Hyperbranched Thermotropic Liquid Crystalline Polyesters Composed of Aromatic Ester Type Mesogens and Polymethylene Spacers

Seong-Ho Choi, Nam-Heui Lee, Soon Wook Cha, and Jung-Il Jin*

Division of Chemistry and Molecular Engineering and Center for Electro- and Photo-Responsive Molecules, Korea University, Seoul 136-701, Korea

Received April 3, 2000; Revised Manuscript Received January 12, 2001

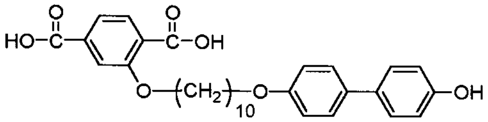
ABSTRACT: Two pairs of new isomeric hyperbranched polyesters composed of aromatic ester type mesogenic units and penta- or decamethylene spacers were prepared and their liquid crystallinity was studied. Branch points in these polymers are connected to each other through the nonmesogenic spacers. All the polyesters were found to be amorphous, but thermotropic, regardless whether the terminal groups are esters or free carboxylic acid or phenolic groups. Although these polymers form nematic phases, their apparent melt viscosity appears to be much higher than those of conventional nematic liquid crystalline polyesters (LCPs), indicating that linear alignment of the mesogens in these polymers may not be as readily achieved as in the common LCPs that are known to have very low melt viscosities in nematic state. Thermal and LC properties were studied by differential scanning calorimetry and X-ray diffractometry and by the observation of the optical textures on a polarizing microscope.

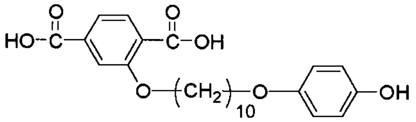
Introduction

Among a huge number of dendrimers and hyperbranched polymers many structures have been reported to be liquid crystalline (LC).[1−21] In 1992 Kim[1] reported synthesis of lyotropic LC hyperbranched aromatic polyamides by direct polycondensation of 5-aminoisophthaloyl dichloride in *N*-methylpyrrolidinone containing $CaCl_2$. It is rather interesting to note that the polyamides described by Kim are all meta-linked, and therefore they are bent rather than linear. In other words, they do not contain linear rigid rodlike structural units. Moreover, up until now, no other lyotropic hyperbranched polyamides have been reported. Around the same time Percec et al.[2] reported an exciting discovery in that a hyperbranched polymer containing disklike mesogens displays a thermotropic columnar hexagonal mesophase. They[3−5] also reported the first hyperbranched thermotropic LCs exhibiting a nematic mesophase. These were the aromatic polyethers containing flexible spacers that can undergo conformational adjustment in such a way that the conventional treelike dendritic architecture of the molecules are transformed into more compact, branched collinear structures. Since then, the Percec's group[6−11] has reported a series of pioneering findings on supramolecular self-assemblies of dendrimers. In particular, they could control the structure of self-assemblies through a systematic changes of molecular parameters such as generation number, nature of tapered tails and so on. The basic structural unit in many of their compositions which can be called mesogenic structure in a classical sense is benzylphenyl or benzylbiphenyl ether. This unit may be readily adaptable to the formation of a wide variety of supramolecular structures due to the presence of the oxymethylene bridge between the two phenylene rings.

Ringsdorf et al.[12] prepared a hyperbranched polyester composed of biphenyl *p*-oxybenzoate type mesogenic structures and decamethylene spacers. They reacted this polymer with a chirally substituted aromatic compound, and the resulting polymer revealed a thermotropic cholesteric mesophase. Kumar and Ramakrishnan[13] incorporated potentially mesogenic biphenyl units into hyperbranched poly(dioxybenzoate) containing aliphatic spacers by 1:1 copolymerization of the AB_2 type monomers with the promesogenic A-type monomer. They did not, however, observe any liquid crystallinity from the resulting polyesters.

Recently, Kricheldorf et al.[14] found that only when the degree of branching is low is stability of nematic phase achieved. They varied the branching density of hyperbranched polyesters by controlling the feed ratio between linear monomers and a branching monomer, triacetylgallic acid. We[15] previously reported LC properties of hyperbranched polyesters prepared from the following monomers:



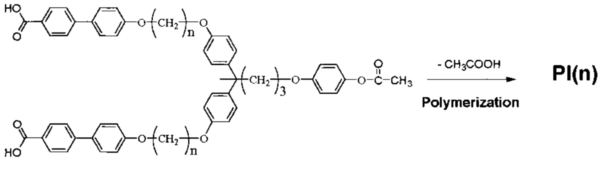


Both polymers contain aromatic ester type mesogenic units and polymethylene spacers. Branches emanate from the central part of mesogenic units through spacers. The first polymer has biphenol moieties, and the second has hydroquinone moieties. Both polymers were found to be thermotropic only when they have carboxylic acid terminals. They, however, became nonliquid crystalline, when the carboxylic terminals were esterified. This observation was explained by the assumption that the hyperbranched architectures make the formation of ordered mesophases difficult. However, the terminal carboxylic acids form cyclic dimeric structures via intermolecular hydrogen bonds, providing enough long rigid rodlike units, which results in the formation of nematic phases.

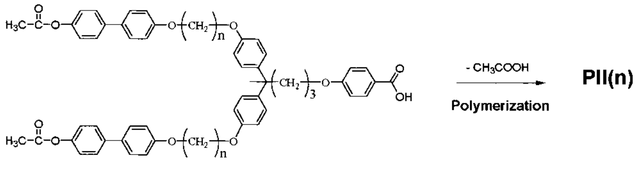
In this work, as a part of our continued effort to synthesize new thermotropic hyperbranched polyesters, we have prepared the following two series of AB_2 type monomers, and the thermotropic liquid crystallinity (LC) of the hyperbranched polyesters derived therefrom

10.1021/ma000591d CCC: $20.00

was investigated. Thermotropic LC properties of the polymers whose terminal carboxylic acid groups were esterified, also were studied. We were particularly interested in the examination if inclusion of even more rigid mesogenic units as the ones in the present polymers can lead to the formation of thermotropic LC states.



MI(n) (n= 5, 10)



MII(n) (n= 5, 10)

In the above equation, **M** stands for monomers and **PI(*n*)** or **PII(*n*)** for the polyester derived from either monomer **I(*n*)** or **II(*n*)**. The number ***n*** designates the number of the methylene groups in spacers. Thermal properties, crystallinity, and liquid crystallinity of the obtained polymers were investigated by differential scanning calorimetry (DSC), X-ray diffractometry, thermogravimetry, and also by observation of optical textures on a polarizing microscope equipped with a hot-stage.

Experimental Section

Synthesis of Monomer I(5) (MI(5)) and I(10) (MI(10)), 1-(4-Acetoxyphenoxy)-4,4-bis{4-(4′-carboxy-1,1′-biphenyl-4-oxypentamethyleneoxy)phenyl}pentane or -decamethyleneoxy)phenyl}pentane. For the synthesis of **MI(5)** and **MI(10)** refer to synthetic Scheme 1. Since all the synthetic steps involve known reactions, synthetic details are given in the Supporting Information.

Synthesis of Polymer I(5) (PI(5)) and I(10) (PI(10)) and Esterification of PI(5). Synthesis of PI(5). Monomer **I(5)** (1.0 g) was placed in a small polymerization tube equipped with a ministirrer, an argon inlet, and a vacuum connection. The oil bath in which the tube was immersed, was heated stepwise to and maintained at 160, 180, 200, 220 and 240 °C for 1 h at each temperature, and then the pressure inside the tube was reduced to 0.1 Torr and the temperature of the oil bath was kept at 240 °C for 30 min and 250 °C for 30 min. The polymer obtained was ground and subjected to Soxhlet extraction, for 3 d using acetone. Polymer thus obtained was dissolved in THF and precipitated into methanol. The polymer yield was 0.75 g (80%)

Anal. Calcd for $C_{531}H_{522}O_{81}$ (for DP = 9.0): C, 77.78; H, 6.42. Found: C, 77.91; H, 6.38.

IR spectrum (KBr; cm^{-1}): 3600−2400 (acidic O−H stretching), 3037 (aromatic C−H stretching), 2931 (aliphatic C−H stretching), 2848 (C−H stretching of $ArOCH_2-$), 1741 (ester C═O stretching), 1689 (acid C═O stretching), 1295, 1241, 1180 (C−O stretching).

