, dissolving in toluene, washing with aqueous HCl, then with distilled water, with aqueous $NaHCO_3$, and again with distilled water until neutral. Finally the solutions were dried over $MgSO_4$, precipitated slowly into methanol, and the products were vacuum dried until constant weight at 60°C.

Extraction Studies

The amount of homopolymer contamination was determined by selective solvent extraction. Thus, a cellulose thimble was loaded with about 5 g of the crude sample and Soxhlet extracted first with boiling MEK (solvent for the glassy outer block, nonsolvent for PIB), followed by boiling *n*-pentane (solvent for PIB, nonsolvent for the glassy outer block), each for 48 hours. The solvents were removed by rotary evaporation and the extracted products were dried in a vacuum oven at 60°C for 5 days. Percent extractables were determined gravimetrically. The overall composition of the extracted products was determined by ^1H-NMR spectroscopy [1, 5].

Characterization

The molecular weights of the center PIB blocks and their molecular weight distributions (MWDs) were obtained by a Waters high-pressure GPC assembly (model 6000A pump, 5 μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å UV and RI detectors) using PIB calibration. The molecular weights and overall compositions of triblocks were determined by ^1H-NMR spectroscopy (see Ref. 1) using a Varian Gemini 200 MHz spectrometer and $CDCl_3$ solvent.

T_gs were determined by a Dupont 910 DSC module with a Dupont 9900 computer/thermal analyzer at a heating rate of 10°C/min.

Mechanical Testing

Microdumbells were stamped from homogeneous bubble-free optically clear films cast from toluene solution (20 wt%) and were vacuum dried at 60°C for a week. Stress-strain measurements were carried out on microdumbells at room temperature by an Instron Tensile Tester. Strain rate: 3.94 min^{-1}. Shore A2 hardness was measured by a Shore Durometer, according to ASTM D2240. The averages of six samples were recorded.

RESULTS AND DISCUSSION

Synthesis and Characterization of P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt)

Table 1 is a comprehensive compilation of the synthesis, characterization, and mechanical property results obtained. For comparison, T_g and other information collected with similar triblocks containing PInd and PpMeSt homopolymer glassy segments are also shown.

TABLE 1. Synthesis, Characterization, and Select Mechanical Properties of P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt)

	Synthesis and characterization											Mechanical properties			
	PIB midsegment[a]				Triblock[b]				Compositions						
Expt.	Con-version, %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	I_{eff},[d] %	Conversion of Ind and pMeSt, %	$\overline{M}_n$[e] triblock	$\overline{M}_n$[f] outer block	$\overline{M}_w/\overline{M}_n$[c]	Overall composition of triblock rubber/glass, w/w	Composition of outer block Ind/pMeSt, w/w	T_g, Rubber/glass °C	Tensile strength, MPa	Modulus (300%), MPa	Elon-gation, %	Hard-ness shore A2
C1	100	71,600	1.07	98	84	105,300	16,900	1.25	68/32	82/18	−61/189	18.8	12.0	410	64
C2	95	66,200	1.07	100	89	101,900	17,900	1.39	65/35	61/39	−61/175	21.3	14.8	450	62
C3	99	70,200	1.08	101	100	115,000	22,400	1.34	61/39	41/59	−63/148	23.4	14.6	460	56
C4	106	79,700	1.10	93	100	160,900	40,600	1.54	47/53	56/44	−60/162	—	—	—	—
M1[g]	—	—	—	—	—	116,000	19,200	1.24	67/33	0/100	−63/113	14.1	9.1	420	53
I1[h]	—	—	—	—	—	83,200	13,100	1.29	70/30	100/0	—	17.0	12.1	400	55
I2[h]	—	—	—	—	—	93,400	19,600	1.39	59/41	100/0	−65/209	20.5	17.0	400	60

[a] Conditions of IB polymerization: DiCumCl = 1.5 mM, $TiCl_4$ = 20.0 mM, IB = 1.87 M, Et_3N = 1.5 mM, CH_3Cl/nC_6H_{14} = 4/6 (v/v), V_0 = 150 mL, 2 hours, −80°C.

