Thermotropic Hyperbranched Polyesters Prepared from 2-[(10-(4-Hydroxyphenoxy)decyl)oxy]terephthalic Acid and 2-[(10-((4′-Hydroxy-1,1′-biphenyl-4-yl)oxy)decyl)oxy]terephthalic Acid

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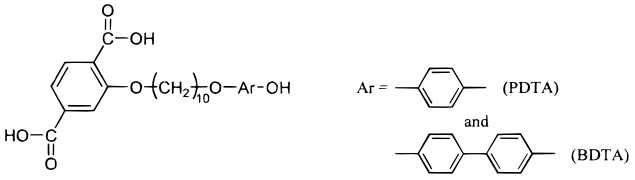
ABSTRACT: Two new thermotropic, liquid crystalline (LC) hyperbranched polyesters with carboxylic acid end groups were synthesized by direct polycondensation of two pseudo AB_2 type monomers, 2-[(10-(4-hydroxyphenoxy)decyl)oxy]terephthalic acid and 2-[(10-((4′-hydroxy-1,1′-biphenyl-4-yl)oxy)decyl)oxy]-terephthalic acid. Their LC properties were characterized by DSC and optical microscopy. The carboxylic acid groups of the polyesters were converted to the corresponding methyl esters, and their properties were also investigated. The number average molar masses of the polymers were 7000 and 15 000, respectively, corresponding to average degrees of polymerization of about 17 and 31. The degrees of branching of the polymers determined by ^{13}C NMR spectroscopy were 37 ± 10% and 43 ± 10%, respectively. The polyesters with the carboxylic acid end groups form the nematic phase above their glass transition temperatures (T_g), whereas their methyl ester counterparts are not liquid crystalline. This observation indicates that the formation of hydrogen bonds between the carboxylic acid terminals plays an important role in mesophase formation by the present polyesters. All the polymers are amorphous and are soluble in common organic solvents such as THF, DMF, NMP, pyridine, and DMSO. The T_g values of the methyl ester polymers are substantially lower than those of the polymers having acid terminals.

Introduction

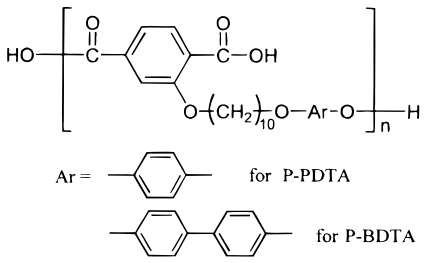
Dendritic and hyperbranched polymers are interesting new classes of materials not only for their unique molecular shapes[1−5] but also for their possible utilization[6−12] in such a variety of applications as in chemical reagents, biological and pharmaceutical uses, catalysts, and other functions. Among the large number of dendritic and hyperbranched structures, only a few liquid crystalline hyperbranched polymers have been reported: aromatic polyethers,[13−16] polyesters[17] containing aliphatic spacers, and aromatic polyamides.[18,19] The polyethers and polyesters were reported to be thermotropic, whereas the polyamides were lyotropic.

We became interested in the synthesis of hyperbranched aromatic polyesters containing oxydecamethyleneoxy spacers between the rigid units of aromatic ester type in order to examine if they were able to form mesophases thermotropically. We expected to observe the formation of LC phases by these polymers if the spacers were indeed flexible enough to allow the alignment of mesogenic units to occur readily. The structures of the monomers utilized in this investigation are as follows:



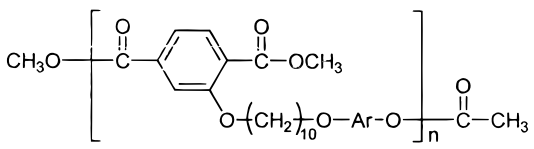
The monomers contain two carboxylic acid groups and one phenolic hydroxyl group. Because the two carboxylic acid groups are not exactly equivalent, their reactivities are not the same. Therefore, these compounds cannot be taken as typical AB_2 type monomers but only as pseudo AB_2 type compounds and, thus, the polyesters to be formed are not of exactly hyperbranched type.

