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Novel Thermoplastic Elastomer Triblocks of a Soft Polyisobutylene Midblock Connected to Two Hard PMMA Stereocomplex Outer Blocks

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ABSTRACT: This paper concerns the synthesis, characterization, and select physical properties of novel thermoplastic elastomers (TPEs) consisting of two hard poly(methyl methacrylate) (PMMA) stereocomplex outer blocks flanking a soft polyisobutylene (PIB) midblock. The preparation of the starting material, a PMMA-*b*-PIB-*b*-PMMA triblock with syndiotactic PMMA (sPMMA) outer blocks, was the subject of a previous publication;[1] this report focuses on the preparation of PMMA stereocomplexes as outer blocks by blending isotactic PMMA (iPMMA) with the sPMMA of the triblocks. Stereocomplex formation was demonstrated by DSC studies. The melting temperature of iPMMA/sPMMA stereocomplexes (170–200 °C) is affected by the relative amounts of the i- and sPMMA in the outer blocks and is much higher than either of the T_g's of the i- and sPMMA (~52 and ~102 °C, respectively) components. The blending solvent, i- and sPMMA molecular weights, and annealing affect stereocomplexation. Stereocomplexation elevates the T_g of these TPEs and leads to enhanced tensile strengths, moduli, and elongations combined with desirably low hardness values.

1. Introduction

A variety of thermoplastic elastomer (TPE) triblock and star block polymers have recently been described comprising a soft polyisobutylene (PIB) midblock (or core in star-blocks) flanked by various hard blocks, e.g., polystyrene,[2,3] poly(*p*-chlorostyrene),[4] polyindene,[5] and cyclized polyisoprene.[6] These syntheses followed the common strategy of initiating a bidirectional (or tridirectional for star blocks) living polymerization of isobutylene, yielding the midblock, and, after sufficient growth of the soft segment, adding to the living charge a second monomer which produces the hard outer blocks.

A limitation of these sequential monomer addition methods is that only cationically polymerizable monomers can be used. The scope of this field has recently been expanded by cationic → anionic transformation; after the living carbocationic polymerization (LC^+Pzn) of isobutylene was complete, the chain ends were quantitatively transformed to polymerization-active anions so that additional blocks could be built by subsequent anionic techniques. An example of this methodology was the synthesis of PMMA-*b*-PIB-*b*-PMMA triblock in which living $^+PIB^+$ dications were transformed into $^-PIB^-$ dianions and the polymerization was completed by the addition of MMA:[1]

$$\mathrm{IB} \xrightarrow{\mathrm{LC^{+}Pzn}} {}^{+}\mathrm{PIB}^{+} \xrightarrow{\text{transformation}} {}^{-}\mathrm{PIB}^{-} \xrightarrow{\mathrm{MMA}} \mathrm{PMMA{-}PIB{-}PMMA}$$

The final step was the polymerization of methyl methacrylate (MMA) in THF at −78 °C, a process which yields largely (~75%) syndiotactic PMMA (sPMMA). The T_g of this sPMMA is ~102 °C so that the resulting sPMMA–PIB–sPMMA triblocks were interesting novel TPEs.[1]

About 15 years ago, Challa et al.[7-11] and Spevacek et al.[12] found that blending sPMMA with isotactic PMMA (iPMMA) yields crystalline stereocomplexes in which the largely sPMMA and iPMMA chains were intimately intertwined, resulting in significant rigidification of the "composite" as indicated by thermal (mainly DSC) and NMR studies. The decomplexation or melting temperature of iPMMA/sPMMA stereocomplexes is in the 170–220 °C range.[7-11,13] Stereocomplexation of i- and sPMMA chains and the resulting rigidificaiton have been ingeniously exploited by Hogen-Esch et al.[13] for the preparation of interesting novel TPEs comprising two hard PMMA stereocomplex outer blocks flanking a soft midblock of polybutadiene or polysiloxane.