[b] Conditions of block polymerization: To the above living $^+PIB^+$ charge at −80°C were added, in CH_3Cl (12 mL)/nC_6H_{14} (18 mL), the following comonomer mixtures. C1: Ind 0.06_2 mol/pMeSt 0.015 mol. C2: Ind 0.046 mol/pMeSt 0.030 mol. C3: Ind 0.031 mol/pMeSt 0.046 mol. C4: Ind 0.077 mol/pMeSt 0.076 mol.

[c] By GPC (using PIB calibration).

[d] Calculated for $(W_p/\overline{M}_n)$/(mole of initiator).

[e] Calculated from overall composition by ^{1}H-NMR spectroscopy assuming 100% blocking efficiency of Ind-*co*-pMeSt.

[f] Calculated from $(\overline{M}_{n\text{Triblock}} - \overline{M}_{n\text{PIB}})/2$.

[g] Data of Tsunogae and Kennedy [7].

[h] Data of Kennedy, Midha, and Tsunogae [6, 8].

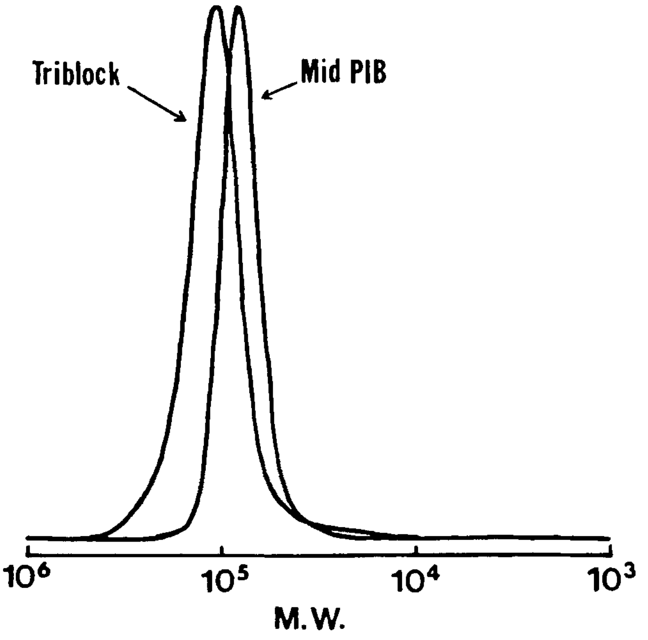

FIG. 1. GPC traces of the PIB midsegment and the triblock polymer (Cl in Table 1).

Figure 1 shows the GPC traces of a representative PIB midsegment and of the corresponding final product. All products gave similar GPC traces ($\overline{M}_w/\overline{M}_n$ = 1.2–1.5). The symmetry and the narrowness of the peak associated with the triblock copolymer suggests high structural purity.

Efforts to analyze the products by selective solvent extraction using MEK and subsequently *n*-pentane were only partially successful because the MEK-insoluble fraction gave stable emulsions in *n*-pentane. However, even partial solubility data provided valuable information in respect to product composition and process details. For example, a sample (Sample C3, Table 1) gave 5.4% of a MEK-soluble fraction of $\overline{M}_n$ = 19,500 whose composition by ^{1}H-NMR spectroscopy was found to be essentially devoid of PIB. Evidently very little if any chain transfer occurs during the growth of the glassy outer segments. Further, the compositions of the glassy Ind-*co*-pMeSt copolymers in the crude sample as well as in the MEK-soluble and -insoluble fractions were quite similar (41/59 ± 5 wt%), indicating efficient blocking and selective solvent separation by molecular weight (that is, not by composition).

A separate series of Ind-*co*-pMeSt random copolymerization experiments were carried out by the use of various Ind/pMeSt composition charges to gain insight into the solubility characteristic of these copolymers. These experiments showed that the copolymers were soluble in MEK provided the pMeSt contents of the products were in excess of ~40 wt%.

These solubility studies, together with GPC information (see, for example, Fig. 1), strongly suggest a close to 100% blocking efficiency (B_{eff}) in these experiments.