^1H NMR spectrum ($CDCl_3$/DMSO, δ, ppm): 1.45−1.7 (m, 9H, $-C\mathit{H}_2CH_2CH_2O-Ar-OCO-$, $C\mathit{H}_3C(Ar-)_2-$, $-OCH_2CH_2C\mathit{H}_2CH_2CH_2O-$), 1.8−1.9 (m, 8H, $-OCH_2C\mathit{H}_2CH_2C\mathit{H}_2CH_2O-$), 2.1−2.2 (m, 2H, $-CH_2C\mathit{H}_2CH_2O-Ar-OCO-$), 3.8−4.05 (m, 10H, $-CH_2CH_2C\mathit{H}_2O-Ar-OCO-$, $-ArOC\mathit{H}_2CH_2-$, $-C\mathit{H}_2OArArCOO-$), 6.8−8.2 (m, 28H, $Ar-\mathit{H}$).

Synthesis of PI(10a). When this polymer was prepared from monomer **I(10)** in the exact same manner as for the preparation of **PI(5)**, the polymer yield was 77%.

Anal. Calcd for $C_{400}H_{452}O_{52}$ (for DP = 5.8): C, 78.86; H, 7.48. Found: C, 78.93; H, 7.33.

IR spectrum (KBr; cm^{-1}): 3600−2400 (acidic O−H stretching), 3038 (aromatic C−H stretching), 2923 (aliphatic C−H stretching), 2847 (C−H stretching of $ArOCH_2-$), 1737 (ester C═O stretching), 1686 (acid C═O stretching), 1296, 1245, 1180 (C−O stretching).

^1H NMR spectrum ($CDCl_3$/DMSO, δ, ppm): 1.35−1.8 (m, 37H, $-C\mathit{H}_2CH_2CH_2O-Ar-OCO-$, $-OCH_2CH_2\ (C\mathit{H}_2)_6\ CH_2CH_2O-$, $C\mathit{H}_3C(Ar-)_2-$, $-OCH_2C\mathit{H}_2\ (CH_2)_6\ C\mathit{H}_2CH_2O-$), 2.1−2.2 ((m, 2H, $-CH_2C\mathit{H}_2CH_2O-Ar-OCOCH_3$), 3.8−4.05 (m, 10H, $-CH_2CH_2C\mathit{H}_2O-Ar-OCO-$, $-ArOC\mathit{H}_2CH_2-$, $-C\mathit{H}_2OArArCOO-$), 6.8−8.2 (m, 28H, $Ar-\mathit{H}$).

Synthesis of PI(10b) at Higher Temperature. Another sample of **PI(10)** was prepared by heating the monomer **I(10)** for 1 h each at 170, 190, 210, 230, and 250 °C, followed by polymerization for 30 min each at 250 and 270 °C under a pressure of 0.1 Torr. The polymer sample obtained after Soxhlet extraction for 3 d using acetone was dissolved in a mixture of trifluoroacetic acid and chloroform (1:3 by volume), and then precipitated into methanol. The polymer yield was 71%.

Anal. Calcd: C, 78.83; H, 7.48. Found: C, 78.79; H, 7.31.

IR spectrum (KBr, cm^{-1}): 3600−2400 (acidic O−H stretching), 3038 (aromatic C−H stretching), 2923 (aliphatic C−H stretching), 2847 (C−H stretching of $ArOCH_2-$), 1737 (ester C═O stretching), 1686 (acid C═O stretching), 1296, 1245, 1180 (C−O stretching).

^1H NMR spectrum ($CDCl_3$/DMSO, δ, ppm): 1.35−1.8 (m, 37H, $-C\mathit{H}_2CH_2CH_2O-Ar-OCO-$, $-OCH_2CH_2\ (C\mathit{H}_2)_6\ CH_2CH_2O-$, $C\mathit{H}_3C(Ar-)_2-$, $-OCH_2C\mathit{H}_2\ (CH_2)_6\ C\mathit{H}_2CH_2O-$), 2.1−2.2 ((m, 2H, $-CH_2C\mathit{H}_2CH_2O-Ar-OCOCH_3$), 3.8−4.05 (m, 10H, $-CH_2CH_2C\mathit{H}_2O-Ar-OCO-$, $-ArOC\mathit{H}_2CH_2-$, $-C\mathit{H}_2OArArCOO-$), 6.8−8.2 (m, 28H, $Ar-\mathit{H}$).

Synthesis of PI (5-Ester) and esterification of PI(5). PI(5) (0.2 g) was dissolved in 10 mL of thionyl chloride. The solution was refluxed for 3 h under a nitrogen atmosphere. Excess thionyl chloride was removed by distillation. Dry THF (10 mL) was added to the residue to dissolve the polymeric acid chloride formed. To this solution added dropwise was a solution prepared from 2.0 mL of dry methanol,[22] 2.0 mL of dry pyridine,[22] and 6 mL of dry THF.[22] The mixture, after being stirred for 30 min at room temperature, was poured into 100 mL of distilled water, containing 10 mL of 10 M HCl. The precipitate formed was thoroughly washed with distilled water and then with methanol. After being dried, the polymer was dissolved in 10 mL of chloroform and reprecipitated into hexane. The polymer yield was 0.168 g (85.5%).

Anal. Calcd for $C_{541}H_{542}O_{81}$(for DP = 9.0): C, 77.91; H, 6.55. Found: C, 77.97; H, 6.63.

IR spectrum (KBr; cm^{-1}): 3044 (aromatic C−H stretching), 2940 (aliphatic C−H stretching), 2858 (C−H stretching of $ArOCH_2-$), 1725 (ester C═O stretching), 1279, 1245, 1184 (C−O stretching).

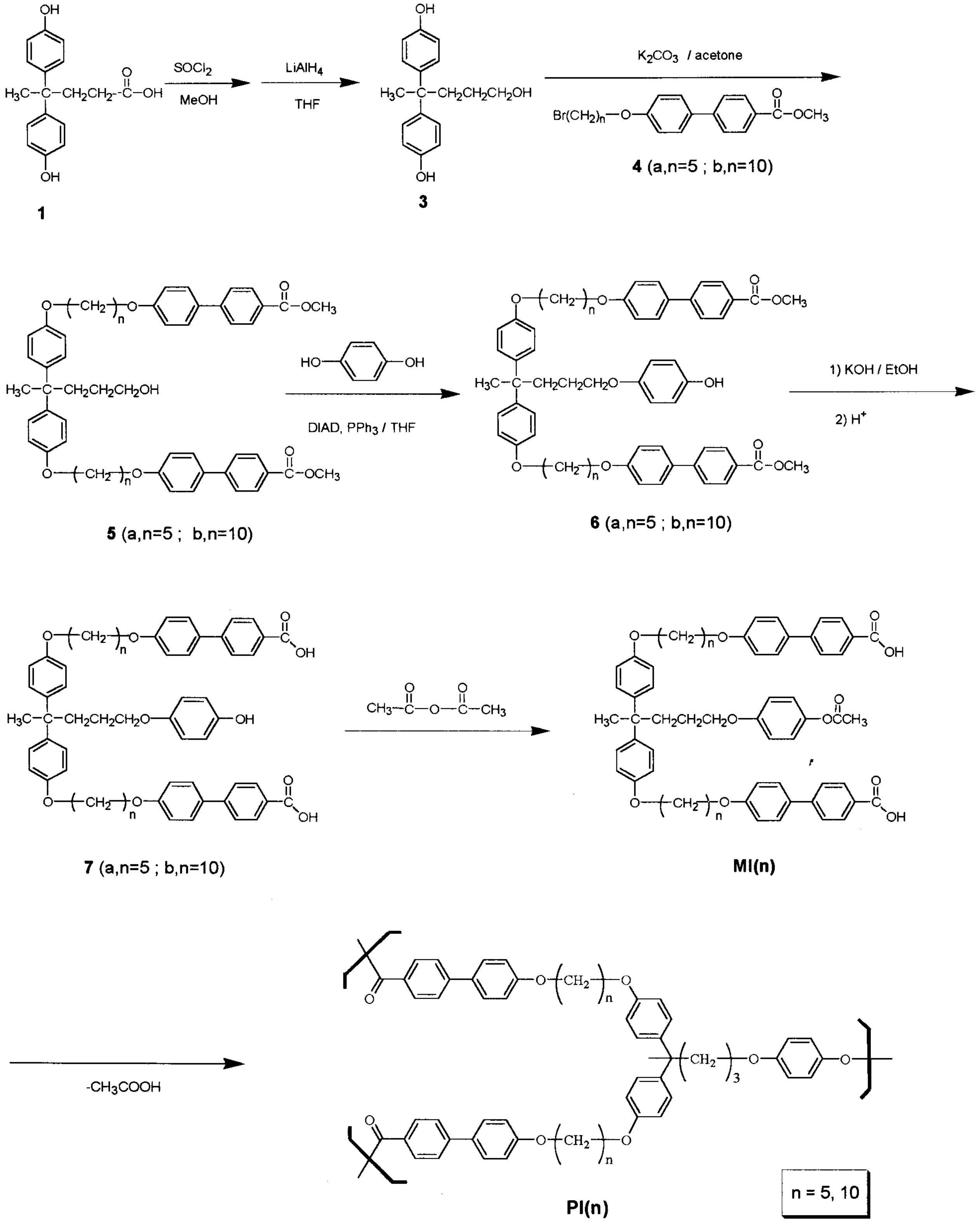
^1H NMR spectrum ($CDCl_3$; δ, ppm): 1.5−2.0 (m, 17H, $-C\mathit{H}_2CH_2CH_2O-Ar-OCO-$, $C\mathit{H}_3C(Ar-)_2-$, $-OCH_2CH_2C\mathit{H}_2CH_2CH_2O-$, $-OCH_2C\mathit{H}_2CH_2C\mathit{H}_2CH_2O-$), 2.1−2.2 (m, 2H, $-CH_2C\mathit{H}_2CH_2O-Ar-OCO-$), 3.8−4.1 (m, 13H, $-CH_2CH_2C\mathit{H}_2O-Ar-OCO-$, $-ArOC\mathit{H}_2CH_2-$, $-C\mathit{H}_2OArArCOO-$, $-CH_2OArArCOOC\mathit{H}_3-$), 6.8−8.2 (m, 28H, $Ar-\mathit{H}$).