This paper concerns the synthesis, characterization, and select physical properties of novel TPEs comprising a soft PIB midblock connected to two iPMMA/sPMMA stereocomplex outer blocks. The synthesis of the starting material sPMMA–PIB–sPMMA has been described earlier:[1] we now focus on the synthesis of iPMMA/PIB–sPMMA/iPMMA stereocomplex TPEs by blending homo-iPMMA to the sPMMA outer blocks, the characterization of the resulting iPMMA/sPMMA stereocomplex outer blocks, and some properties of these composite TPEs. This is the first time that some physical properties of stereocomplex TPEs are being reported.

2. Experimental Section

2.1. Materials. The synthesis and purification of 1,3-bis(2-methoxy-2-propyl)-5-*tert*-butylbenzene (*t*Bu-*m*-DiCuOMe) have been described.[14] The source and purification of isobutylene (IB), methyl chloride (CH_3Cl), *n*-hexane,[15] $TiCl_4$,[16] methyl methacrylate (MAA),[17] toluene,[18] tetrahydrofuran (THF), 1,1-diphenylethylene (DPE), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA)[1] have also been described. *sec*-Butyllithium (*s*BuLi; Aldrich; 1.3 M solution in cyclohexane) was used after checking its functionality by titration.[1] *tert*-Butylmagnesium chloride (*t*BuMgCl; Aldrich; 2.0 M solution in diethyl ether), *N,N*-dimethylformate (DMF; Aldrich), triethylaluminum (Aldrich; 1.0 M solution in hexane), sodium potassium tartrate (Fisher Scientific Co.), dimethylacetamide (DMA; Aldrich), $AlCl_3$ (Fisher Scientific Co.), $CaCl_2$ (Fisher Scientific Co.), acetone (Fisher Scientific Co.), methanol (Fisher Scientific Co.), and $CDCl_3$ (Aldrich) were used as received.

2.2. Polymerization. 2.2.1. Block Copolymerization. Polymerization of IB was carried out in a drybox under a dry-nitrogen atmosphere in a 2-L round-bottomed flask equipped with a me-

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Table I
Precursor for the Midblock: Preparation of α,ω-Ditolylpolyisobutylene[a]

sample	yield, g	conv, %	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff},[b] %
${}^tCl-PIB-Cl^t$	86.9	87	70 350	61 000	1.15	85
$CH_3Ph-PIB-PhCH_3$	71.5	100	64 600	54 700	1.18	

[a] Step 1: preparation of α,ω-dichloropolyisobutylene; *t*Bu-*m*-DiCuOMe/DMA/$TiCl_4$ (mole) = $1.68 \times 10^{-3}/3.03 \times 10^{-2}/8.0 \times 10^{-2}$; CH_3Cl/*n*-hexane = 40/60 (v/v); isobutylene, 4 × 31.5 mL/20 min, −80 °C. Step 2: alkylation of toluene by *t*Cl–PIB–Cl*t*; *t*Cl–PIB–Cl*t* (88.5 g)/*n*-hexane (150 mL)/toluene (100 mL)/$AlCl_3$ (55.6 g); −78 °C, 7 h. [b] I_{eff} (%) = (polymer yield (g)/$\bar{M}_n$ of PIB)/(number of moles of initiator).

chanical stirrer. Details of the experimental technique have been described.[1,14-16] The conditions and procedure for block copolymerization to obtain the starting material sPMMA–PIB–sPMMA have also been described.[1] Briefly, the synthesis steps involved the Friedel–Crafts alkylation of toluene by α,ω-di-*tert*-chloropolyisobutylene (*t*Cl–PIB–Cl*t*) and lithiation of the α,ω-ditolylpolyisobutylene ($CH_3Ph-PIB-PhCH_3$) to α,ω-dibenzyllithiopolyisobutylene ($^-CH_2Ph-PIB-PhCH_2^-$), which in turn was reacted with DPE to give the corresponding dianion. After dilution with THF and cooling to −78 °C, the addition of MMA gave the sought PMMA–PIB–PMMA triblock. Table I summarizes the synthesis conditions used for the preparation of *t*Cl–PIB–Cl*t* and $CH_3Ph-PIB-PhCH_3$.

