Synthesis and Characterization of Thermotropic Poly(benzobisthiazole)s

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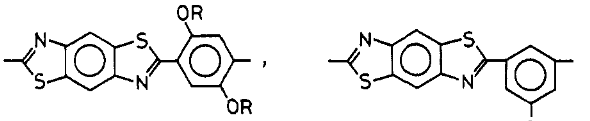
ABSTRACT: Thermotropic polymers containing the benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl unit combined with 2,5-bis(*n*-alkoxy)-1,4-phenylene (C*n*-PTBT) or 5-(alkyloxy)-1,3-phenylene units (C*n*-PIBT) were synthesized via precursor polyamides prepared by low-temperature solution polycondensation. The polyamides were converted into C*n*-PTBT or C*n*-PIBT by heating at 250 °C. All polymers except for one containing 2,5-bis(*n*-butyloxy)-1,4-phenylene showed anisotropic melt phases in the range of 280–450 °C. Characterization of these polymers by differential scanning calorimetry, thermal optical analysis, X-ray diffraction, and thermogravimetric analysis is reported. The polymers were not stable at high temperatures due to decomposition of the alkyloxy side chains.

Introduction

Recently, there has been a consistent interest in wholly aromatic polymers, especially with regard to the production of high-performance materials.[1] In this study, a series of aromatic heterocyclic rodlike polymers, such as poly[(benzo[1,2-*d*:5,4-*d'*]bisoxazole-2,6-diyl)-1,4-phenylene] (PBO),[2] poly[(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)-1,4-phenylene] (PBT),[3] and poly[(benzo[1,2-*d*:4,5-*d'*]bisimidazole-2,6-diyl)-1,4-phenylene] (PBI),[4] that form liquid crystalline solutions has been developed as a new class of materials having not only the mechanical but also the thermal capabilities. Liquid crystalline solutions of these poly(benzazole)s (PBZs) have produced highly ordered fibers of extremely high tensile modulus (close to the theoretical values) and high strength.[5] PBZs, however, show no melting temperatures and therefore they are not amenable to melt processing. This low tractability is probably the greatest limitation to broader commercial use.

Among the various studies of liquid crystalline polymers, there have been many theories and attempts to convert lyotropic liquid crystalline polymers into thermotropic liquid crystalline polymers by introducing side chains in order to create new meltable materials while retaining the stiffness of the polymer backbone.[6-10] Polyamides having flexible side chains showed thermotropicities and their thermotropic characteristics were investigated.

Many studies about substituted PBZs had also been reported to improve the solubility or mechanical property and new attractive PBZs were obtained thus far.[11-18] In these studies, PBTs having flexible side chains were prepared via silylation methods and meltability was suggested.[12] This work showed elegant synthetic procedures for obtaining substituted PBTs; however, the essential thermal behaviors and properties have not yet been clarified. Thus, it is the purpose of the present work to synthesize thermotropic PBTs by introducing flexible side chains, that is, polymers comprised of the benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl unit combined with 2,5-bis(*n*-alkyloxy)-1,4-phenylene (C*n*-PTBT) or 5-(alkyloxy)-1,3-phenylene units (C*n*-PIBT) as shown in Figure 1, and report their thermal properties.



Cn-PTBT Cn-PIBT

C4-PTBT : R= n-C_4H_9
C6-PTBT : R= n-C_6H_{13}
C8-PTBT : R= n-C_8H_{17}
C10-PTBT : R= n-$C_{10}H_{21}$
C12-PTBT : R= n-$C_{12}H_{25}$
C10-PIBT : R= n-$C_{10}H_{21}$
C12-PIBT : R= n-$C_{12}H_{25}$

Figure 1. Chemical structures of C*n*-PBTs.

Table 1. Results of Polymerization

	polyamide		C*n*-PBT
polymer	yield (%)	η_{inh} (dL/g)[1]	η_{inh} (dL/g)[a]
C4-PTBT	92	0.12	0.18
C6-PTBT	89	0.20	0.71
C8-PTBT	82	0.11	0.42
C10-PTBT	85	0.33	0.23
C12-PTBT	95	0.17	0.30
C10-PIBT	92	0.40	0.18
C12-PIBT	92	0.23	0.17

[a] Measured by using a 0.2 g/100 mL solution in methanesulfonic acid at 30 °C.