Synthesis of Monomer II(5) and II(10), 1-(4-Carboxyphenoxy)-4,4-bis{4-(4′-acetoxy-1,1′-biphenyl-4-oxypentamethyleneoxy)phenyl}pentane or -decamethyleneoxy)phenyl}pentane. Refer to synthetic Scheme 2 for the synthesis of **MII(5)** and **MII(10)**.

Synthetic detail can be found in the Supporting Information.

Synthesis of Polymer II(5) (PII(5)) and Polymer II(10) (PII(10)). Preparation of PII(5). Monomer **II(5)** (0.50 g; 0.51 mmol) was placed in a polymerization tube equipped with a micro stirrer, an argon inlet and a vacuum connection. The oil bath in which the polymerization tube was immersed, was heated one each hour at 160, 180, 200, 220, and 240 °C, and then the pressure inside the tube was reduced to 0.1 Torr while

Scheme 1. Synthetic Route to Monomer I, MI(*n*), and Polymer I, PI(*n*)



the temperature was maintained at 240 °C. The temperature was finally raised to and kept at 260 °C for 30 min. The polymer obtained was subjected to Soxhlet extraction for 3 d using acetone. The polymer thus obtained was dissloved in a mixture of *p*-chlorophenol and 1,1,2,2-tetrachloroethane (1:1 by volume) and precipitated into methanol. The recovered polymer yield was 0.39 g (83%).

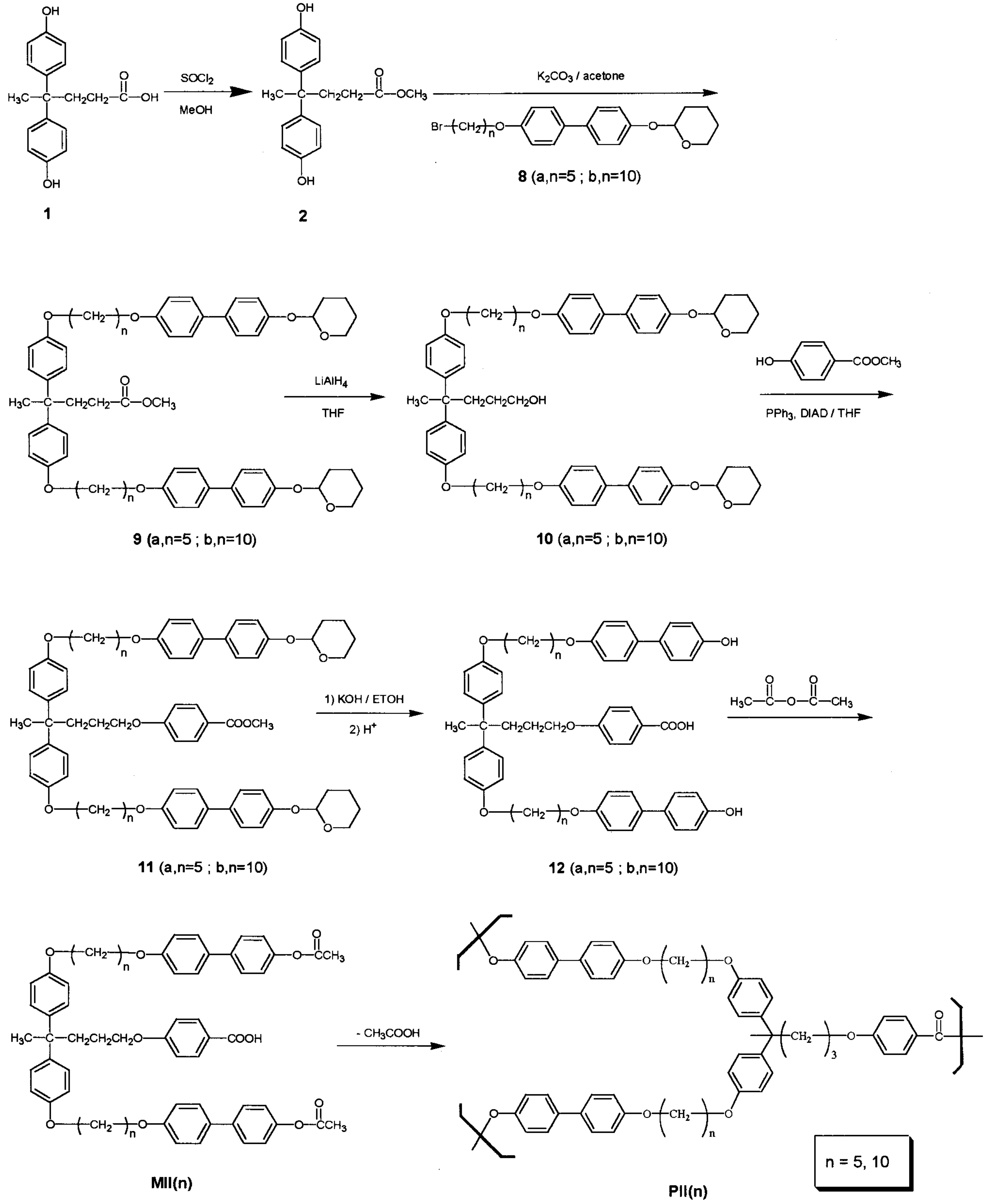
Anal. Calcd: C, 77.90; H, 6.54. Found: C, 77.97; H, 6.58.

IR spectrum (KBr; cm^{-1}): 3029 (aromatic C−H stretching), 2913 (aliphatic C−H stretching), 2842 (C−H stretching of ArOCH$_2$−), 1726 (ester C=O stretching), 1286, 1238, 1178 (C−O stretching).

