Novel Thermoplastic Elastomers: Polyisobutylene-*block*-polyamide Multiblocks

Bernd Zaschke[†] **and Joseph P. Kennedy***

Institute of Polymer Science, University of Akron, Akron, Ohio 44325-3909

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ABSTRACT: The synthesis and characterization of a series of novel thermoplastic elastometers, $(AB)_n$ multiblock copolymers, containing polyisobutylene as the soft phase and polyamides as the hard phase are described. First, carboxyl ditelechelic polyisobutylene prepolymers and isocyanate ditelechelic polyisobutylene prepolymers were synthesized, both of which were subsequently reacted under solution polycondensation conditions with dicarboxylic acids and diisocyanates (see eqs 1 and 2). Molecular weights and molecular weight distributions were determined by GPC and light scattering on trifluoroacetylated samples. The melting points of the polyamide hard phases were in the 223–284 °C range. The decomposition temperatures (296–337 °C) in air and nitrogen of these TPEs made by eq 1 were quite similar; in contrast, these properties of polytetrahydrofuran-based TPEs were noticeably lower in air. Melt processing of these novel PIB-based TPEs is possible.

1. Introduction

A considerable body of literature exists on the synthesis and properties of polyisobutylene (PIB)-based linear and three-arm star thermoplastic elastomers (TPE) containing a variety of hydrocarbon hard phases with T_g's[1–6] or in one case T_m[7,8] in the 100–240 °C range. In contrast, there is a dearth of information on related $(AB)_n$-type multiblocks comprising rubbery PIB blocks connected to glassy or crystalline segments, and only PIB multiblocks with polyurethane[9–11] and poly(butylene terephthalate)[12,13] hard phases have been described.

In the course of our fundamental studies aimed at the synthesis of novel PIB-based TPEs we decided to explore the possibility of preparing $(AB)_n$-type TPEs with PIB soft segments connected to polyamide (PA) as hard segments. PAs promise to yield desirably high melting crystalline blocks (mp = 220–280 °C) coupled with outstanding thermal, chemical, and environmental resistance and melt processibility, and all this for a reasonably low cost. This paper concerns initial investigations in this field and demonstrates that $(PIB-PA)_n$ TPEs exhibiting a combination of desirable properties can readily be prepared.

2. Synthetic Strategy

We have considered several alternatives for the synthesis of $(PIB-PA)_n$ multiblocks. In view of experimental limitations (i.e., immiscibility of nonpolar PIB and polar PA ditelechelic prepolymers in the melt, cumbersome preparation of NH_2-ditelechelic PIB[14] the simplest route to our target appeared to be the solution polycondensation of HOOC- or OCN-ditelechelic PIBs with various diisocyanates and dicarboxylic acids. Equations 1 and 2 show the two routes selected and explored for the synthesis of $(PIB-PA)_n$ multiblocks.

In regard to experimental conditions, we modified for our needs Chen et al.'s procedure[15] that has been developed for the synthesis of $(polyether-PA)_n$ multiblocks. Orienting experiments showed that all the envisioned polar and nonpolar ingredients could be readily dissolved in tetramethylene sulfone (TMS)/xylene, γ-butyrolactone/xylene, and TMS/*o*-dichlorobenzene mixed solvent systems at an elevated temperature. The boiling points of all these solvent systems are above 150 °C (for the mixing ratios we used), a desirable temperature for the polycondensations contemplated. Among the various catalysts employed by earlier workers to accelerate the polycondensation (e.g., 1,3-dimethyl-3-phospholene 1-oxide, 1,3-dimethyl-2-phospholene 1-oxide,[15,16] CH_3ONa, CH_3OLi, PhOLi,[17] and lithium lactamates[18]) we have selected CH_3ONa because of its commercial availability and low cost.

3. Experimental Section

3.1. Materials. Dicarboxylic acids (Aldrich Chemical Co.) were dried in vacuum (1 Torr, 25 °C, 24 h) before use. Diisocyanates (Aldrich Chemical Co. or Pfaltz & Bauer) were used without further purification. The OCN functionality was checked by back-titration with di-*n*-butylamine followed by HCl. The dicarboxylic acids and diisocyanates in Chart 1 were used.

3.2. Characterization. GPC. Molecular weights and molecular weight distributions were determined by using a Waters high-pressure GPC instrument equipped with RI, UV, and a three-angle light scattering detector (Minidawn by Wyatt Technology Corp.). Five Ultrastyragel columns (100, 500, 1000, 10 000, 100 000 Å) and THF solutions (injection 100 μL) were used. The calibration curve was obtained with PIB standards. Because of the strong hydrogen bonds between the amide groups, polyamides are insoluble in THF; however, after *N*-trifluoroacetylation of the amide groups (see eq 3), both homopolymers and block copolymers became soluble in THF, rendering GPC and light scattering characterization possible.[19] Thus all our GPC determinations have been carried out by the use of trifluoroacetylated polymer.