Results and Discussion

Polymer Synthesis. C*n*-PBTs were prepared by low-temperature solution polycondensation as described in Scheme 1, modified from the previous method.[19] First, polyamides 4 were synthesized from 1 and 2,5-bis(*n*-alkyloxy)terephthaloyl chloride (3) in *N*-methyl-2-pyrrolidone (NMP) at room temperature. The dihydrochloride salt 1 was used as a monomer owing to the instability of 2,5-diamino-1,4-benzenedithiol (2). Lithium carbonates were added to the solution of 1 in NMP in order to complete dehydrochlorination prior to an addition of 3 and enhance the solubility of polyamide into NMP by means of lithium chloride by product. This procedure gave precursor polyamides 4 with inherent viscosities in the range of 0.11–0.40 dL/g as measured in MSA at 30 °C (see Table 1). All polyamides showed limited solubility in MSA, which was

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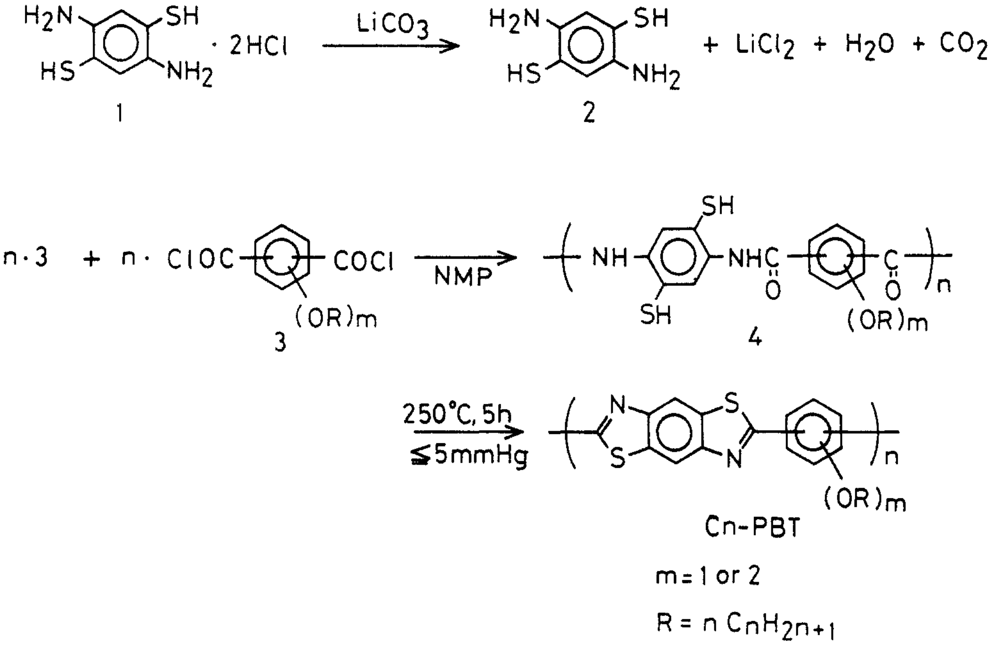
Scheme 1. Polymer Synthesis of C*n*-PBTs via Precursor Polyamides



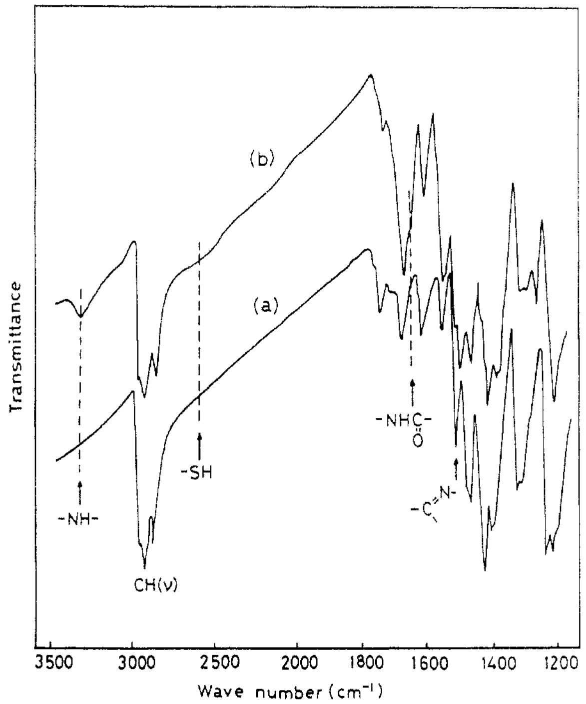


Figure 2. Infrared spectrum of (a) C6-PTBT and (b) the corresponding precursor polyamide.