^{1}H NMR spectrum (CDCl$_3$/CF$_3$COOD, *δ*, ppm): 1.3−2.4 (m, 19H, $-C\mathit{H}_2CH_2CH_2O-ArCOO-$, $C\mathit{H}_3C(Ar-)_2-$, $-OCH_2CH_2C\mathit{H}_2CH_2CH_2O-$, $-OCH_2C\mathit{H}_2CH_2C\mathit{H}_2CH_2O-$, $-CH_2C\mathit{H}_2CH_2OArCOO-$), 4.0−4.2 (m, 10H, $-CH_2CH_2C\mathit{H}_2O-Ar-COO-$, $-ArOC\mathit{H}_2CH_2-$, $-C\mathit{H}_2OArArOCO-$), 6.8−8.2 (m, 28H, Ar−*H*).

Preparation of PII(10). Monomer **II(10)** was polymerized as described above for the polymerization of **II(5)**. The polymer

Scheme 2. Synthetic Route to Monomer II, MII(*n*), and Polymer II, PII(*n*)



obtained was purified as for **PII(5)**. The recovered polymer yield was 72%.

Anal. Calcd: C, 78.92; H,7.57. Found: C, 78.98; H, 7.63.

IR spectrum (KBr; cm^{-1}): 3026 (aromatic C−H stretching), 2912 (aliphatic C−H stretching), 2832 (C−H stretching of $ArOCH_2-$), 1725 (ester C=O stretching), 1291, 1240, 1176 (C−O stretching).

^1H NMR spectrum ($CDCl_3/CF_3COOD$, δ, ppm): 1.3−2.1 (m, 39H, $-CH_2CH_2CH_2O-Ar-COO-$, $-OCH_2CH_2(CH_2)_6$-CH_2CH_2O-, $CH_3C(Ar-)_2-$, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$, $-CH_2CH_2CH_2O-Ar-COO-$), 3.8−4.0 (m, 10H, $-CH_2CH_2$-$CH_2O-Ar-COO-$, $-ArOCH_2CH_2-$, $-CH_2OArArOCOO-$), 6.8−8.2 (m, 28H, $Ar-H$).

Instrumentation and Characterization. IR and ^1H NMR spectra of intermediates, monomers, and polymers were recorded on a Bomem MB- series FT-IR instrument and a Bruker AM 300 NMR spectrometer. Elemental analyses were conducted on an Eager 200 elemental analyzer by the Organic

Research Institute of Sogang University, Seoul, Korea. Thermal properties of liquid crystalline intermediates, monomers and polymers were studied on a differential scanning calorimeter (Metter DSC 821^e) at the heating and cooling rate of 10 °C/min under a nitrogen atmosphere and also on a hot stage (Mettler FP-82HT) attached to a polarizing microscope (Olympus BH −2). Optical textures and transition temperatures could be simultaneously examined on the microscope. Indium metal was employed as the reference for calibration of temperature and enthalpy changes (ΔH). The initial inflection points from the baseline on the DSC curves were taken as the glass transition temperatures (T_gs), while the temperatures of peak maxima or minima were taken for other transitions such as melting (T_m) and isotropization (T_i).

The wide-angle X-ray diffractograms (WAXD) of polymers were obtained on a Philips X's PERT MPD instrument by the Korea Basic Science Institute, Seoul branch, Seoul, Korea. The curved graphite monochromator filtered Cu Kα line was utilized as X-ray radiation source. The solution viscosity values of the polymers were obtained using a Ubelhode-Ostwald type viscometer at 30 °C, for a solution of 0.2 g/dL in a mixed solvent of *p*-chlorophenol and 1,1,2,2-tetanchloroethane (1:1 by vol.). Absolute molecular weights of **PI(5)** and **PII(5)** were determined by gel-permeation chromatography (GPC) on a Waters GPC 410 system using THF as an eluent. Polystyrene standards were employed for calibration.

Results and Discussion

Synthesis and Liquid Crystallinity of Intermediates, Monomer I(5) (MI(5)), and I(10) (MI(10)). Monomers **I(5) (MI(5))** and **I(10) (MI(10))** were prepared via the multistep synthetic route shown in Scheme 1. The only structural difference between the two monomers lies in the length of the spacers, i.e., pentamethylene vs decamethylene. Both monomers are symmetric AB_2 type compounds containing one acetylated phenolic moiety and two biphenyl carboxylic acid groups. Compounds **5a** and **5b** were separately condensed with hydroquinone to produce compounds **6a** and **6b** in the presence of a specific condensing agent pair of diisopropyl azodicarboxylate and triphenylphosphine. This condensing agent pair[23] is known to be very efficient in the preparation of aromatic−aliphatic mixed ethers from phenolic compounds and aliphatic alcohols. To avoid the formation of dimeric ethers, excess hydroquinone was used in this step. For many steps, column chromatographic separation and purification were required to obtain pure enough compounds. Silica gel columns were utilized. The structure and purity of intermediates and the final monomers were confirmed by IR and ^{1}H NMR spectroscopy, elemental analysis, and thin-layer chromatography.

Some of the intermediates and monomers were found to be thermotropic. This is not surprising in light of the fact that many derivatives of 4′-hydroxy-4-biphenylcarboxylic acid are known to be liquid crystalline.[24] Both the dicarboxylic compounds **7a** and **7b** and the two monomers are enantiotropically liquid crystalline (LC). According to their optical textures in melt, they form nematic LC phases as shown in Figure 1, parts a and b. DSC thermograms given in Figure 2 clearly show that there are two endothermic processes in thermal transitions of these compounds. The lower temperature peaks correspond to crystal-to-nematic phase transitions and the higher temperature ones to nematic-to-isotropic phases transitions i.e., isotropization. These transitions occur reversibly on cooling too (Figure 2). The isotropization peak of **MI(10)** shown in Figure 2 is very broad centered around 195 °C on the heating thermogram due to the fact that polymerization of the monomer occurs even before reaching its isotropization temperature. The intermediate **7a**, however, appears to be much more stable exhibiting a rather sharp isotropization endothermic peak at 201.4 °C. In general, a higher degree of supercooling is observed for LC phase-to-crystal transitions or crystallization than isotropic-to-LC phase transitions. This phenomenon is observed commonly in LC compounds and suggests that much more molecular reorientation is required for crystallization than for an isotropic-to-LC phase transition.[25−27]

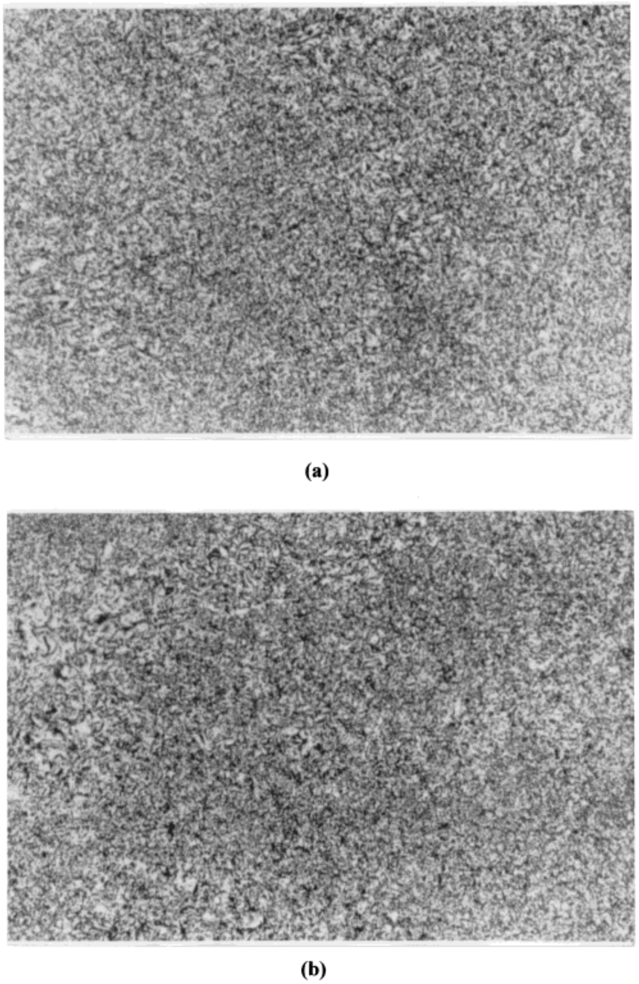

(a)
(b)

Figure 1. Photomicrographs of (a) **7b** taken at 178.2 °C and (b) **MI(10)** taken at 165.5 °C (magnification 200×).