2.2.2. MMA Polymerization for Complexation Study. To model the stereocomplexation, sPMMA and iPMMA were synthesized. The conditions to obtain sPMMA were the same as those used for sPMMA–PIB–sPMMA synthesis except *s*BuLi was used as the initiator. To obtain iPMMA, MMA was polymerized with *t*BuMgCl as the initiator in toluene at −78 °C [*t*BuMgCl (2.0×10^{-3} mol)/toluene (50 mL)/MMA (10 mL)].[18] After polymerization, the charge was quenched by prechilled methanol and the polymer was reprecipitated twice from acetone into a large excess of *n*-hexane and dried in a vacuum oven at room temperature.

2.2.3. Solvent Extraction Studies. The amount of homopolymer contaminants in the triblocks was determined by selective solvent extraction (Soxhlet). Thus, a cellulose thimble was loaded with about 5 g of crude block copolymer, and it was extracted for 24 h with *n*-hexane (a good solvent for PIB and a nonsolvent for PMMA) followed for 24 h by acetone (a good solvent for PMMA and a nonsolvent for PIB). Percent extractables were determined gravimetrically. The composition of the extracts was determined by a Varian Gemini 200-MHz ^1H NMR spectrometer.

2.2.4. Preparation of Stereocomplexes. Stereocomplex samples were prepared by mixing dilute solutions of the components.[10,11] A strongly complexing solvent,[8] mostly THF, was used. Thus, 1 wt % solutions of iPMMA plus sPMMA or iPMMA plus sPMMA–PIB–sPMMA triblocks were mixed in THF so that the iPMMA/sPMMA weight ratios were 1/2. The solutions were stirred for 20 h at room temperature, then concentrated to 20% by evaporating the solvent (rotovap), and used for casting (see below). This procedure was similar to that described by Challa et al.,[11] with the difference that the earlier author used DMF for mixing the PMMA stereoisomers. Most castings were carried out by the use of THF; however, in certain instances we have also employed THF/toluene (50/50, v/v) mixtures. The rationale for using solvent mixtures was to reduce the rate of evaporation of the casting medium. Detailed conditions and data are shown in the table and figure captions. Annealing of stereocomplexes was carried out for 24 h at 140 °C.[7,8] The annealed sheets exhibited a tan to brown discoloration which may indicate surface oxidation or some degradation.

2.3. Characterization. Molecular weights and molecular weight distributions (MWD) were obtained by a Waters high-pressure GPC assembly (Model 6000A pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, a Model 410 differential refractometer, a Model 440 UV absorbance detector, and a WISP 710B automatic sampler). The flow rate of THF was 1 mL/min. Calibration curves were obtained with narrow molecular weight PIB and polystyrene standards. Absolute molecular weights and block polymer compositions were determined by ^1H NMR spectroscopy. ^1H NMR spectra were taken on a Varian Gemini 200-MHz spectrometer using $CDCl_3$ as solvent. Block copolymer compositions were calculated by comparing the signal intensities corresponding to the CH_3O- resonance of the PMMA segment and the $-CH_2-$ resonance of the PIB segment (3.6 and 1.4 ppm, respectively) by ^1H NMR.[19,20] A representative ^1H NMR spectrum of a sPMMA–PIB–sPMMA is shown in Figure 1. Tacticities were also determined by signal intensities of the i, s, and heterotactic (h) α-methyl resonances of the PMMA segments.[19]

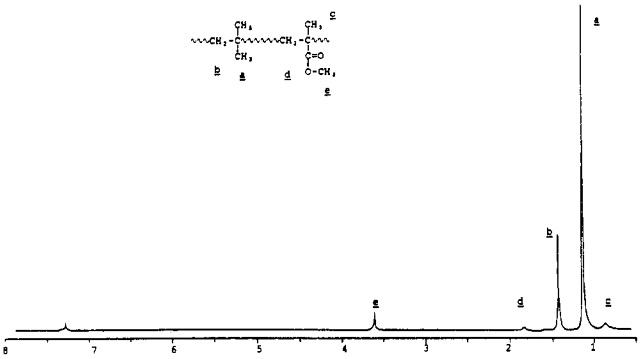


Figure 1. ^1H NMR spectrum of a representative sPMMA–PIB–sPMMA (B1 in Table II).