NMR. ^1H- and ^{13}C-NMR spectra were obtained at ambient temperatures by a Varian Gemini-200 spectrometer operating at 200 and 50 MHz, respectively, using $CDCl_3$ solutions in 5 mm tubes. Sample concentrations were 20 mg/mL for proton and 300 mg/mL for carbon spectroscopy. Typically, 128 transients were accumulated for the proton spectra with 60° pulses (18 μs), 2.7 s acquisition time, and 4 s delay. ^{13}C-NMR spectra were obtained with the ^1H decoupler turned on only during the acquisition time to suppress the NOE (gate decoupling). The following parameters were used: 60° pulses (14.7 μs), 1 s acquisition time, 4 s delay, and 12 h accumulation.

DSC: (DSC 2910 DuPont Instruments) sample weight, 5–12 mg; heating rate, 10 °C/min. All the DSC data reflect the second heating cycle.

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* Corresponding author.

[†] Present address: BASF Schwarzheide GmbH, 01986 Schwarzheide, Germany.

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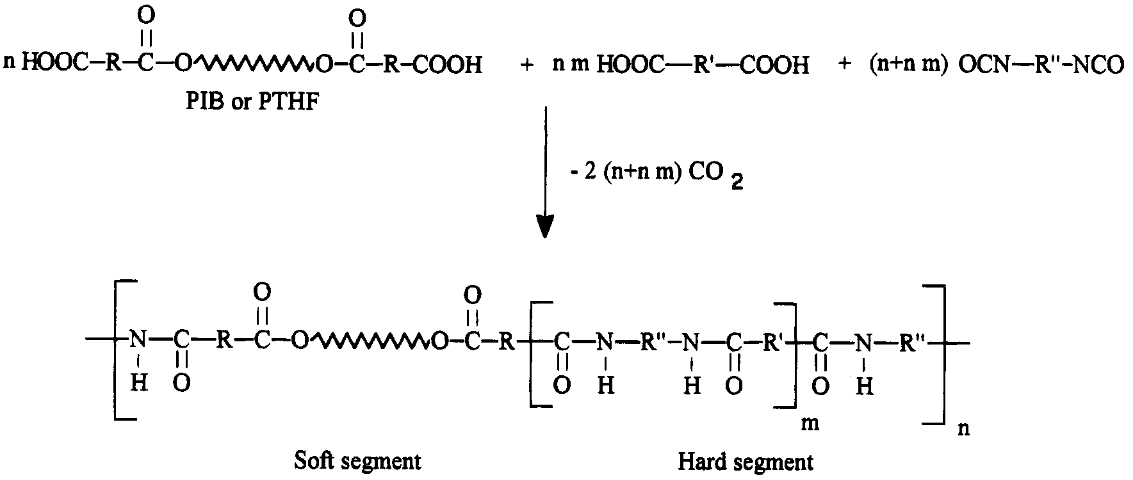

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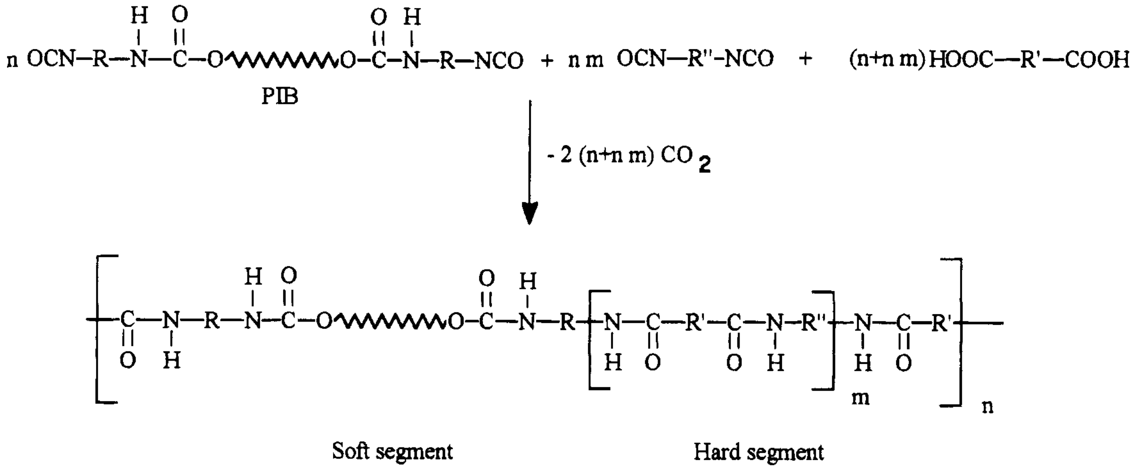