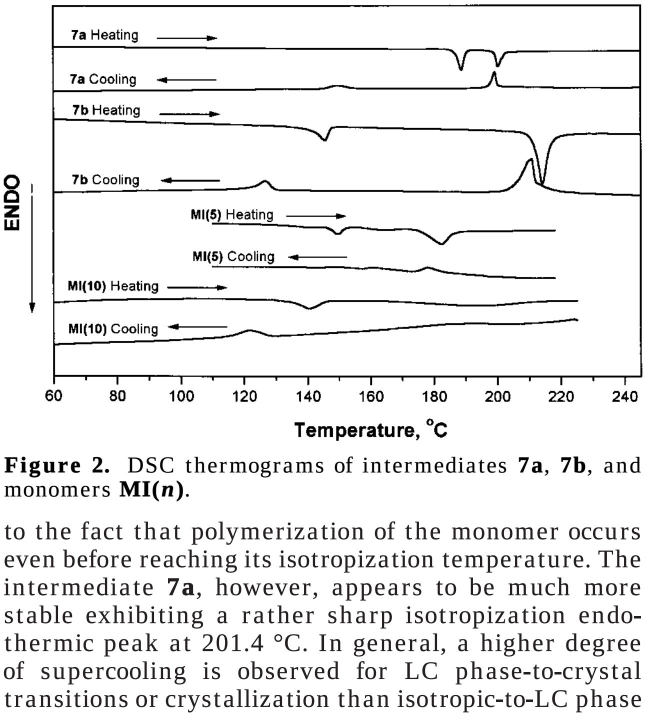
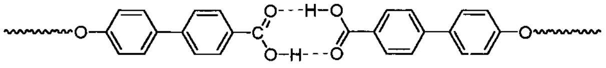


Figure 2. DSC thermograms of intermediates **7a**, **7b**, and monomers **MI(*n*)**.

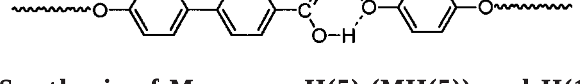
Another point to be noted is that the liquid crystalline temperature ranges ($T_i - T_m$) of compound **7b** and monomer **I(10)** are about 69 and 48 °C, respectively, which are much wider than those of **7a** (14 °C) and monomer **I(5)** (29 °C) (Table 1). Therefore, it is concluded that the compounds with longer spacers, i.e., the decamethylene groups, exhibit liquid crystallinity over a wider temperature range than the compounds with shorter spacers, i.e., the pentamethylene group.

Table 1 compares the thermodynamic parameters associated with phase transitions of compounds **7a** and **7b** and the two monomers. We note that transitions temperatures and the magnitude of thermodynamic parameters, i.e., ΔH's and ΔS's, are greater for compounds **7a** and **7b** than for the monomers. The only structural difference between the two groups of compounds lies in the fact that the intermediates **7a** and **7b** contain the phenolic hydroxy group while the monomers have the functional group esterified. Consequently, the intermediates are prone to form more hydrogen bonds than the monomers, which is expected to result in higher values in thermodynamic parameters and transition temperatures. Another interesting phenomenon observed is that the values of enthalpy and entropy changes for isotropization, ΔH_i and ΔS_i, of the present compounds are only slightly lower (compound **7a**) or much greater than the corresponding ΔH_m and ΔS_m values. Probably, this can be ascribed to the unexpectedly low ΔH_m and ΔS_m Values of **7a**, **MI(5)** and **MI(10)**, when compared with reported ΔH_m and ΔS_m values[28] for the homologous series of p−*n*-alkoxybenzoic acids, about 15−20 kJ/mol and 35−40 J/mol·K, respectively. It is very possible that the solid compounds prepared in the manner as described in this investigation have much crystal defects resulting in low ΔH_m and, thus, ΔS_m values. Nonetheless, the magnitudes of ΔH_i and ΔS_i values are unusually high, which can be ascribed to the fact that molecules in the mesophase are involved in the formation of hydrogen bonding, resulting in polymerlike chains as described below.

One common structural feature that compounds **7a** and **7b** and the two monomers, **MI(5)** and **MI(10)**, possess is the presence of two 4′-alkoxy-4-biphenylcarboxylic acid moieties in the molecules. This moiety is able to form intermolecularly hydrogen-bonded cyclic dimers through the carboxylic acid terminals. The resulting rigid rodlike structures are expected to provide the driving force for the compounds to form LC phases.[29−32]



More complicated hydrogen-bonded structures are expected from compounds **7a** and **7b** due to the presence of the phenolic hydroxy group in addition to the carboxylic acid terminals. Additional intermolecular hydrogen bonding between a carboxylic acid terminal and a phenolic hydroxyl group also is expected to produce a rigid rodlike structure as shown below:



Synthesis of Monomer II(5) (MII(5)) and II(10) (MII(10)). The synthetic route to **MII(5)** and **MII(10)** is shown in Scheme 2. Both **MII(5)** and **MII(10)** are AB_2 type monomers containing one carboxylic acid group and two acetylated biphenolic moieties. The only structural difference in the monomers again is in the length of the spacers, i.e., pentamethylene vs decamethylene. Exchange of the position of the carboxylic acid group with the position of acetoxy group in the molecules converts **MI(*n*)** monomers to **MII(*n*)** monomers.

Compounds **10a** and **10b** were separately condensed with *p*-carbomethoxy phenol, an aromatic alcohol, to yield compound **11a** and **11b**, respectively. A combination[23] of diisopropyl azodicarboxylate and triphenyl phosphine was again employed for this step. The structures of intermediates and the final monomers were confirmed as described in the Experimental Section.

None of the intermediates and the two monomers, **MII(5)** and **MII(10)**, was able to form any mesophase in melt. This is in a great contrast to the LC character of some of the intermediates and the **I(5)** and **I(10)** monomers shown in Scheme 1. A close examination of the literature[33] reveals that derivatives of 4′-hydroxy-4-biphenylcarboxylic acid have a greater tendency to be liquid crystalline than derivatives of 4,4′-biphenol. Higher polarity of the former ones is considered to be responsible for this difference.

Synthesis and General Properties of Polymers. As shown in the synthetic Schemes 1 and 2, all of the present polymers were prepared by melt polymerization. In general, monomer melts were heated stepwise either to 240 °C (**PI(5)**, **PI(10a)**, **PII(5)** and **PII(10)**) or to 250 °C (**PI(10b)**) under a steady stream of argon. Then followed the evacuation of the polymerization tube to 0.1. The polymerizing melts were finally stirred at 240−270 °C for 1 h under 0.1 Torr. The polymers obtained were purified by Soxhlet extraction using acetone followed by a dissolution-precipitation process using a solvent−nonsolvent pair, as described in the Experimental Section. **PI(5)** and **PI(10a)**, after being extracted with acetone, were dissolved in THF and reprecipitated into methanol. The solvent−nonsolvent pair used for the final purification of **PI(10b)** were a mixture (1:3 by volume) of trifluoroacetic acid and chloroform and methanol. **PII(5)** and **PII(10)** were purified by dissolving them in a mixture (1:1 by volume) of *p*-chlorophenol and 1,1,2,2-tetrachloroethane and reprecipitating into methanol. The polymers finally were washed thoroughly with methanol.

To prepare **PI(5-ester)**, **PI(5)** was reacted first with thionyl chloride to transform to the corresponding acid chloride, which was then reacted with methanol in the presence of an HCl acceptor, pyridine. **PI(5-ester)** thus obtained was purified by dissolving in chloroform and reprecipitating in hexane. The precipitate polymer was thoroughly washed with hexane.

PI(5) and **PI(10a)** were found to have relatively lower molecular weights and were soluble in THF and chlorinated hydrocarbons such as 1,1,2,2-tetrachloroethane (see Table 2). The rest of the polymers were not soluble in conventional solvents but only in a mixed solvent of *p*-chlorophenol and 1,1,2,2-tetrachloroethane. **PI(10b)** is of higher molecular weight than **PI(10a)** judging by its higher solution viscosity value and poorer solubility. **PI(10b)** was prepared at the final temperature of 270 °C in comparison with **PI(10a)** prepared at the final temperature of 250 °C. The solution viscosity value of **PI(10b)** was significantly higher ($\eta_{inh} = 0.85$ dL/g) than the value (0.41 dL/g) of **PI(10a)**.