The sPMMA–PIB–sPMMA sheets (~0.7 mm thick) cast from THF solution on taut cellophane films were invariably somewhat hazy and their surfaces were uneven, reminiscent of pig skin. Haziness and the "pig skin" surface were attributed to overly rapid THF evaporation and consequent insufficient microphase separation. Efforts were made to reduce the rate of THF evaporation by covering the casting area with an inverted glass funnel (7.5 cm diameter) and further reducing the rate of solvent evaporation by tightly wrapping aluminum foil around the narrow opening (0.5 cm) of the funnel stem. However, none of these measures improved the optical appearance of our films. During these casting experiments we discovered that optically clear and smooth-surface films could be prepared by the use of THF/toluene (50/50, v/v) casting solutions. Evidently the slower rate of evaporation of the higher boiling solvent, toluene, led to improved phase separation of the sPMMA and PIB microdomains.

In contrast, THF cast films of iPMMA/sPMMA–PIB–sPMMA/iPMMA invariably gave clear films and smooth surfaces under the same casting conditions.

After 1 week, when the odor of THF disappeared and the optically clear films were judged largely free of THF, the films were dried for an additional 7–10 days in a vacuum oven under reduced pressure (~15 mmHg) at 40–50 °C. These products were used for the preparation of microdumbbells for tensile testing.

Stress–strain measurements were carried out with an Instron tensile tester according to ASTM D412. The data reported are averages of three determinations. Shore A hardness values were measured by a Shore Durometer according to ASTM D2240. DSC measurements were performed on a Du Pont instrument (Model 910 differential scanning calorimeter, Model 9900 computer/thermal analyzer).

3. Results and Discussion

Thermoplastic elastomers comprising glassy–rubber–glassy architectures are useful materials under intensive investigation in both academic and industrial laboratories.[21-24] The upper use-temperature of these triblocks is set by the thermal properties, usually the T_g, of the glassy segment. The upper use-temperature of sPMMA–PIB–sPMMA would also be determined by the T_g of the sPMMA, ~102 °C.

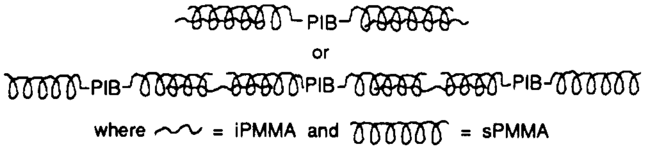
In the course of our fundamental research on novel TPEs, it occurred to us that the usefulness of our recently synthesized sPMMA–PIB–sPMMA could be enhanced by

Table II
Synthesis of sPMMA–PIB–sPMMA Triblocks[a,b]

synthesis					extractables, %		sPMMA–PIB–sPMMA			
sample	CH_3Ph–PIB–$PhCH_3$, mL (g)	MMA, g	yield, g	conv, %	*n*-hexane: $\bar{M}_n{}^c/\bar{M}_w/10^{-3}\bar{M}_n$	acetone: $\bar{M}_n{}^d/\bar{M}_w/10^{-3}\bar{M}_n$	sum of *n*-hexane + acetone insoluble fractions, g	$\bar{M}_n$ (×10^{-3})[e] sPMMA–PIB–sPMMA	A_w/A_n	PMMA, %
B1	30 (4.50)	2.30	6.67	98	15/54/1.26	10/7.4/1.14	4.67	7.0–54.7–7.0	1.27	20
B2	32 (4.80)	3.51	8.21	99	13/52/1.27	12/10.6/1.16	5.42	10.3–54.7–10.3	1.30	27
B3	32 (4.80)	5.27	9.00	89	10/53/1.26	25/14/1.14	6.11	14.3–54.7–14.3	1.30	34
B4	35 (5.25)	4.07	9.36	100	9/52/1.25	8.10/1.11	6.00	9.9–54.7–9.9	1.28	27
B5	35 (5.25)	1.92	7.02	98	35/55/1.19	7/7.5/1.25	3.90	7.3–54.7–7.3	1.23	21
B6	20 (3.00)	1.74	4.73	100	47/46/1.26	7/21/1.49	1.76	16.5–53.2–16.5	1.28	38