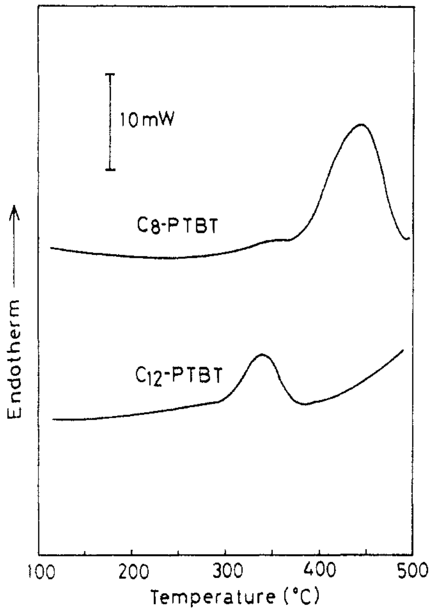


Figure 3. DSC profiles of C8-PTBT and C12-PTBT.

indicative of cross-linking. Mercapto groups of 1 seemed to be slightly susceptibile to the nucleophilic acyl substitution.

The polyamides 4 are then converted into C*n*-PBTs by thermal cyclodehydration at 250 °C for several hours under reduced pressure. The obtained C*n*-PBTs had inherent viscosities in the range of 0.17–0.71 dL/g as measured in methanesulfonic acid (MSA) at 30 °C as shown in Table 1. The formation of C*n*-PBTs was confirmed by infrared spectroscopy. A typical spectrum of C6-PTBT and the corresponding precursor polyamide are shown in Figure 2 where NH, SH, and C=O stretching bands disappear completely, the C=N stretching band of benzothiazole ring appears, and the CH stretching band does not change after heat treatment. These spectra are consistent with the proposed structure of the polyamide and C6-PTBT.

Thermal Properties. The thermotropicities of C*n*-PBTs were evaluated by DSC and thermal optical analysis under crossed polarizers. The samples for these analyses were polymerized C*n*-PBTs which were cured at 250 °C for thermal cyclodehydration of polyamides. Typical DSC profiles are shown in Figure 3 and the results are summarized in Table 2. All polymers except for C4-PTBT showed thermal transitions from solid phase to anisotropic melt phase in the range of 280 and 450 °C. C4-PTBT did not exhibit any transition up to 600 °C. These polymers are not thermally stable over 270 °C even under a nitrogen atmosphere due to the thermal instability of alkyloxy side chains as discussed later. Therefore, DSC measurements were performed with a very rapid heating rate of 100 °C/min under nitrogen and thermal optical analyses were also performed with a maximum heating rate of 40 °C/min under nitrogen in order to avoid the influence of thermal decomposition. The differences between Tend and Ts-a in Table 2 were attributed to the difference in these heating rates. Anisotropic melt phases were observed under crossed polarizers. A typical photomicrograph of an anisotropic melt phase of C10-PTBT is shown in Figure 4 and it was obtained from the specimen which was molten at 400 °C in the absence of externally applied shear and

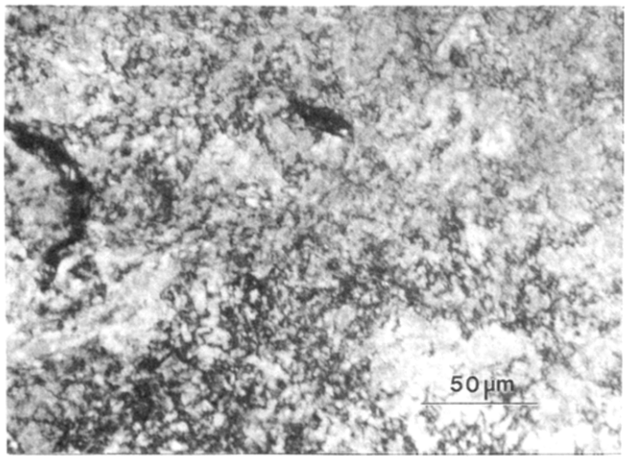


Figure 4. Photomicrograph with crossed polarizers of C10-PTBT quenched from the anisotropic melt phase.