Table 1. Phase Transition Data for Intermediates and MI Monomers[a]

compd	T_m (°C)	T_i (°C)	ΔH_m (kJ/mol)	ΔS_m (J/mol·K)	ΔH_i (kJ/mol)	ΔS_i (J/mol·K)
7a	187.8	201.4	15.41	33.44	13.19	27.81
7b	145.2	214.5	7.20	17.21	26.30	53.93
MI(5)	149.3	(178.7)[b]	2.94	6.97	7.80	17.26
MI(10)	141.8	(189.7)[b]	6.08	14.65	9.06	19.57

[a] All the data were obtained from first heating DSC thermograms at the heating rate of 10 °C/min. [b] Transition temperature ranges observed on the thermograms (see Figure 2) are so broad that the numbers are to be taken only as approximate values.

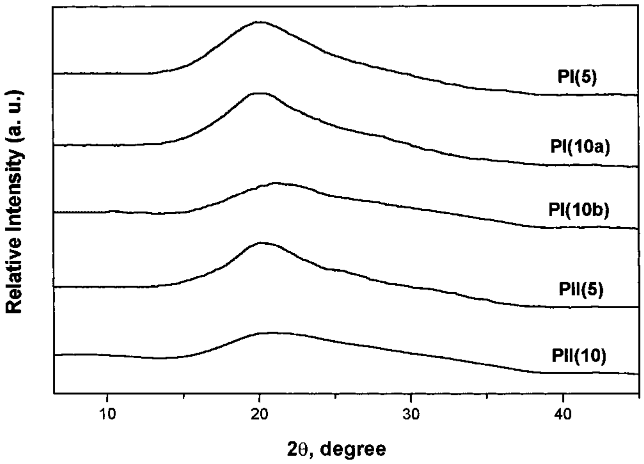


Figure 3. Wide-angle X-ray diffractograms of **PI(*n*)** and **PII(*n*)** at room temperature.

The **PII** polymers appear to be less soluble than the **PI** polymers. Although molecular weights could be examined only for **PI(5)** and **PI(10a)** by GPC, the degree polymerization of the present polymers appear not to be very high. It is lowest (5.8) for **PI(10a)** but the rest are thought to be at least about 10 **(PI(5))** or higher judging by the solution viscosity values (Table 2). It should be noted that the relatively large size of the repeating units of the present polymers lends itself to a fairly high molar mass despite the relatively low degree of polymerization. Polydispersity index (PDI) values of **PI(5)** and **PI(10a)** are 1.49 and 2.15, respectively, which are much lower than the values reported[34−36] for other hyperbranched polymers prepared by step-reaction polymerization. This is probably due to the fact that the present polymers were purified in two precipitation steps in which low molar mass fractions were removed from the final polymer product. This is reflected by the moderate recovered yields of the present polymers: 67−78%.

It should be pointed out that the molecular weights of hyperbranched polymers determined by GPC can be erroneous due to various reasons: their smaller size and more compact shape than linear polymers with the same MW, possible interaction with the GPC column owing to the large number of terminal groups, use of a nonideal reference standard, and so on.[37,38] The solution viscosity values of the present polymers indicate that their real MW's are relatively high, much higher than the values shown in Table 1 determined by GPC, according to literature on the molecular weight of hyperbranched aromatic polyesters.[39, 40]

According to wide-angle X-ray diffractograms obtained at room temperature (see Figure 3), all the polymers are amorphous. They show a very broad diffraction from about $2\theta = 15°$ (5.9 Å) to about $2\theta = 40°$ (2.3 Å) with their maximum positions located at about $2\theta = 20°$ (4.4 Å). Such a broad diffraction over the wide-angle region is derived from spacings arising from various aromatic−aromatic, aromatic−aliphatic, and aliphatic−aliphatic interchain distances in the amorphous state. The glass transition temperatures of the polymers were determined by DSC analysis (Figure 4). **PI(5)** and **PII(5)**, both of which contain pentamethylene spacers, exhibit T_g values of 127 and 134 °C, respectively. These values are significantly higher when compared with the value for **PI(10b)** and **PII(10)**, i.e., 112 and 109 °C, respectively. It is evident that the longer spacer results in lowered T_g values owing to their easier conformational changes. The T_g value for **PI(10a)** whose molecular weight is much lower than that for **PI(10b)** is only 73 °C. This must be due to its very low degree of polymerization. The T_g range of about 110−135 °C for the present hyperbranched polyesters, with the exception of **PI(10a)**, are similar to those reported[41−44] for aromatic polyesters and aromatic polyesters containing flexible spacers. Since the present polymers contain two aromatic rings in the spacers and the aromatic ester units are derived from biphenyl derivatives, their T_g values are somewhat higher than ordinary polyesters. This is particularly true when compared with the T_g values of the hyperbranced polyesters reported earlier by us.[15] Last, the T_g value of **PI(5-ester)** was 121 °C, which is slightly lower than the value (127 °C) of **PI(5)**. **PI(5-ester)** was prepared by methylating the carboxylic terminal groups of **PI(5)**.

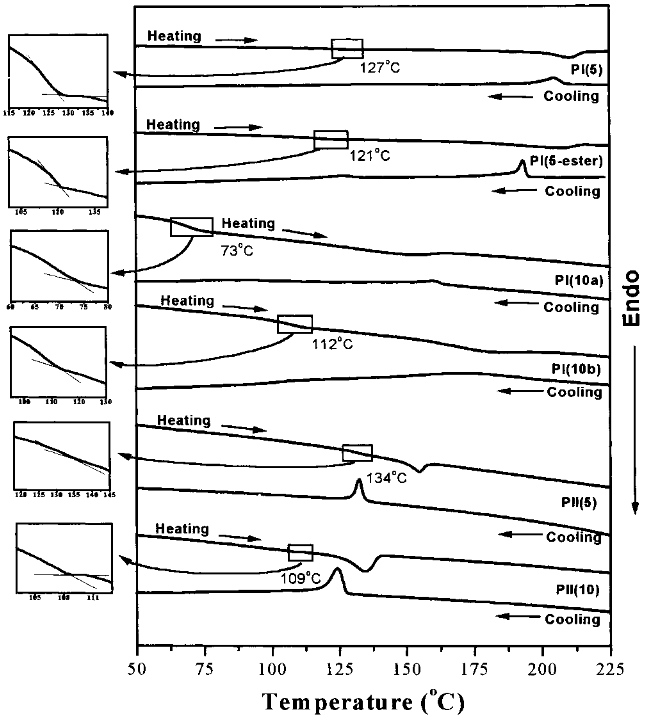


Figure 4. DSC thermograms of polymers [**PI(*n*)**, **PI(5-ester)**, and **PII(*n*)**].

Consequently, hydrogen bonding between the terminal carboxyl groups of **PI(5)** is eliminated in **PI(5-ester)**. This must have caused a slight lowering of the T_g value of **PI(5-ester)** when compared with that of **PI(5)**. A similar phenomenon was reported earlier by us[15] for other series of hyperbranched polyesters.

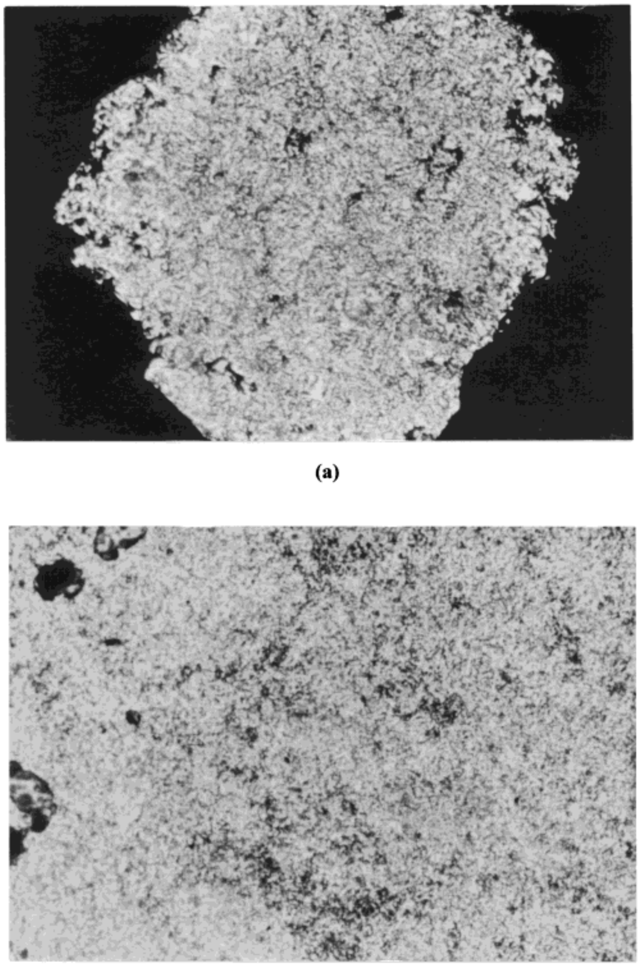
Liquid Crystalline Properties of Polymers

The DSC thermograms (Figure 4) of all of the polymers show two endothermic peaks on the heating curves. The first peak corresponds to the glass transition and the second to mesophase → isotropic phase transitions or isotropization. These transitions are reversible, as one can see from the cooling DSC curves. Since the polymers all are amorphous, they do not exhibit any melting transition. This sequence of transitions could be easily confirmed by the observation of optical textures during heating and cooling of the polymers on a polarizing microscope.