[a] Synthesis conditions: 15% CH_3Ph–PIB–$PhCH_3$ in *n*-hexane (two chain ends)/TMEDA/*s*BuLi = 2/8/4 molar ratio, 0 °C for 48 h; add DPE (4 M excess per polymer chain end) and 100 mL of THF, cool to −78 °C, add MMA dropwise, and stir for 1.5 h. [b] Samples for DSC and tensile testing. B1, B2, and B4–B6: dissolved in THF, concentrated to ~20%, and cast. B3: dissolved in THF, concentrated to ~20%, toluene (v/v = 50/50) added, and cast. [c] Based on PIB calibration. [d] Based on PSt calibration. [e] By ^1H NMR.

blending iPPMA to these triblocks, in other words, that we could obtain improved TPEs with rubbery PIB soft segments connected to high-melting stereocomplex hard segments: iPMMA/sPMMA–PIB–sPMMA/iPMMA. In addition to this well-defined microarchitecture, homo-iPMMA may also function as "tie-blocks" connecting two sPMMA–PIB–sPMMAs.[13] Schematically:



The final products were of course expected to contain a combination of these microstructures. In any event, the large polarity difference between the soft PIB and hard PMMA components was expected to manifest in extensive microphase separation, a prime requirement for high-quality TPEs.

3.1. Synthesis and Extraction. The first phase of our experimental work focused on the preparation and characterization of the starting materials sPMMA–PIB–sPMMA, homo-iPMMA, and model iPMMA/sPMMA blends. Table II is a compilation of the sPMMA–PIB–sPMMAs prepared. The $\bar{M}_n$ of the PIB was selected to be in the 50–60 × 10^3 g/mol range. This selection was based on previous experience with triblock TPEs.[1,22,24] The crude triblocks were sequentially extracted with hexane (good solvent for PIB and nonsolvent for PMMA) and acetone (good solvent for PMMA and nonsolvent for PIB), and the extracted products, assumed to be pure sPMMA–PIB–sPMMA, were characterized. This assumption may not be correct, and the extracted product may contain sPMMA–PIB diblocks; however, according to GPC evidence (uniform narrow traces; see, for example, Figure 2), the extracted products were largely triblocks.

Since the alkylated PIB chain end/*s*BuLi ratio was 2/4, one may expect the acetone extract to contain homo-PMMA (due to chain transfer). However, the facts that the $\bar{M}_n$'s of the acetone extracts and those of the PMMA segments in the triblock were virtually identical and that the molecular weight dispersities of the extracts were very narrow argue against this possibility. (We thank one of the reviewers for bringing this to our attention). An earlier report from this laboratory focused on the precision synthesis and characterization of sPMMA–PIB–sPMMA.[1]

Table III summarizes representative microstructure results obtained by ^1H NMR spectroscopy. Sample s1, obtained by *s*BuLi initiation of MMA polymerization under the same conditions as the triblock was synthesized, is a model for the sPMMA blocks present in our triblocks; i1 and i2 are iPMMAs prepared by us or purchased, respectively, and have been used for blending with sPMMA–PIB–sPMMA. According to these data the syndiotactic content of sPMMA was ~76% and the isotactic content of the iPMMA was ~83 and ~69% depending on the molecular weight of the product.

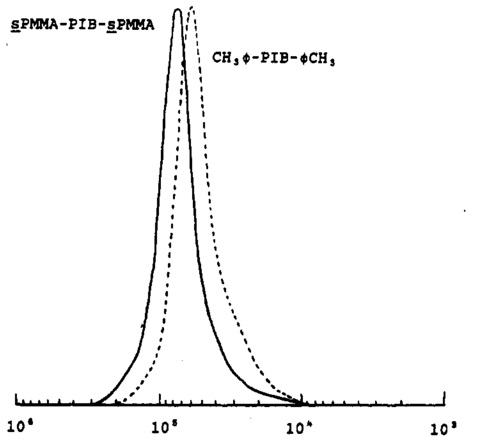


Figure 2. GPC traces of CH_3Ph–PIB–$PhCH_3$ (dotted line) precursor and sPMMA–PIB–sPMMA triblock (solid line) obtained under conditions given in Table I (CH_3Ph–PIB–$PhCH_3$) and II (B1).