The structure of the polymers can be simplified as shown below:



An idealized structure of P-PDTA with all of the methylene units in trans, anti conformations is shown in Figure 1.

The terminal groups of the polymers were also esterified in order to compare their properties with those of P-PDTA and P-BDTA.



For the sake of simplicity, these polymers will be called P-PDTA(ester) and P-BDTA(ester), respectively.

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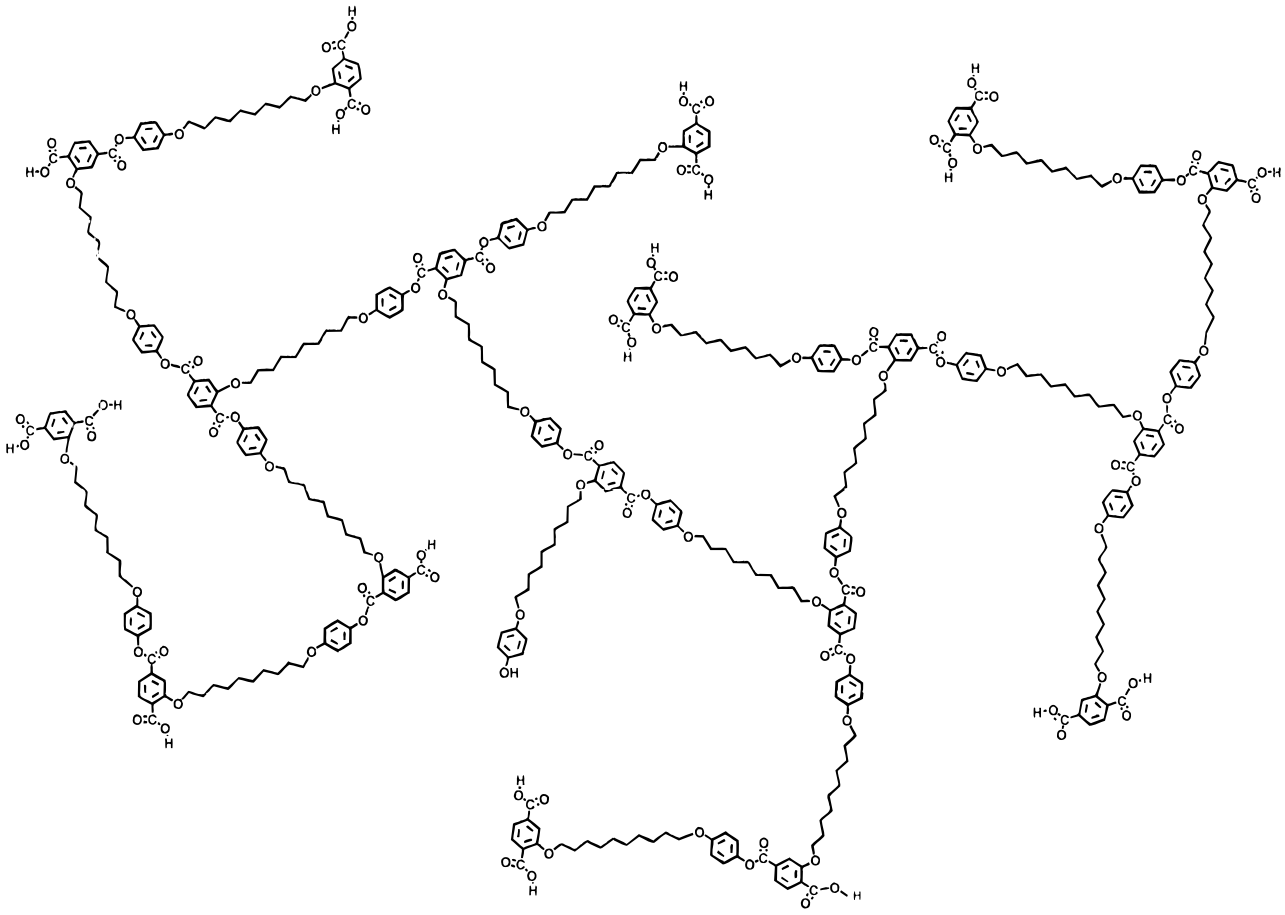


Figure 1. An idealized structure of P-PDTA.