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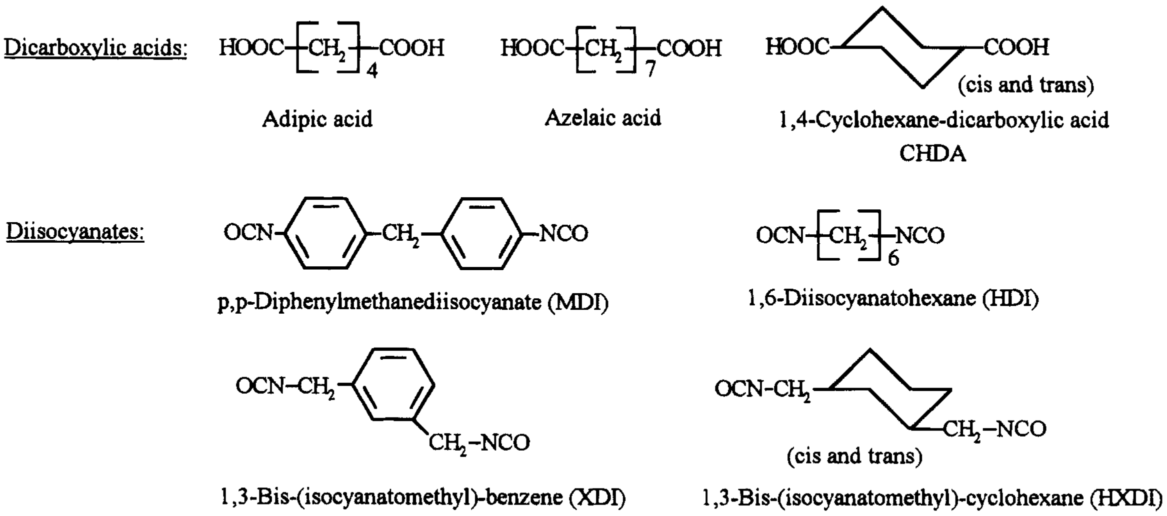
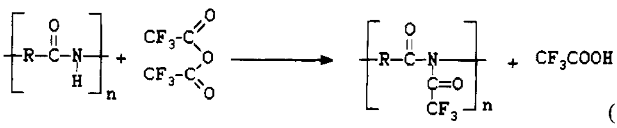
Chart 1





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TGA: (DuPont Instruments, 951 Thermogravimetry Analyzer) heating rate, 10 °C/min; gas flow, 60 mL/min, N_2 or air. Decomposition temperature = 5% weight loss.

Mechanical Properties. Compression-molded sheets were obtained in a Carver press (≈20 °C above the mp of the PA moieties, at ≈50 kN). Mechanical properties were determined on dumbbells (British Standard 903, Part A2, Type E) punched from the above sheets by the use of a Monsanto Tensiometer 10. Rate: 50.8 and 508 mm/min.

3.3. Preparation of Soft Segment Prepolymers. HO–PTHF–OH. Hydroxyl ditelechelic PTHF (Aldrich Chemical Co.) was used without further purification. Product characteristics are shown in Table 1. The subscripts in the symbols in the column heading indicate $\bar{M}_N$ of the PIB or PTHF segments.

HO–PIB–OH. Hydroxyl ditelechelic PIBs were prepared by a well-established procedure outlined by eq 4.

The aim was to prepare prepolymers of $\bar{M}_N \approx 1000$ and ≈2000 and narrow molecular weight distributions, capped by exactly two terminal HO groups ($\bar{F}_N$ = number average

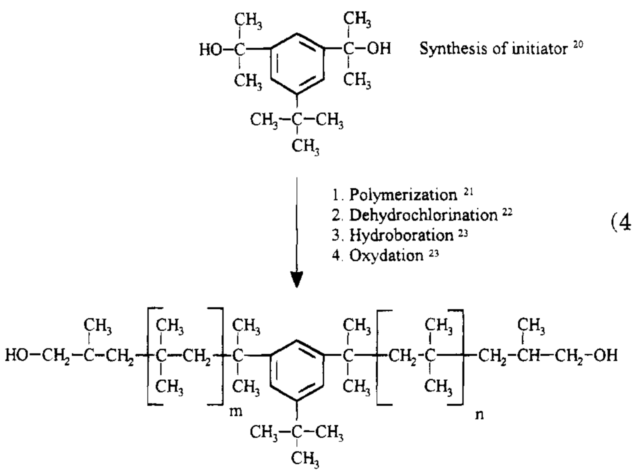
Table 1. Characteristics of Hydroxyl ditelechelic Prepolymers

	HO−PTHF$_{1000}$−OH	HO−PIB$_{1000}$−OH	HO−PIB$_{2000}$−OH
$\bar{M}_N$ (^{13}C-NMR)	1000	975	1950
$\bar{M}_N$ (^{1}H-NMR)	930	1060	2140
HO $\bar{F}_N$ (^{1}H-NMR; ^{13}C-NMR)		1.97	1.98
$\bar{M}_W/\bar{M}_N$ (GPC)	1.535	1.057	1.036
T_g or mp (°C)	23 (mp)	−49 (T_g)	−61 (T_g)
dec temp. (°C) in N_2	274	358	382

Table 2. Molecular Weight, Molecular Weight Distribution, and Composition of Carboxyl Ditelechelic Prepolymers

prepolymer	preparation eq	$\bar{M}_N$ (^{13}C-NMR^a)	$\bar{M}_w/\bar{M}_N$ (GPC)	product composition from GPC traces (%)	HOOC $\bar{F}_N$
HOOC−PTHF$_{1000}$−COOH	5	NA	1.78	broad trace	≈2.0^b
HOOC−PIB$_{2000}$−COOH	6	2200	1.04	92	1.93−1.95
		4270^c	1.03	8	
HOOC−PIB$_{1000}$−COOH	6	1230	1.07	90	1.93−1.95
		2320^c	1.04	10	