Table III
Characterization of PMMAs Used

			tacticity, %			
sample	$\bar{M}_n{}^a$	$\bar{M}_w/\bar{M}_n$	s	h	i	T_g, °C
s1	11 900	1.16	76.3	20.5	3.2	102.1
i1	4 700	2.29	10.8	6.5	82.7	51.8
i2[b]	65 500	2.49	12.3	19.1	68.6	67.9

[a] By GPC, caibrated by polystyrene standards. [b] Purchased from Polysciences Inc.

3.2. DSC Studies. Figure 3 shows evidence for stereocomplex formation upon solution-mixing of iPMMA plus sPMMA and iPMMA plus sPMMA–PIB–sPMMA. Specifically, the trace CO (for control) is the DSC thermogram of a 1/2 (w/w) iPMMA/sPMMA blend of iPMMA ($\bar{M}_n$ ~ 4700) and sPMMA ($\bar{M}_n$ ~ 11 900). The blend was prepared by the procedure given in ref. 11. Stereocomplexation is evident by the strong endotherm at ~162 °C. The minor shoulder at ~86 °C is probably due to a minor amount of uncomplexed material.

Trace B1 is the thermogram of the triblock, as specified in Table II. It shows a distinct low-temperature transition due to the PIB microdomain; however, the high-temper-

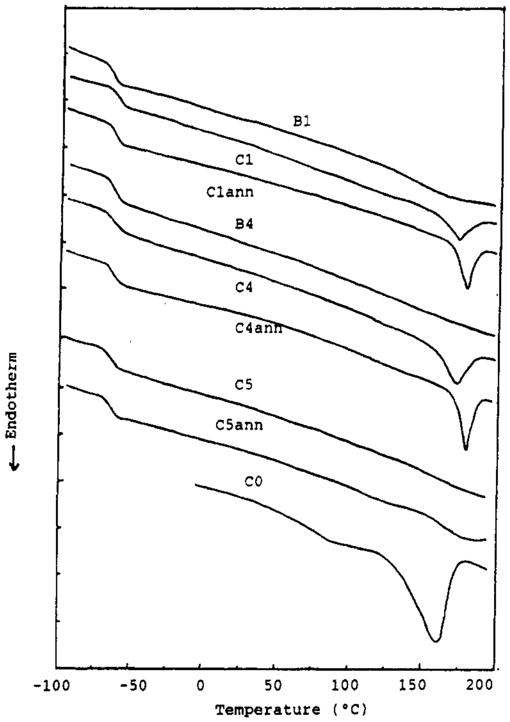


Figure 3. DSC thermograms of sPMMA-PIB-sPMMAs and iPMMA/sPMMA-PIB-sPMMA/iPMMAs. C1, C4, and C5 were prepared, respectively, by blending B1 + i1 and B5 + i2. The total PMMA contents of these blends were 28, 35, and 29%, respectively.

ature transition due to the sPMMA is very diffuse because the relatively low amount and low molecular weight sPMMA is the product. Trace C1, obtained with a blend of homo-iPMMA plus B1 triblock, exhibits the low-temperature transition and a strong endotherm at ~172 °C indicating stereocomplexation. Trace $C1_{ann}$ shows the thermogram of the same blend after annealing for 24 h at 140 °C. These annealing conditions have been found by earlier authors[7,8] to maximize stereocomplex formation. The high-temperature transition due to the stereocomplex became much stronger and shifted to a higher temperature (~178 °C), indicating enhanced stereocomplexation. The three thermograms, B4, C4, and $C4_{ann}$, obtained with triblock B4 (see Table II), its blend with iPMMA, and the latter after annealing, indicate the same trends obtained with a TPE having a relatively higher molecular weight hard block. Evidently blending of iPMMA with sPMMA-PIB-sPMMA, particularly after annealing, produces stereocomplexes with enhanced thermal transitions relative to the starting materials.