Experimental Section

Synthesis of Monomers. Synthesis of 2-[(10-(4′-Hydroxyphenoxy)decyl)oxy]terephthalic Acid (PDTA). The synthetic route to this compound is shown in Scheme 1. The numbers used in the description of the compounds in the synthetic procedure are the same as those in the scheme.

2-Hydroxyterephthalic Acid, 1. This compound was prepared by starting from 2,5-dimethylanisol via the two steps shown in Scheme 1. The overall yield for the two steps was 63%, mp 317−320 °C (lit.[20] 317−320 °C).

Dimethyl 2-Hydroxyterephthalate, 2. Compound **1** (14.5 g; 0.80 mmol) was dissolved in 400 mL of methanol. To this solution was slowly added with stirring under a nitrogen atmosphere 54 mL (75 mmol) of purified thionly chloride[21] over a period of 1 h. The mixture was stirred for 15 h at room temperature. Then the reaction mixture was poured into a large excess distilled water. To the slurry was added a 30% aqueous solution of Na_2CO_3 until the mixture became neutral. The precipitate formed was collected on a filter and washed thoroughly with distilled water. The product was recrystallized from a mixture of acetone and water (2:1 by volume). The yield was 14.6 g (87%), mp 95 °C (lit.[22] 92−93 °C).

Dimethyl 2-[(10-Bromodecyl)oxy]terephthalate, 3. Compound **2** (15.0 g; 71 mmol) and 150 g (0.50 mol) of 1,10-dibromodecane were dissolved in 200 mL of acetone. To this solution were added 20 g of K_2CO_3 and 0.20 g of KI. The mixture was refluxed for 24 h under a nitrogen atmosphere. The solid residue was removed by filtration. Acetone in the filtrate was distilled out using a rotary evaporator followed by removal of 1,10-dibromodecane via vacuum distillation. The residue was chromatographed on a silica gel column using a mixture of *n*-hexane and ethyl acetate (6:1 by volume) as an eluent. The yield was 22.5 g (74%), mp 34 °C.

Anal. Calcd for $C_{20}H_{29}BrO_5$: C, 55.95; H, 6.81%. Found: C, 55.91; H, 6.67%. IR spectrum (neat; cm^{-1}): 2932 (aliphatic C−H stretching), 2855 (C−H stretching of ArOCH_2), 1725 (C═O stretching), 1257, 1114, 1083, and 1011 (C−O stretchings), and 643 (C−Br stretching). ^{1}H NMR spectrum (acetone-d_6; δ, ppm): 1.25−1.65 (m, 12H, −OCH$_2$CH$_2$(CH_2)$_6$CH$_2$CH$_2$Br), 1.79−1.95 (m, 4H, −OCH$_2$$CH_2$(CH$_2$)$_6$$CH_2CH_2$Br), 3.5 (t, 2H, −$CH_2$-Br), 3.8 (s, 3H, O$CH_3$), 3.9 (s, 3H, O$CH_3$), 4.15 (t, 2H, −O$CH_2$), and 7.55−7.8 (m, 3H, ArH).