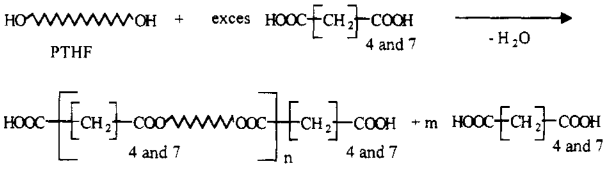
^{a} $\bar{M}_N$ by GPC are unreliable below $\bar{M}_N \approx 3000$. ^{b} Assumed value. ^{c} Chain-extended product.



(4)

terminal functionality = 2.0 ± 0.05). According to ^{13}C-NMR spectroscopy we have essentially attained our targets. The T_g's of our rather low molecular weight products, −49 and −61 °C, are higher than that of conventional high molecular weight PIB (−73 °C),[24] most likely because of the relatively large initiator fragment ($\bar{M}_N$ 216) in the statistical middle of the short PIB chain. Molecular characterization data are collected in Table 1.

HOOC−PTHF−COOH. This prepolymer was prepared by Chen et al.'s process.[15]



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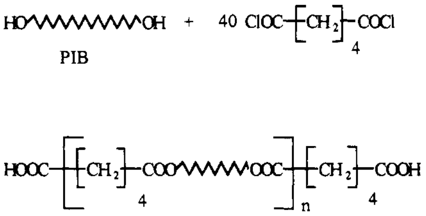
The advantage of this route is that the product can be used in subsequent polycondensations without prior purification since the unreacted adipic and azelaic acids are consumed during PA formation. ^{1}H- and ^{13}C-NMR analyses showed that the terminal hydroxyl groups were quantitatively converted. Table 2 shows the data collected.

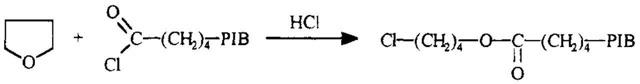
HOOC−PIB−COOH. Efforts to adapt the route used for the synthesis of HOOC−PTHF−COOH (see above) for the preparation of HOOC−PIB−COOH failed because of excessive foaming, an even after close to 3 days of refluxing (Dean-Stark apparatus), only 56% of the hydroxyl groups have reacted.

Various routes for the synthesis of carboxyl ditelechelic PIB have been considered. Among the available processes some gave incompletely COOH-functionalized products[6,25,26] and another was deemed cumbersome.[27] The best process to date seemed to be that developed by Liao and Kennedy[28] which was used in the present investigations:



(6)

A solution of 20 g of HO−PIB−OH (2 wt % in THF) was added dropwise to charges of 40-fold excess (to suppress chain extension) of adipoyl chloride. The THF solvent employeed by the earlier authors[28] consumed 2−5% of the PIB end groups, probably by the following side reaction:



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By substitution of benzene for THF this side reaction has been avoided and useful products were obtained. After removing the excess adipic acid, water, and pyridine, ^{1}H-NMR, ^{13}C-NMR, and GPC characterizations indicated satisfactory end functionalization and the formation of only a small amount (8−10%) of chain-extended product. Table 2 summarizes the characterization data.

OCN−PIB−NCO. The target isocyanate ditelechelic PIB employed in synthesis by eq 2 was prepared by reacting HO−PIB−OH with excess MDI (eq 8). Although the HO−PIB−OH + MDI reaction has been studied extensively,[9−11]conditions for the preparation of the sought prepolymer (i.e., by the use of HO−PIB−OH plus excess MDI) have not been described and had to be developed. Table 4 (feed composition) shows the reagent stoichiometries employed. After removal of the solvent, the products were used in polycondensations without further purification. Depending on the HO−PIB−OH:MDI ratio, the products contained different amounts of chain-extended PIB and unreacted MDI. Table 3 provides this information, generated by GPC (RI) eluograms. In the course of the polycondensation the excess MDI is consumed and gives the hard PA phase.

A typical synthesis was carried out as follows: Under a blanket of nitrogen in a four-neck flask equipped with a magnetic stirrer, pressure-equalized dropping funnel, thermometer, and a reflux condenser, a solution (25 wt %) of the diisocyanate in THF (dried over CaH_2) was added to a solution of 4−7 g of HO−PIB−OH (25 wt %) in dry THF. Table 4 shows the HO−PIB−OH:MDI ratio used. The mixture was refluxed for 2.5 h, and after removing the THF by vacuum, diisocyanate telechelic prepolymer was obtained.