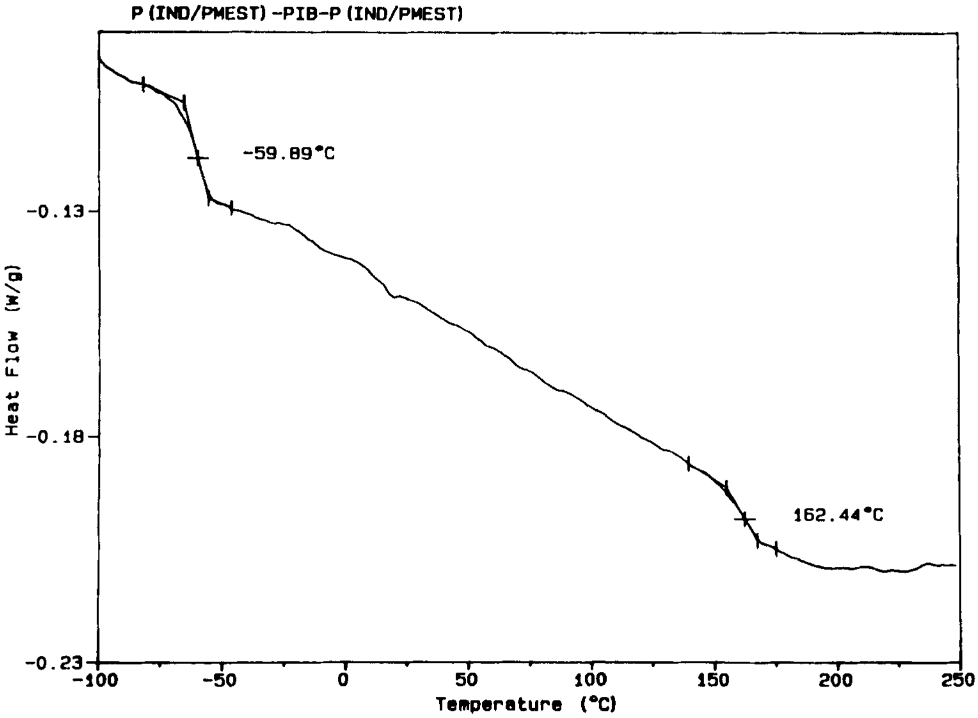

FIG. 2. DSC trace of a representative triblock (C4 in Table 1).

As described and discussed in previous papers concerning the syntheses of PInd-*b*-PIB-*b*-PInd [6, 8] and PpMeSt-*b*-PIB-*b*-PpMeSt [7], high B_{eff} can be obtained when Ind or pMeSt are added to $^{+}$PIB^{+} macrocations of sufficiently high molecular weight in CH_3Cl/nC_6H_{14} solvent mixtures. These desirable B_{eff}s were ascribed to the reduced rate of propagation relative to that of cationation during the blocking step [6–8]. Similarly to these earlier observations, high random-copolymerization blocking-efficiencies were also obtained in the present experiments despite the fact that model experiments with 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ showed relatively slow initiation [1]. Similar failures of the TMPCl model to predict the actual blocking behavior have also been observed in the PIB/PInd [6, 8] and PIB/PpMeSt [7] blocking systems. As discussed in these references, the rate of Ind propagation from $^{+}$PIB^{+} macroinitiator decreased with increasing molecular weight of $^{+}$PIB^{+}. The GPC trace of product initiated by low molecular weight PIB ($\overline{M}_n$ = 1400) showed two peaks: High molecular weight peak ($\overline{M}_n$ = 60,000) and low molecular weight peak ($\overline{M}_n$ = 1400) corresponded to the block and PIB homopolymer, respectively. The peak corresponding to PIB decreased in size as $\overline{M}_n$ of PIB macroinitiator was increasing, and a narrow MWD final product was obtained above $\overline{M}_{n(\mathrm{PIB})}$ = 45,000 [6, 8]. This means that the blocking of Ind and pMeSt from high molecular weight $^{+}$PIB^{+} yields high B_{eff}s (although the TMPCl model would predict otherwise) because the rate of diffusion of the styrenic monomers through the high molecular weight coil to the macroinitiator site is reduced, which in turn increasingly reduces the rate of propagation (R_p) of the block