In the above experiments the molecular weights of the iPMMA homopolymer (~4700) and the sPMMAs in the triblocks (~7000 and ~9000) were not too far from each other. A series of experiments were carried out in which these molecular weights were quite dissimilar; i.e., iPMMA ~ 65 500 and sPMMA ~ 7300. Thermograms of C5 and $C5_{ann}$ show the results. Apparently, when the molecular weights of the PMMAs are very different, significant stereocomplexation does not occur even after annealing (the diffuse endotherm at ~170 °C may indicate a limited extent of stereocomplex formation).

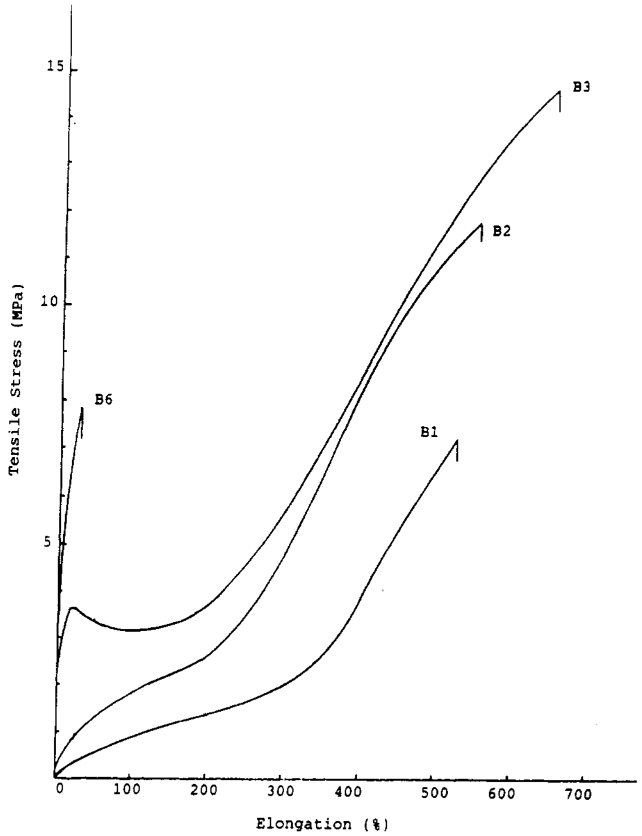


Figure 4. Stress-strain curves for sPMMA-PIB-sPMMA triblocks.

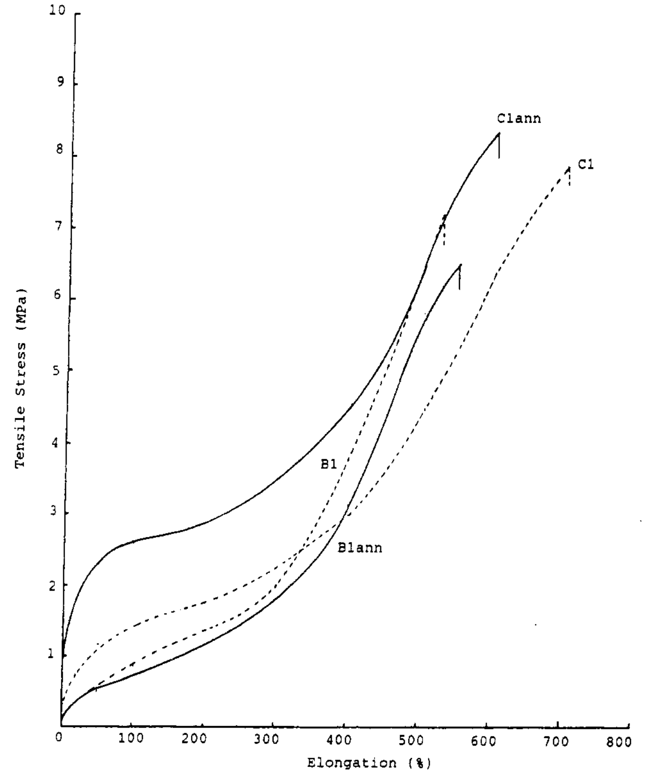


Figure 5. Stress-strain curves for sPMMA-PIB-sPMMA triblock (B1 in Table II) and a blend with iPMMA (C1; B1 + i1).