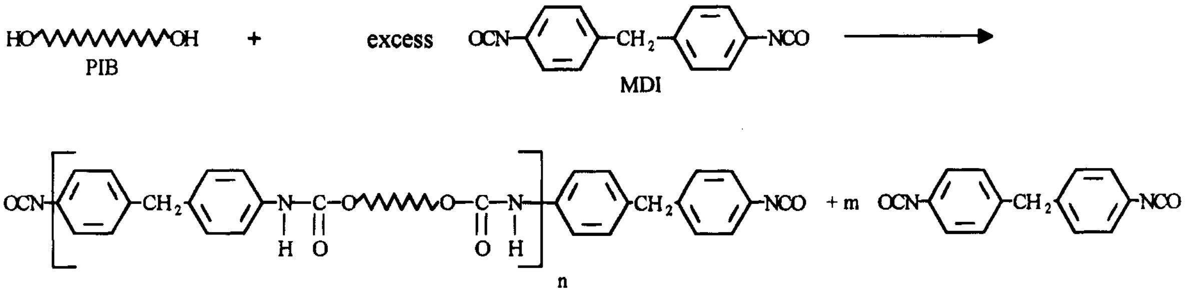

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Table 3. Composition of Isocyanate Ditelechelic Polyisobutylenes[a]

products	unreacted MDI m (eq 8)	OCN–PIB–NCO $n = 1$ (eq 8)	once chain extended $n = 2$ (eq 8)	twice chain extended $n = 3$ (eq 8)	three times chain extended $n = 4$ (eq 8)
OCN–PIB$_{1000}$–NCO (**1**)	2.4	20.1	27.4	50.1	
OCN–PIB$_{1000}$–NCO (**2**)	4.1	21.7	21.7	16.5	36.0
OCN–PIB$_{1000}$–NCO (**3**)	48.3	48.0	3.7		
OCN–PIB$_{1000}$–NCO (**4**)	47.3	47.8	5.9		
OCN–PIB$_{1000}$–NCO (**5**)	43.7	56.3			

[a] Characterization by GPC; % values calculated from RI-signal area.

3.4. Polycondensation. Synthesis of Polyamides (PA) and Multiblocks (PTHF-PA)$_n$ and (PIB-PA)$_n$ by Eq 1. The syntheses of PAs, (PTHF–PA)$_n$, and (PIB–PA)$_n$ according eq 1 (see section 2) were carried out by modifying Chen et al.'s solution polycondensation method.[15] The synthesis of the PAs and the PTHF-based multiblocks were carried out in TMS. Because of the simultaneous use of polar and nonpolar ingredients in the (PIB–PA)$_n$ synthesis, we employed polar/nonpolar solvent mixtures, such as TMS/xylene. Polycondensation conditions are described in Table 4.

A typical polycondensation was carried out under a blanket of nitrogen in a four-neck flask equipped with a magnetic stirrer, pressure-equalized dropping funnel, and thermometer. Solvents were dried over CaH_2 and distilled under a blanket of N_2. Before use all carboxyl ditelechelic prepolymers were dried in vacuum (1 Torr, 40 °C, about 5 days) to constant weight. The carboxyl ditelechelic PIB (3–8 g), the low molecular weight dicarboxylic acids, and about 20 mg of $NaOCH_3$ were dissolved in 40–55 mL of xylene/TMS (60/40 up to 75/25 vol %) under stirring and heating. (Homo polyamides PA1–PA5: 3.5–4.5 g of low molecular weight dicarboxylic acids and 20 mg of $NaOCH_3$ were dissolved in 25 mL of TMS.) At the preselected temperature a solution of diisocyanate in 20–30 mL of xylene/TMS (50/50 up to 0/100 vol %) was added dropwise (70% of the diisocyanate during the first 2 h, 80% after 3 h, and then dropwise very slowly the rest). The reaction was accompanied by gas evolution. After the reaction was completed, the charge was precipitated into 500 mL of acetone, after 12 h the precipitate was filtered out and washed for 24 h in 500 mL of methanol under stirring, and after filtration the product was dried in vacuum (1 Torr) for 5 days for 60 °C.

Synthesis of (PIB–PA)$_n$ by eq 2. The polycondensation was carried out under a blanket of nitrogen in the same reaction vessel used for the synthesis of OCN–PIB–NCO prepolymer. Solvents were dried over CaH_2 and distilled under a blanket of N_2. After addition of the low molecular weight dicarboxylic acids (NCO:COOH = 1:1.08), we added about 20 mg of $NaOCH_3$ and 35–50 mL of xylene/TMS (65:35 vol %), and the charge was quickly heated to the polycondensation temperature. Gas evolution and viscosity increase occurred during the heating period. Stirring for an additional 4 h resulted in a decrease in the viscosity. Subsequently, a solution of MDI in 20 mL of TMS was added over a period of 1 h until the desired COOH:NCO ratio (see Table 4) was achieved. The product was recovered as described above for the products by eq 1.

4. Results and Discussion

The objective of this research was the preparation of novel (PIB–PA)$_n$ multiblock TPEs consisting of thermally stable rubbery PIB blocks connected to thermally stable crystalline PA blocks having mp's in the 220–280 °C range. This combination of soft and hard moieties promised to yield not only outstanding physical–mechanical properties but also melt processibility. On the basis of our examination of background information, we concluded that the target TPEs could be made by solution polycondensation of HOOC- or OCN-ditelechelic PIBs according to eq 1 or 2 (see section 2). Thus our results can be best discussed in terms of (**1**) orienting experiments aimed at the preparation of hard PA blocks and (2) solution polycondensation of soft PIB prepolymers by eqs 1 and 2.