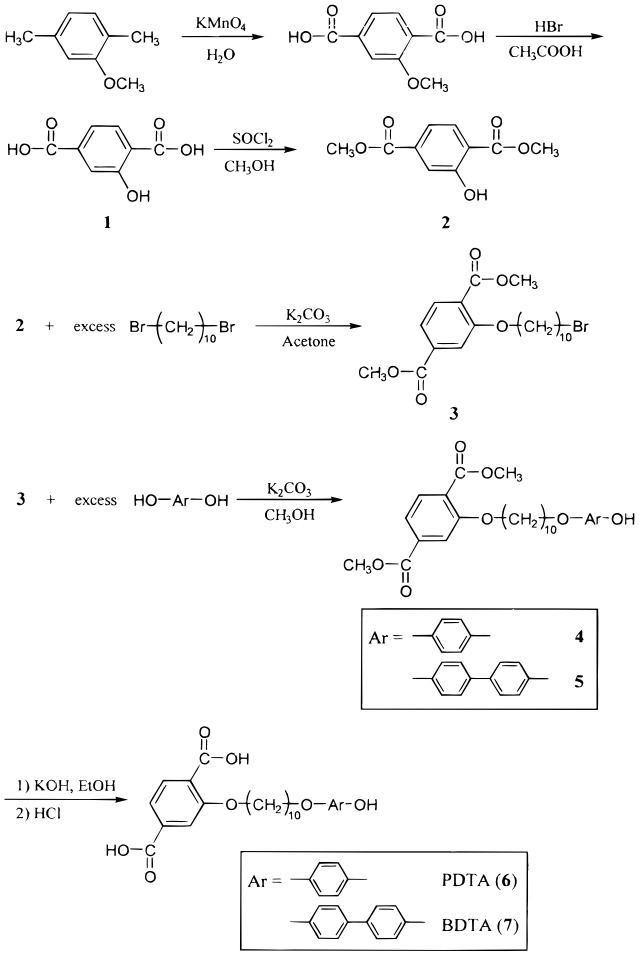
Dimethyl 2-[(10-(4-Hydroxyphenoxy)decyl)oxy]terephthalate, 4. Compound **3** (13.60 g; 3.2×10^{-2} mol), 24.60 g (24.60 g; 0.22 mol) of hydroquinone, 17.7 g (0.13 mol) of K_2CO_3, 0.2 g of tetrabutylammonium bromide, and 3.0 g of $Na_2S_2O_4$ were mixed in 150 mL of methanol.

The mixture was refluxed for 12 h under a nitrogen atmosphere. And then the reaction mixture was acidified to pH = 1 by adding concentrated H_2SO_4. The mixture was poured into a large excess of cold distilled water. The precipitate was collected on a filter and washed thoroughly with distilled water. The final product was obtained by recrystallizing the crude product from a mixture of methylene chloride and *n*-hexane (4:1 by volume). The yield was 8.5 g (59%), mp 96 °C.

Anal. Calcd for $C_{26}H_{34}O_7$: C, 68.10; H, 7.47. Found: C, 67.96; H, 7.57. IR spectrum (KBr; cm^{-1}): 3427 (O−H stretching), 3032 (aromatic C−H stretching), 2936 (aliphatic C−H stretching), 2855 (C−H stretching in ArOCH_2), 1715 (C═O stretching) and 1297, 1230, 1085, and 1015 (C−O stretchings). ^{1}H NMR spectrum (DMSO-d_6; δ, ppm): 1.2−1.5 (m, 12H, −OCH$_2$CH$_2$(CH_2)$_6$CH$_2$CH$_2$O−), 1.6−1.8 (m, 4H, −OCH$_2$$CH_2$(CH$_2$)$_6$-$CH_2CH_2$O−), 3.7−3.9 (m, 8H −O$CH_3$ and HOArOCH_2−), 4.1 (t, 2H, ArOCH_2−), 6.6−6.8 (m, 4H, HO*Ar*O−), and 7.5−7.8 (m, 3H, ArH).