Isotropization temperatures (T_is) are significantly higher for **PIs** than for **PIIs**; 210 °C for **PI(5)** vs 155 °C for **PII(5)** or 182 °C for **PI(10b)** vs 134 °C for **PII(10)**. This is due to the fact[33] that LC phase of the esters of 4′-hydroxybiphenyl-4-carboxylic acid are much more thermally stable than those of the corresponding esters of 4,4′-biphenol. Another point to be noted is that the T_i values of **PI(5)** and **PII(5)** of pentamethylene spacers are much greater than the T_i values of **PI(10)** and **PII(10)** of longer decamethylene spacers. There are a number of reports[45,46] describing poor thermal stability of mesophase for symmetric twin LCs containing longer central polymethylene spacers. Apparently, longer spacers in those structures and the present polymers tend to destabilize the mesophases due to their lowered resistance to conformational changes, i.e., in short, due to their higher flexibility. The glass transition of **PI(10a)** and **PI(10b)** occurs over a broad temperature range and, thus, their DSC thermograms show very broad endothermic (heating) or exothermic (cooling) peaks (Figure 4). The T_i values mentioned above correspond to the temperature where peak minima are observed on the heating DSC curves.

All of the present polymers including **PI(5-ester)** exhibit liquid crystalline optical textures above their T_gs. Either polished marble textures or simple Schlieren textures were observed (see Figure 5, parts a and b), which are the characteristic of nematic phases. Figure 6 compares wide-angle X-ray diffractograms obtained at the temperatures of (a) below T_g, (b) the liquid crystalline state, and (c) above T_i. Diffractograms in parts a and b of Figure 6 show practically the same diffraction patterns with peak maximum at $2\theta = 21.5°$ (4.1 Å) and an fwhm of 7.6°, whereas the diffractogram in Figure 6c shows the peak maximum at $2\theta = 21.3°$ (4.2 Å) with an fwhm of 8.9 °. In other words, the wide-angle diffraction (short spacing) moves slightly toward increased spacing side and peak-width broadens as the temperature was increased from LC phases to isotropic phase. Increased molecular motions and chaotic orientations in the isotropic phase compared to the LC phase are expected to broaden the X-ray diffraction.

This contrasts with our earlier observation[15] that the hyperbranched aromatic polyesters of similar structures to the present ones formed mesophase only when they had carboxylic acid terminals through which they could form cyclic dimeric forms resulting in long and linear rigid structures. The only difference in structures between the earlier and the present series can be found in the position of branches. In the earlier series, the branching points are directly attached to the central part of rigid mesogenic units, whereas in the present ones they are located at the midpoints of the flexible spacers. Wholly aromatic linear polyesters lose their capability to form LC phases even with a relatively low level of branching. For example, Kumar and Ramakrishman[13] reported that 1:1 copolyesters derived from ethyl 3,5-bis(ω-hydroxyoligo(ethyleneoxy))benzoates and ethyl 4-(4-butoxyphenyl)benzoate are not liquid crystalline. Kricheldorf et al.[14] recently described thermotropic LC properties of several copolyesters containing hyperbranching units. They exhibited LC behavior only when the concentration of the branching units were low. Earlier, Ringsdorf et al.[12] reported formation of the


(a)

(b)

Figure 5. Photomicrographs of (a) **PI(10b)** taken at 161.8 °C (annealed for 20 h) and (b) **PII(10)** taken at 105.0 °C (annealed for 8 h) (magnification 200×).

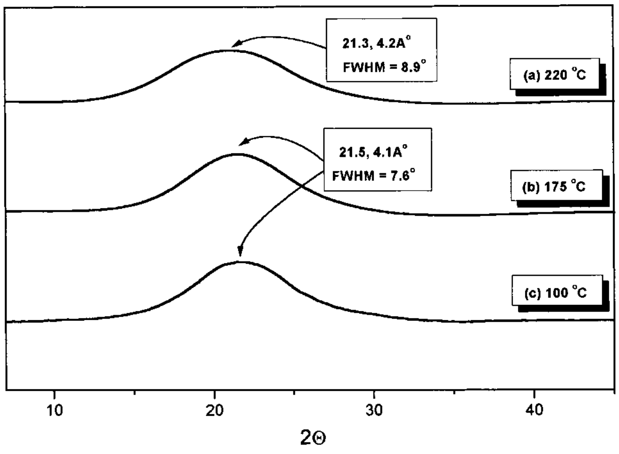


Figure 6. Wide-angle X-ray diffractograms of **PI(5)** at (a) 220, (b) 175, and (c) 100 °C.

Table 2. General Properties of Polymers

polymer	final polym temp, °C/0.1Torr	$\overline{M_w}^a$ ($\overline{M_n}^a$)	PDI^a	$\overline{DP}^a$	η_{inh}, dL/g	T_g,^{d} °C	T_i,^{d} °C	ΔH_i, kJ/mol (ΔS_i, J/mol·K)
PI(5)	250	12 160 (8144)	1.49	9.0	0.42^b	127	210	8.6 (17.6)
PI(5-ester)						121	208	11.6 (24.7)
PI(10a)	250	13 080 (6085)	2.15	5.8	0.41^b	73	151	
PI(10b)	270				0.85^b	112	182	
PII(5)	260				0.50^c	134	155	9.2 (21.4)
PII(10)	260				0.68^c	109	134	16.1 (39.4)

[a] The value was obtained from GPC (eluent: THF; standard: polystyrene). [b] Inherent viscosities were measured at 30 ± 0.1 °C on 0.2 g/dL in a mixed solvent of *p*-chlorophenol/1,1,2,2-tetrachloroethane (v/v = 1:1). [c] Inherent viscosities were measured at 30 ± 0.1 °C on 0.2 g/dL in a mixed solvent of *p*-chlorophenol/1,1,2,2-tetrachloroethane /chloroform (v/v/v = 10:3:3). [d] Estimated from the DSC thermograms of the first heating cycle at the heating rate of 10 °C/min.

cholesteric phase by a hyperbranched polymer. However, it is not clear whether the LC nature of this particular hyperbranched polymer is due to its peripheral mesogenic structures constructed on to the precursor hyperbranched polyester. The report did not make any comment on the LC properties of the precursor itself. Recently, Shibaev et al.[20a] and Frey et al.[20b] also reported LC properties for dendrimers whose peripheral terminals contain mesogenic units. It is clear, in this case, that peripheral mesogenic units provide a driving force to form a mesophase in melt. Pesak and Moore reported[47] the formation of columnar LC phases by novel dendritic molecules of rigid disk-shape.