4.1. Synthesis of PAs. To control the mp of the PA moieties, orienting experiments were carried out with various diisocyanates plus different dicarboxylic acids, and by adipic/azelaic acid mixtures. The mixtures of adipic and azelaic acids were chosen because the mp of PAs made with different proportions of these acids can be readily controlled over the desirable 240–320 °C range.[29]

The first group of data in Table 4 shows reaction conditions and corresponding results for the preparation of various PAs (PA1 to PA5).

Assuming that the polymer composition is equivalent to the feed composition (and that all amide groups have been trifluoroacetylated), the value m (see eq 1) and the average number of amide bonds per chain ($2m$) can be readily calculated from the molecular weights of the polycondensation products and the starting materials. Column 15 in Table 4 shows the estimated average number of amide bonds per chain (22–97) in the PAs obtained.

The two melting points of PA1 may be due to crystallites containing unequal proportions of adipic/azelaic acids. This PA exhibited outstanding thermal resistance (5% decomposition at 352 °C). PA2 prepared with CHDA plus MDI melted at 249 °C, was only sparingly soluble in TMS, and exhibited a barely acceptable decomposition temperature (274 °C) for melt processing. The solubility characteristics of PA3 and PA4 prepared with "kinked" diisocyanates (HXDI, XDI) were good; however, their melting points were less than desirable and exhibited poor crystallization behavior (i.e., after the first melting, repeated heating/cooling cycles by DSC gave irreproducible melting point readings). PA5 obtained with adipic acid plus HDI formed in excellent

Table 4. Experimental Conditions and Results

conditions									results									
			feed composition (molar equiv)							GPC		in eqs 1 and 2			DSC			
																hard phase		
product designation^{a}	dicarboxylic acid	diiso-cyanate	pre-poly	dicarb acid	diiso-cyan	hard phase in charge^{e} (wt %)	time (h)	temp (°C)	yield (%)	$\bar{M}_N$	$\bar{M}_w/\bar{M}_N$	m	n	amide group per chain^{g} $2m$ or $n(2m+2)$	soft phase T_g (°C)	T_g (°C)	T_m (°C)	dec temp in N_2/in air
Homo Polyamides																		
PA1	Adip/Azel^{b}	MDI	0	1	1.07	100	5.5	170	77	8000	1.40	15		30		103	232, 257	352
PA2	CHDA	MDI	0	1	1.08	100	3	170	72	5800	1.43	11		22		46	249	274
PA3	Adip/Azel	HXDI	0	1	1.08	100	5	170	28	7800	1.52	17		33		64	137^{c}	162
PA4	Adip/Azel	XDI	0	1	1.08	100	5	170	82	9300	1.64	20		40		49	130^{c}	275
PA5	Adip	HDI	0	1	1.08	100	5	170	98	20 200	1.57	48		97		102	232	305
Multiblock Copolymers from HOOC–PTHF–COOH																		
$PTHF_{1000}$–PA1 (1)	Adip/Azel	MDI	1	0.30	1.40	40	5.5	170	84	29 300	1.68	0.3	17	45	−77		194^{d}	355/277
$PTHF_{1000}$–PA2 (1)	Adip/Azel	MDI	1	2.04	3.28	58	5.5	170	96	24 800	1.75	2.04	9.5	58	−77	66	226	340/284
Multiblock Copolymers from HOOC–PIB–COOH																		
PIB_{2000}–PA1 (1)	Adip/Azel	MDI	1	3.13	4.48	35	8.5	160	75	11 800	1.37	3.13	2.8	23	−49	107	227, 255	324/320
PIB_{2000}–PA2 (1)	Adip	HDI	1	2.92	4.61	24	5.5	150	94	19 200 (93%)	2.35	2.92	5.2	41	−49	108	240^{d}	337/337
										115 000 (7%)	2.37							
PIB_{1000}–PA1 (1)	Adip/Azel	MDI	1	1.27	2.45	43	8	150	69	12 700	1.37	1.27	5.8	26	−18		284	310/296
PIB_{1000}–PA2 (1)	Adip/Azel	MDI	1	1	2.16	40	8	150	91	21 400	1.70	1	10	40	−18		223	337/332
Multiblock Copolymers from OCN–PIB–NCO																		
PIB_{1000}–PA1 (2)	Adip/Azel	MDI	1^{f}	0.92	1.92	24	5.5	144	36	29 200	2.07				−4			286
PIB_{1000}–PA2 (2)	CHDA	MDI	1^{f}	0.79	1.79	21	5.5	144	40	23 500	1.61				−8			286
PIB_{1000}–PA3 (2)	Adip/Azel	MDI	1^{f}	4.08	5.31	70	5.5	150	34	17 500	2.12				−28	123	230	286
PIB_{1000}–PA4 (2)	Adip/Azel	MDI	1^{f}	4.01	5.21	62	5.5	150	30	17 800	2.13				−21	136	279	298
PIB_{1000}–PA5 (2)	Adip/Azel	MDI	1^{f}	3.01	4.21	57	5.5	150	46	12 800	1.81				−21	123	234^{d}	267