Table 2. Results of Thermal Transition of C*n*-PBTs

polymer	composition (wt %)[a] Rs	Rb	Ts-a,[b] (°C)	DSC[c] Tend (°C)	ΔH (kcal/mol)	ΔS (cal/K·mol)
C4-PTBT[d]	35.6	64.4				
C6-PTBT	43.4	56.6	402	447.2	10.00	13.88
C8-PTBT	49.4	50.6	396	444.2	5.71	7.96
C10-PTBT	54.3	45.7	385	438.8	8.09	11.36
C12-PTBT	58.4	41.6	324	344.5	0.66	1.07
C10-PIBT	39.5	60.5	346	386.1	0.44	0.66
C12-PIBT	43.1	56.9	275	288.0	0.01	0.02

[a] Rs, weight ratio of side chains; Rb, weight ratio of phenylenebenzobisthiazole unit. [b] Ts-a, transition temperature from solid phase to anisotropic melt phase measured by thermal optical analysis with a heating rate of 40 °C/min in nitrogen under crossed polarizers. [c] Tend, peak top temperature of endothermic peak measured by DSC with a heating rate of 100 °C/min in nitrogen. [d] Thermal transition was not detected.

then quenched rapidly to room temperature to avoid thermal decomposition. However, the characteristic properties of anisotropic melt phases could not be investigated due to the following occurrence of thermal decomposition. The transition temperatures C*n*-PTBTs were higher than those of C*n*-PIBTs and decreased with the content of side chains (Rs) from C6 to C10. A drastic change was observed between C10 and C12 (see Figure 5). Here, the content of side chains (Rs) and phenylenebenzobisthiazole units (Rb) are described as follows.

$$\mathrm{Rs}\ (\%) = \frac{\text{molecular weight of side chains in repeating}}{\text{molecular weight of repeating}} \times 100$$

$$\mathrm{Rb}\ (\%) = 100 - \mathrm{Rs}$$

The decrease of transition temperatures may be explained as a diluting effect of phenylenebenzobisthiazole units by side chains. It may be interpreted that flexible side chains act like solvents of lyotropic solutions in an anisotropic melt phase and the stiff polymer backbones are solvated by side chains. However, why the drastic drop of the transition temperature exists between C10 and C12 is not yet clear. Further study is required.

The thermal stabilities of C*n*-PBTs were evaluated by thermogravimetric analysis (TGA). The results are summarized in Table 3. Thermal decomposition started around 270–300 °C under nitrogen and around 250–270 °C under air. Temperatures of 5 wt % loss and char yields at 550 °C under nitrogen correlated very well with the content of side chains (Rs) and char yields at 550 °C are in good agreement with Rb. The infrared spectra of these chars are identical with those of poly[(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-1,4(or 1,3)-phenylene] which is the polymer backbone of C*n*-PBTs. From these results, the conclusion is that the thermal instabilities of C*n*-PBTs are owed mainly to the decomposition of the alkyloxy side chains.

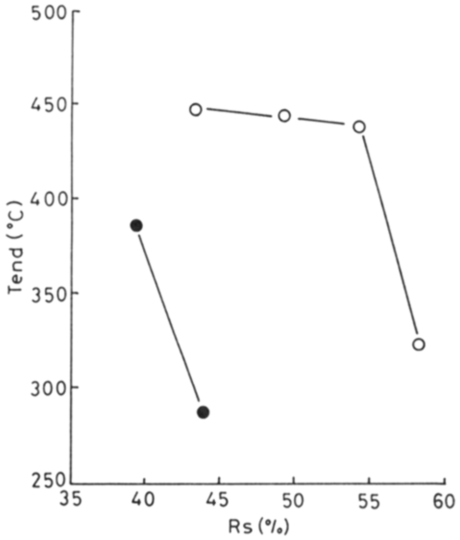


Figure 5. Anisotropic transition temperatures (Tend) plotted as a function of the weight ratio of side chains (Rs): ○, C*n*-PTBT; ●, C*n*-PIBT.

Table 3. Results of Thermal Stability of C*n*-PBTs[a]

polymer	composition (wt %)[b] Rs	Rb	onset (°C) nitrogen	air	5 wt % loss (°C) nitrogen	air	char yield[c] (wt %)
C4-PTBT	35.6	64.4	298	260	370	333	61.9
C6-PTBT	43.4	56.6	294	260	373	322	58.6
C8-PTBT	49.4	50.6	286	266	356	324	53.2
C10-PTBT	54.3	45.7	280	252	350	318	46.6
C12-PTBT	58.4	41.6	278	252	336	306	42.9
C10-PIBT	39.5	60.5	276	268	375	323	62.6
C12-PIBT	43.1	56.9	275	265	365	320	58.2

[a] Evaluated by TGA performed with a heating of 10 °C/min. [b] Rs and Rb are the same as described in Table 2. [c] Residue at 550 °C under nitrogen.