3.3. Tensile Properties and Hardness. Efforts were made to produce clear films for testing of physical properties. Initial castings of sPMMA-PIB-sPMMA from THF (good solvent for both PIB and PMMA) yielded hazy films (pig skin surfaces). In contrast, iPMMA/sPMMA-PIB-sPMMA/iPMMA stereocomplexes needed about a day longer for casting because of the higher viscosity of the solution but yielded clear smooth films under the same conditions. The initially higher viscosity of the latter solutions may have lengthened the time of THF evaporation and gave better microphase-separated, smaller

Table IV
Tensile Properties of sPMMA-PIB-sPMMAs and iPMMA/sPMMA-PIB-sPMMA/iPMMAs

	B1[a] (B1$_{ann}$)[c]	B2[a]	B3[b]	B4[a] (B4$_{ann}$)[c]	B6[a]	C1[a] (C1$_{ann}$)[c]	C4[a] (C4$_{ann}$)[c]
total PMMA, wt %	20	27	34	27	38	28	35
modulus (300%), MPa	2.03 (1.65)	4.77	5.83			2.25 (3.52)	2.39 (4.38)
tensile strength, MPa	7.23 (6.52)	11.82	14.52		7.69	7.90 (8.42)	6.20 (5.48)
elongation, %	525 (550)	550	650		25	700 (600)	700 (550)
hardness (Shore A)	42 (40)	48	63	49 (48)	68	53 (55)	66 (72)

[a] Cast from ~20% THF solution. [b] Cast from ~20% THF/toluene 50/50 (v/v) solution. [c] B1$_{ann}$, B4$_{ann}$, C1$_{ann}$, and C4$_{ann}$ were obtained by annealing B1, B4, C1, and C4, respectively, for 24 h at 140 °C.

domain size films. By the use of 50/50 THF/toluene mixtures (toluene is a much less volatile good solvent for both PIB and PMMA) optically clear smooth films were obtained even with uncomplexed triblocks.

Figure 4 shows representative stress-strain data obtained with sPMMA-PIB-sPMMA samples whose characteristics are given in Table II. Samples B1, B2, and B6 were obtained with THF cast films, whereas B3 was produced by casting from THF/toluene. The molecular weights of the PIB phases were about the same in all samples; thus the data reflect the differences due to the sPMMA molecular weights and the casting solvent. A comparison of the data obtained with films B1 and B2 indicates strength enhancement due to increasing the molecular weight of the sPMMA block. A comparison of the data of films B3 and B6, i.e., films whose overall compositions (structure) were quite similar, shows dramatically the effect of the casting method on stress-strain properties; while film B3 obtained by very slow evaporation from THf/toluene gave a relatively strong high-modulus TPE, sample B6 prepared by casting from THF was a weak brittle solid.

The softness of these TPEs is noteworthy: films with 34-38% sPMMA (B3 and B6) exhibit 63-68 Shore A hardness by durometry. (We agree with the comment of one of the reviewers that higher tacticity PMMAs would yield higher tensiles and elongations with desirably low hardness values). Figure 5 shows representative stress-strain traces of triblock starting materials (B1), the same after annealing (B1$_{ann}$), the same after blending with iPMMA (C1), and the latter after annealing (C1$_{ann}$). Tables IV shows some additional information (durometer data) together with results obtained with other samples. A comparison of the data obtained with samples B1 and B2 shows that increasing the sPMMA content from 20 to 27% results in significant tensile strength and modulus enhancement combined with a small hardening. A look at the data of sample B3 with 34% sPMMA may indicate a further property enhancement; however, the latter information is not strictly comparable with those obtained with B1 and B2, because the casting conditions were different (see footnotes in Table IV).

A comparison of the data generated with B1 (containing 20% sPMMA) and C1 (containing about the same amount of sPMMA plus 9% stereocomplexed iPMMA) shows that stereocomplexation enhances somewhat the tensile strength and modulus and, further, that annealing of the latter yields some additional improvement.

A comparison of the results obtained with C1 and C4 shows the modulus and hardness enhancing effect due to increased total PMMA content (from 28 to 35%).

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