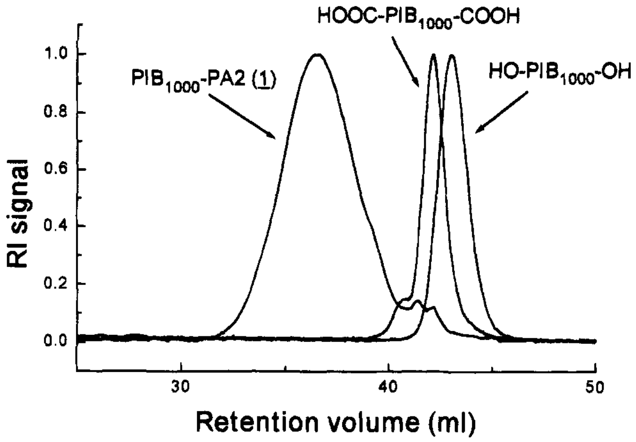

Figure 1. GPC curves of HO−PIB$_{1000}$−OH, HOOC−PIB$_{1000}$−COOH, and PIB$_{1000}$−PA2 (eq 1).

yield, was of high molecular weight, exhibited an acceptable melting point, and showed excellent thermal resistance. The repeat structures of PA5 and nylon-6,6 are, necessarily, identical; however our PA exhibits mp = 232 °C (in contrast to commercial nylon-6,6 with mp = 265 °C[30] most likely because the molecular weight of the former is lower than the conventional material.

According to these experiments PA1 and PA5, because of their relatively high melting points and excellent thermal resistance, appear suitable to provide the hard phases in (PIB−PA)$_n$ multiblock copolymers.

4.2. Multiblock Synthesis by Eq 1. As outlined in section 2 (see eq 1), (PIB−PA)$_n$s were synthesized by reacting HOOC−PIB−COOH plus dicarboxylic acids with stoichiometric amounts of diisocyanates (small excess). Since the prepolymers were prepared by eq 5 or 6, the hard/soft phase boundary in these (PIB−PA)$_n$s is predominantly formed by ester groups.

Prior to experimentation with HOOC−PIB−COOH, orienting experiments were carried out with HOOC−PTHF−COOH. The second group of data in Table 4 show respective experimental conditions and results. High yields of pale yellow high molecular weight products were obtained with mp's at 194 and 226 °C. The products were thermally quite stable in nitrogen; however, in air at ≈150 °C they started to gain weight (≈1.5%), indicating the onset of oxidation. At ≈280 °C significant decomposition accompanied by heat evolution and weight loss (burning) occurred. According to these observations the oxidative resistance of PTHF-based TPEs at temperatures above 150 °C under air are less than satisfactory.

The third group of data in Table 4 show the conditions and results of experiments carried out with HOOC−PIB−COOH. Evidently, reasonable to high yields (69−94%), high molecular weights, and desirably high mp's (from 223 to 284 °C) of products were obtained. The two mp's exhibited by PIB$_{2000}$−PA1 (eq 1) are most likely due to crystallites with different adipic:azelaic acid ratios. The same phenomenon has been observed with PA1 obtained in orienting runs (see section 4.1).

Figure 1 shows representative GPC traces obtained in the course of the synthesis of PIB$_{1000}$−PA2 (eq 1) (see Table 4). The molecular weight of the HOOC−PIB$_{1000}$−COOH prepolymer (see Table 2) is shifted to somewhat higher values (lower elution counts) relative to the HO−PIB$_{1000}$−OH starting material on account of the two additional adipic acid units. The small peak of the HOOC−PIB$_{1000}$−COOH trace indicates the presence of ≈10% chain-extended material. The large broad peak of PIB$_{1000}$−PA2 (eq 1) shifted to higher molecular weights relative to the prepolymers and the two small peaks in the 41−42 elution count range suggest a contribution by lower molecular weight components.

The samples were also characterized by light scattering (LS). Polymers with $\bar{M}_N \geq 15\,000$ gave good signals, and the molecular weight data obtained by LS and GPC were in reasonable agreement.

The values for n and m in eq 1 (n = average number of PIB segments per chain; m = average number of hard segment repeating units which can be controlled by the HOOC−PIB−COOH:HOOC−R′−COOH ratio) can be calculated by assuming that the charge and product compositions are equal (or equivalent at less than complete conversions). From n and m one can calculate the average number of amide bonds formed per chain: $n(2m + 2)$. Columns 13−15 in Table 4 show the data according to which number of amide bonds in (PIB−PA)$_n$s prepared in eq 1 were in the 23−41 range.

PIB$_{2000}$−PA2 (eq 1) was cross-linked because of the relatively large quantity of diisocyanate employed (the sum of the −COOH:NCO ratio was 3.92:4.61 (or 1:1.17)) (see Table 4). Cross-linking was due to the formation of acyl urea groups −N(−CO−NH−)−CO− which, however, could be dissolved by stirring the product for 48 h at 80 °C in a mixture of xylene/dimethylformamide (DMF)/di-*N*-butylamine (54/43/3 vol %). The final product (bimodal by GPC) contained ≈7% cross-linked material.