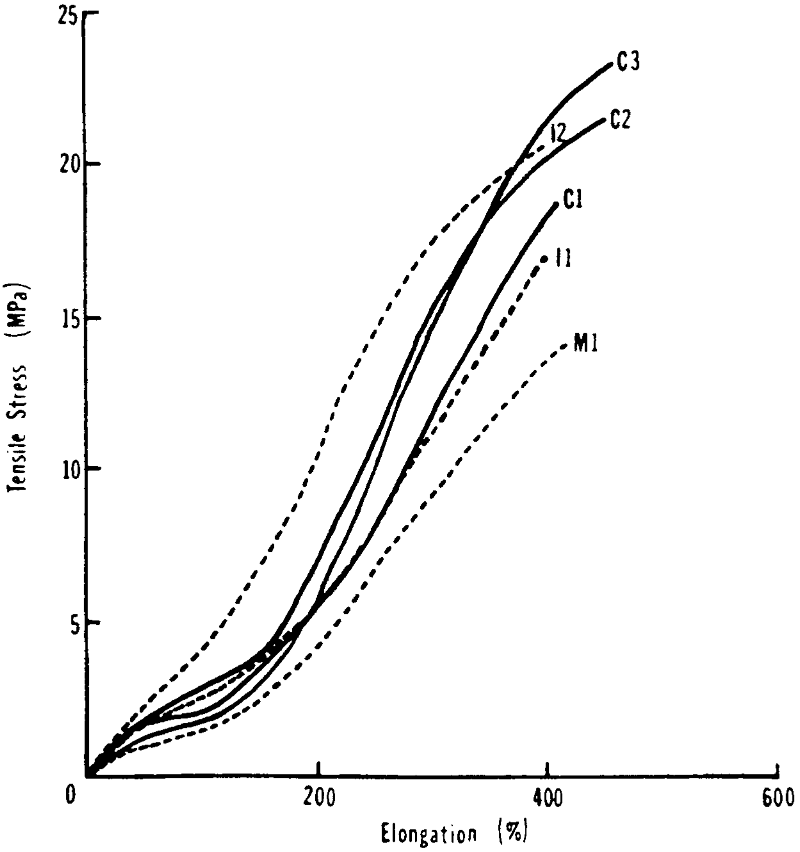

FIG. 3. Stress-strain traces of P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt) (C1-3), PpMeSt-*b*-PIB-*b*-PpMeSt (M1), and PInd-*b*-PIB-*b*-PInd (I1 and I2) triblocks (see Table 1).

segment growth. With the low molecular weight model, monomer diffusion to the active site is relatively unhindered so that the rate of propagation will be high, which in turn gives rise to relatively faster homopolymerization than initiation and consequently to low blocking efficiencies.

The overall composition and the T_g of the triblocks were analyzed by ^{1}H-NMR spectroscopy and DSC, respectively. The results are included in Table 1. Figure 2 shows the DSC trace of a representative triblock (Sample C4 in Table 1). The figure exhibits two transitions characteristic of segregated PIB and P(Ind-*co*-pMeSt) microdomains. The high temperature transition characteristic of the glassy domains in triblocks with low glass contents was difficult to detect. While Samples C1-C3 clearly showed strong transitions for the PIB domain, those characteristic of the glassy domain were much weaker.

The T_gs of the glassy domains can be controlled by the relative Ind/pMeSt composition, and they were found to be very close to the theoretical values calculated by (Ind content) × (T_g of PInd) + (pMeSt content) × T_g of PpMeSt). Evidently the outer segments indeed consist of Ind/pMeSt random copolymers.

Mechanical Properties

As shown by the data in Table 1, triblock copolymers C1–C3 exhibit excellent TPE characteristics. C4 is not a TPE because its glass content is higher than its rubber content. Figure 3 displays the stress-strain profiles obtained. Sample C3 with the highest molecular weight glassy segment exhibits the highest tensile strength, although its Ind content is below those of C1 and C2. Apparently the tensile strengths of these materials are more affected by the molecular weight of the glassy outer block than by the Ind/pMeSt composition.

Evidently the hardness of P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt) triblocks depends of the Ind/pMeSt composition in the outer segment (see Table 1) and increases with increasing Ind content. Thus it seems that hardness is influenced more by the Ind/pMeSt composition than by the overall triblock composition.

CONCLUSIONS

P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt) triblocks of quite narrow dispersities have been synthesized by sequential monomer addition. The triblocks exhibit excellent TPE characteristics. DSC analysis indicates two-phase microdomain morphology. The T_g of the outer random copolymer segment is controlled by the Ind/pMeSt composition. The molecular weight of the glassy outer block, rather than its composition, determines the tensile strength.

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