Conclusion

Thermotropic PBTs having long alkyloxy side chains (C*n*-PBTs) were obtained from precursor polyamides by low-temperature solution polycondensation and following thermal cyclodehydration at 250 °C.

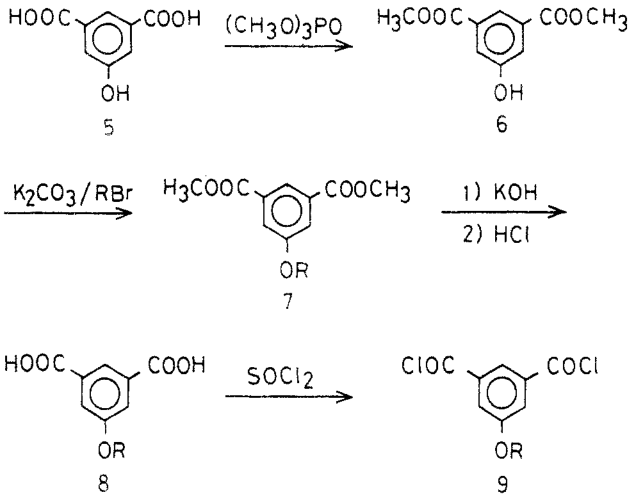
C*n*-PBTs except for C4-PTBT showed a thermal transition from a solid phase to an anisotropic melt phase in the range of 280 to 450 °C. Polymers having longer side chains had lower transition temperatures and it appeared that the transition temperature was controlled by the length of side chains. These polymers, however, were not stable at high temperatures even under nitrogen, due to the decomposition of alkyloxy side chains and, therefore, the characteristic properties of anisotropic melt phases could not be investigated in detail.

Experimental Section

Monomer Synthesis. 2,5-Diamino-1,4-benzenedithiol Dihydrochloride (1). This monomer was prepared as described by Wolfe.[3]

2,5-Bis(*n*-alkyloxy)terephthalic Acid Chlorides. To a solution of 2,5-dioxo-1,4-cyclohexane-2,5-dicarboxylic acid diethyl ester obtained from Aldrich (0.078 mol) in 60 mL of concentrated sulfuric acid was added bromine (0.156 mol) at 0 °C under vigorous

Scheme 2. Synthesis Routes of 5-(*n*-Alkyloxy)isophthaloyl Chlorides



stirring. After being stirred for 3 h at 0 °C, the reaction mixture was poured into ice–water. The pale yellow solid was collected by filtration. The crude product was stirred with 10% aqueous sodium bisulfite and then washed with water until the water was no longer acidic. Two recrystallizations from alcohol yielded pale yellow needle-like crystal of diethyl 2,5-dihydroxyterephthalate (yield 51%): mp 134–135 °C; IR (KBr) 3500–3100 cm^{-1} (OH), 3069 cm^{-1} (aromatic CH), 2977–2855 cm^{-1} (aliphatic CH), 1685 cm^{-1} (C=O). Anal. Calcd for $C_{12}H_{24}O_6$: C, 56.69; H, 5.55. Found: C, 56.75; H, 5.63. The diethyl 2,5-dihydroxyterephthalate was then converted to **3** according to the procedures described in the literature.[7]

5-(*n*-Alkyloxy)isophthaloyl Chlorides 9. These monomers were synthesized by the reaction shown in Scheme 2 by the procedure in the literature.[20] To a solution of **5** obtained from Mitsubishi Gas Chemical (0.055 mol) in 25 mL of xylene were added trimethyl phosphate (0.796 mol) and 50 mL of pyridine. After being stirred for 30 min at reflux, the reaction mixture was allowed to cool and 200 mL of chloroform was added. The reaction mixture was washed with water several times. Evaporation of the chloroform and recrystallization from benzene with charcoal yielded white needle-like crystal of **6** (yield 66%): mp 157–158 °C; IR (KBr) 3700–3100 cm^{-1} (OH), 3000–2960 cm^{-1} (aromatic CH), 1725 cm^{-1} (C=O). Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80. Found: C, 56.99; H, 4.94.