The products swelled in THF, CH_2Cl_2, $HCCl_3$, and xylene at room temperature, however, dissolved (27 g/L) in 90/10 THF/DMF mixtures leaving 2−5% gel. The gels could be solubilized after *N*-trifluoroacetylation,[19] which suggests that this fraction consisted mainly of PAs and/or products with high PA content.

The T_g's of the PIB$_{2000}$−PA and PIB$_{1000}$−PA multiblocks were −49 and −18 °C, respectively, which is much higher than that of the HO−PIB−OH starting materials. This T_g elevation occurs because of the relatively low molecular weights ($\bar{M}_N$ = 1950 and 975) of the soft segments (decreasing free volume in the multiblocks). We noted with interest that the T_g of a PIB-based polyurethane[10] made with HO−PIB−OH of $\bar{M}_N$ = 1800 also exhibited T_g = −49 °C. The T_g of the soft phase could be decreased by increasing the length of the PIB chain or by using PIB prepolymers containing no aromatic initiator fragments (see (PIB−polyurethane)$_n$[9,10]).

Importantly, all the PIB−PAs (eq 1) exhibited satisfactorily high mp's and high decomposition temperatures (excellent thermal stability) in both N_2 and air (see Table 4). This is in contrast to PTHF-based TPEs which showed noticeably lower decomposition temperatures in air. Efforts to generate mechanical property information were hampered by the limited quantities of materials on hand. Notwithstanding, attempts were made to attain stress/strain data with PIB$_{1000}$−PA2 (eq 1). Dumbbells punched from compression-molded transparent slightly yellow sheets gave the following data (averages of three determinations): 17 MPa tensile strength and 84% elongation at 508 mm/min and 14 MPa with 102% elongation at 50.8 mm/min. The low elongation, due to the relatively short effective PIB segments (see also above), could be enhanced by the use of higher molecular weight PIBs.

4.3. Multiblock Syntheses by Eq 2. Multiblock copolymers were obtained by the condensation of diisocyanate telechelic prepolymers with low molecular weight dicarboxylic acids. The prepolymers were OCN−PIB−NCO (partly chain extended) containing some unreacted MDI (see Table 3). Since the prepolymers are formed by the reaction of HO−PIB−OH with MDI (eq 8), the multiblock copolymers contain urethane bonds at the hard/soft phase boundary. Prepolymer synthesis and the polycondensation were carried out in one pot. As the reaction mixture was heated to 150 °C, cross-linking by allophanate groups −N(−CO−NH−)−CO−O− caused the viscosity to increase significantly, which impeded stirring and reduced the yield. Since the allophanate bond is thermally unstable and starts to release isocyanate groups above 150 °C,[30] the viscosity of the charge decreased upon further heating.

As shown by the first two lines of the fourth group of data, the HO−PIB−OH:MDI ratio for the synthesis of the prepolymers OCN−PIB_{1000}−NCO was 1:1.92 or 1.79 (see Table 4). Strongly chain extended prepolymers containing only a small amount of free MDI (see Table 3) were obtained, and only a small amount of PA hard phase was formed during the polycondensation. According to DSC PIB_{1000}−PA1 (eq 2) and PIB_{1000}−PA2 (eq 2) exhibited only one T_g at −4 and −8 °C, respectively. They are not phase separated.

When the HO−PIB−OH:MDI ratio was increased to 1:4.21−5.31 (see lines 3−5 of this group of data in Table 4), low M_N prepolymers which contained 40−50% unreacted MDI were obtained (see Table 3). Hard phase formation was sufficient for good phase separation, and the multiblocks exhibited a T_g in the −21 to −28 °C range (quite similar to the low T_g's obtained with products prepared by eq 1) and, depending on the adipic:azelaic acid ratio used, a PA mp in the 230−279 °C range. The thermostability of the products was adequate albeit somewhat lower (because of the urethane groups) than for those prepared by eq 1.

5. Conclusion

Novel $(AB)_n$ multiblock TPEs consisting of PIB soft phases and PA hard phases were synthesized as outlined by eqs 1 and 2. Syntheses by eq 1 led to high yields and gave high melting PA phases. By varying the structure of the PA, we could adjust the melting points of the hard phase in the range 223−284 °C. The polymers are thermostable in N_2 and in air up to 296−337 °C, and they are melt processible. Compression molding yielded pale yellow transparent and tough sheets. It is anticipated that the use of higher molecular weight PIB prepolymer would decrease the T_g of the soft phase and would improve the mechanical properties, particularly that of elongation.

The synthesis of the diisocyanate telechelic prepolymers (eq 8) and the subsequent polycondensation according eq 2 were carried out in one pot. The products were thermostable up to 267−298 °C under nitrogen. Because the polycondensation according eq 2 is complicated by temporary allophanate cross-linking, eq 1 appears to be the better alternative for the preparation of $(\text{PIB}-\text{PA})_n$ TPEs.

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