Our observations lead us to the conclusion that, unless their branching points are connected through flexible spacers, hyperbranched aromatic polyesters are not prone to be liquid crystalline. This is in line with the structures of hyperbranched polymers and dendrimers reported by others to be thermotropic. Related to the subject under discussion, it is to be noted[47,48] that stilbenoid and tolanoid dendrimers that consist of rigid segments form thermotropically various types of discotic and columnar LC phases. These dendrimers certainly are of disk shape that can lead to molecular stacks. In addition, many of the exciting discoveries described by Percec et al.[17] also provide us with rules that govern the formation of LC phases or ordered supramolecular assemblies by hyperbranched and dendritic polymers. One group[3] of Percec's thermotropic compositions are based on the novel concept of conformational isomerism, which may be applicable to the present polyesters as well. The major difference between the Percec's and the present polymers lies in the fact that conformational isomerism in the former is applicable even to the structural units involving rigid element, in addition to flexible spacers, resulting in generation of longer mesogenic structures and elongated, not spherical, molecular shapes with a greater ease. In the present polymers, however, conformational isomerism must be restricted to the polymethylene spacers.

Table 2 contains thermodynamic parameters for isotropization of the present polymers. The transition enthalpies (ΔH_i) and entropies (ΔS_i) values are surprisingly comparable with those reported[49] for linear thermotropic LC polyesters. This can be taken an indication that molecular ordering of the present polymers in the LC phase is not lowered by their hyperbranched skeletal.

Last, one additional important observation[50,51] made qualitatively was that melt viscosity of present LCP's in liquid crystalline phases was much higher than conventional main chain LCPs including aromatic polyesters and the melts were quite resistant to flow. This indicates that uniaxial alignment of mesogenic units is not readily achieved for hyperbranched LCPs. Detailed rheological studies of hyperbranched LCPs are yet to be conducted in detail.

Conclusion

There have been continuing efforts to establish structure−LC property relationships for various types of thermotropic LCPs. As discussed above, there are many papers describing LC properties of hyperbranched aromatic polyesters and polyethers. The present investigation, in conjunction with earlier reports, appears to give us a guide to the design of structures of thermotropic hyperbranched aromatic polyesters. Hyperbranched aromatic polyesters with totally rigid units are not able to form LC phases in the melt. Inclusion of flexible spacers between mesogenic units helps the hyperbranched polymers become thermotropic. Their presence is not a sufficient, but only a necessary condition. An additional requirement is to have flexible branching units linked to flexible spacers, but not to rigid mesogenic units in the main skeleton. This conclusion is in accord with earlier reports by others, in particular, by Percec et al., who reported many different types of hyperbranched and dendritic polymers revealing thermotropic properties. This means that a very high degree of conformational freedom for the spacers generates the opportunity for the mesogenic units or the rigid rodlike segments to achieve domains in which their directors are oriented more or less along the same direction having LC orders. We are presently preparing new hyperbranched polyesters with the required structural character to be LC using monomers containing built-in mesogenic units. In contrast, the present and earlier polymers can form mesogenic units only through polymerization of the monomers.

Acknowledgment. This research was supported by the Ministry of Science and Technology of Korea and Korea Science and Engineering Foundation through the Center for Electro- and Photo-Responsive Molecules, Korea University. S.-H.C. and S.W.C. wish to express their thanks to the Ministry of Education of Korea for the special assistantship through the Brain Korea 21 program.

Supporting Information Available: Text giving synthetic details of monomers (**MI(5)** and **MI(10)**). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kim, Y.-H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.
(2) Percec, V. *Macromolecules* **1992**, *25*, 1164.
(3) Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843.

(4) Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441.
(5) Percec, V.; Cho, C. G.; Pugh, C.; Tomazos, D. *Macromolecules* **1993**, *26*, 963.
(6) Percec, V.; Schlueter, D.; Ungar, G.; Cheng, S. Z. D.; Zhang, A. *Macromolecules* **1998**, *31*, 1745.
(7) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061.
(8) Hudson, S. D.; Jung, H.-T.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, S. K. *Science* **1997**, *278*, 449.
(9) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161.
(10) Balagurnscuny, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539.
(11) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855.
(12) Bauer, S.; Fischer, H.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1589.
(13) Kumar, A.; Ramakrishnar, S. *Macromolecules* **1996**, *29*, 2524.
(14) Reina, A.; Gerken, A.; Zemann, U.; Kricheldorf, H. R. *Macromol. Chem. Phys.* **1999**, *200*, 1784.
(15) Hahn, S. W.; Yun, Y. K.; Jin, J.-I. *Macromolecules* **1998**, *31*, 6417.
(16) Li, J.; Crandall, K. A.; Chu, P.; Percec, V.; Petschek, R. G.; Rosenblatt, C. *Macromolecules* **1996**, *29*, 7813.
(17) Percec, V.; Chu, P.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1995**, *117*, 11441.
(18) Zhang, X.; Chen, Y.; Gong, A.; Chen, C.; Xi, F. *Liq. Cryst.* **1998**, *25*, 767.
(19) Dardel, B.; Deschenaux, R.; Even, M.; Serrano, E. *Macromolecules* **1999**, *32*, 5193.
(20) (a) Richardson, R. M.; Ponomarenko, S. A.; Boiko, N. I.; Shibaev, V. P. *Liq. Cryst.* **1999**, *26*, 101. (b) Lorentz, K.; Holter, D.; Stuhn, B.; Mulhaupt, R.; Frey, H. *Adv. Mater.* **1996**, *8*, 414.
(21) Saez, I. M.; Goodby, J. W. *Liq. Cryst.* **1999**, *26*, 1101.
(22) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1988.
(23) Mitsunobu, O. *Synthesis* **1981**, 1.
(24) Gray, G. W.; Hartley, J. B.; Jones, B. *J. Chem. Soc.* **1955**, 236.
(25) Jin, J.-I.; Park, J.-H. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 293.
(26) Huh, S.-M.; Jin, J.-I. *Liq. Cryst.* **1998**, *25*, 285.
(27) Maeda, Y.; Yun, Y.-K.; Jin, J.-I. *Thermochim. Acta* **1998**, *322*, 101.
(28) Herbert, A. J. *Trans. Faraday Soc.* **1967**, *63*, 555.
(29) Gray, G. W.; Jones, B. *J. Chem. Soc.* **1954**, 675.
(30) Gray, G. W.; Jones, B. *J. Chem. Soc.* **1953**, 4179.
(31) Byron, D. J.; Gray, G. W.; Wilson, R. C. *J. Chem. Soc.* **1966**, 840.
(32) Gray, G. W.; Jones, B. *J. Chem. Soc.* **1955**, 236.
(33) Goodby, J. W. *Ferroelectric Liquid Crystals Principles, Properties and Applications*; Gordon and Breach Science Publishers: Newark, NJ, 1991, Chapter 2, p 129−130.
(34) Schmaljohann, D.; Häubler, L.; Pötschke, P.; Voit, B. I.; Loontjens; J. A. *Macromol. Chem. Phys.* **2000**, *201*, 49.
(35) Kricheldorf, H. R.; Stöber, O.; Lübbers, D. *Macromolecules* **1995**, *28*, 2118.
(36) Martinez, C. A.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2015.
(37) Fang, J.; Kita, H.; Okamoto, K. *Macromolecules* **2000**, *33*, 4639.
(38) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240.
(39) Kricheldorf, H. R.; Stöber, O.; Lübbers, D. *Macromolecules* **1995**, *28*, 2118.
(40) Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, *26*, 4617.
(41) Zhou, Q. F.; Jin, J.-I.; Lenz, R. W. *Can. J. Chem.* **1985**, *63*, 181.
(42) Jin, J.-I.; Kang, C.-S.; Chang, J.-H. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 259.
(43) Jin, J.-I.; Kang, C.-S. *Polymer* **1993**, *34*, 2407.
(44) Jin, J.-I.; Cho, Y.-I.; Sohn, B.-H.; Kang, C.-S. *Polymer* **1993**, *34*, 3019.
(45) Ober, C. K.; Jin, J.-I.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 103.
(46) Hoshino, H.; Jin, J.-I.; Lenz, R. W. *J. Appl. Polym. Sci.* **1984**, *29*, 547.
(47) Pesak, D. J.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1636.
(48) Meier, H.; Lehamann, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 643.
(49) Jin, J.-I.; Choi, E.-J.; Ryu, S.-C.; Lenz, R. W. *Polym. J.* **1986**, *18*, 63.
(50) Blizard, K. G.; Baird, D. G. *Polym. Eng. Sci.* **1987**, *27*, 653.
(51) Heino, M. T.; Seppälä, J. V. *J. Appl. Polym. Sci.* **1993**, *48*, 1677.

MA000591D