Compound **6** (0.048 mol) was refluxed with powdered potassium carbonate (0.48 mol) in 300 mL of acetone for 10 min and then an excess of *n*-alkyl bromide (1.20 mol) was added to the solution. The reflux of the reaction mixture was continued until the yellow color had disappeared. After the solid potassium bromide and excess potassium carbonate were filtered off, evaporation of acetone and excess *n*-alkyl bromide gave the crude product. Recrystallization from petroleum ether yielded **7**.

Compound **7** was then heated at reflux in 110 mL of 30% aqueous potassium hydroxide under a slow stream of nitrogen for 4 h. The reaction mixture was allowed to cool to room temperature and then acidified with 6 N hydrochloric acid. The white solid was collected by filtration and washed with water. Recrystallization from glacial acetic acid yielded the corresponding **8**.

Compound **9** was prepared from **8** according to the procedures described in the literature.[7] Compound **9** was purified by recrystallization from dried hexane. The yields, melting points and results of elemental analyses of **7**, **8**, and **9** are tabulated in Table 4.

Polymer Synthesis. In a 100-mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet was placed a mixture of **1** (5.97 mmol) and powdered lithium carbonate (5.97 mmol) in 14.6 mL of NMR, and this solution was stirred under a slow stream of nitrogen at room temperature for 20 min. Into this solution was added a solution of **3** (5.97 mmol) in 24.1 mL of NMP under vigorous stirring. The reaction was allowed to proceed for 12 h at room temperature under a nitrogen atmosphere. The viscous reaction mixture was poured into ethanol and the precipitate was collected by filtration. Washing with methanol followed by drying at 50 °C under reduced pressure yielded polyamide **4**. Heating **4** at 250 °C for 4 h under reduced pressure afforded C*n*-PBTs. The results of elemental analyses are found in Table 5. For obtaining C12-PTBT, C10-PIBT, and C12-PIBT, the corresponding **4** was synthesized in a mixture of cyclohexanone and NMP instead of NMP alone.

Table 4. Results of Synthesis of Compounds 7, 8, and 9

compd	R	yield (%)	mp (°C)	elem anal.[a] C	elem anal.[a] H
7	n-$C_{10}H_{21}$	50	50–51	68.55 (68.33)	8.63 (8.61)
7	n-$C_{12}H_{25}$	66	58–59	69.72 (69.81)	9.03 (9.05)
8	n-$C_{10}H_{21}$	93	218–219	67.05 (67.06)	8.12 (8.13)
8	n-$C_{12}H_{25}$	86	169–170	68.51 (68.55)	8.63 (8.53)
9	n-$C_{10}H_{21}$	79	32–34	60.08 (60.17)	6.66 (6.73)
9	n-$C_{12}H_{25}$	92	42–43	62.07 (62.02)	7.25 (7.29)

[a] Found (calcd).

Table 5. Results of Elemental Analysis of C*n*-PBTs

polymer	elem anal. (found/calcd) C	H	N	S
C4-PTBT	62.67/64.36	5.35/5.40	6.53/6.82	14.62/15.62
C6-PTBT	66.13/66.92	6.48/6.48	5.64/6.00	12.79/13.72
C8-PTBT	68.28/68.73	7.37/7.33	4.90/5.36	11.36/12.27
C10-PTBT	69.15/70.55	8.01/8.01	4.59/4.84	10.38/11.08
C12-PTBT	71.39/71.88	8.72/8.57	3.85/4.41	9.02/10.10
C10-PIBT	67.47/65.72	6.35/5.98	6.41/6.39	13.57/14.62
C12-PIBT	68.44/66.92	6.92/6.48	6.06/6.00	12.84/13.72

Polymer Characterization. Inherent viscosities were measured at 30 °C in 0.2% methanesulfonic acid solution (MSA). Transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC) and thermal optical analysis. DSC was performed using a Perkin-Elmer DSC 7 at a heating rate of 100 °C/min in nitrogen. Indium served as a reference for enthalpy estimations of transitions. Thermal optical analysis was performed using a Yanaco MP-500 REX-P-100 at a heating rate of 40 °C/min in nitrogen under crossed polarizers. Thermal stabilities were evaluated by using thermal gravimetric analysis (TGA) with a Shimazu DT-30. TGA was performed with a 5-mg sample and at a heating rate of 10 °C/min in nitrogen and air.

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