2-[(10-(4-Hydroxyphenoxy)decyl)oxy]terephthalic Acid (PDTA), 6. Compound **4** (6.0 g; 1.3×10^{-2} mol) was dissolved in 100 mL of 95% ethanol. To the solution was added a solution of 3.65 g (6.5×10^{-2} mol) of KOH and 2.5 g of $Na_2S_2O_4$ dissolved in 200 mL of distilled water. After the mixture was refluxed for 8 h under a nitrogen atmosphere, it was poured

Scheme 1. Synthetic Route to Monomers



into 300 mL of distilled water. The insoluble fraction was removed by filtration, and the filtrate was mixed with 200 mL of 10 M HCl. The precipitate was collected on a filter and recrystallized from a mixture of water and ethanol (1:2 by volume). The product yield was 4.73 g (84%), mp 154 °C. This compound was found to be nematic and underwent isotropization at 169 °C.

Anal. Calcd for $C_{24}H_{30}O_7$: C, 66.96; H, 7.02. Found: C, 66.81; H, 6.97. IR spectrum (KBr; cm^{-1}): 3600−2400 (acidic O−H stretching), 2923 (aliphatic C−H stretching), 1739 and 1699 (C=O stretchings), and 1303 and 1230 (C−O stretchings). ^{1}H NMR spectrum (DMSO-d_6; δ, ppm): 1.2−1.5 (m, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$, stretching) 1.6−1.8 (m, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 3.8 (t, 2H, HOArO$CH_2-$), 4.11 (t, 2H, ArO$CH_2-$), 6.6−6.8 (m, 4H, HO*Ar*O−), 7.5−7.8 (m, 3H, ArH) and 8.85 (s, 1H, *HO*Ar−).

Synthesis of 2-[(10-((4′-Hydroxy-1,1′-biphenyl-4-yl)oxy-)decyl)oxy]terephthalic Acid (BDTA), 7. Dimethyl 2-[(10-((4′-Hydroxy-1,1′-biphenyl-4-yl)oxy)decyl)oxy]terephthalate, 5. This compound was prepared by following the exact same procedure as the one utilized for the synthesis of compound **4**. After refluxing the reaction mixture for 12 h under a nitrogen atmosphere, the insoluble fraction was removed by filtration. The filtrate was acidified to pH = 1 with concentrated H_2SO_4, and the whole mixture was cooled to and kept at 0 °C for 2 days. The precipitate was collected on a filter and recrystallized from a mixture of acetone and water (3:1 by volume) to remove the remaining biphenol. The purified product was further recrystallized from a mixture of methylene chloride and *n*-hexane (6:1 by volume). The yield was 50%, mp 122−124 °C.

Anal. Calcd for $C_{32}H_{38}O_7$: C, 71.89; H, 7.16. Found: C, 71.63; H, 7.11. IR spectrum (KBr, cm^{-1}): 3452 (O−H stretching), 3020 (aromatic C−H stretching), 2928 (aliphatic C−H stretching), 2850 (C−H stretching in Ar−O−CH_2), 1720 (C=O stretching), and 1230, 1107, 1080, and 1026 (C−O stretchings). ^{1}H NMR spectrum (DMSO-d_6; δ, ppm): 1.2−1.5 (m, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$) 1.6−1.8 (m, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 3.8 (s, 3H, $-OCH_3$), 3.9 (s, 3H, $-OCH_3$), 4.0 (t, 2H, $HOC_6H_4C_6H_4OCH_2-$), 4.1 (t, 2H, ArOCH_2-), 6.8−7.5 (m, 8H, $HOC_6H_4C_6H_4O-$), 7.6−7.8 (m, 3H, ArH), 9.45 (s, 1H, $HOC_6H_4C_6H_4-$).

2-[(10-((4′-Hydroxy-1,1′-biphenyl-4-yl)oxy)decyl)oxy]-terephthalic Acid (BDTA), 7. This compound was prepared in the same manner as the way used for the synthesis of compound **6**. The final product was recrystallized from a mixture of ethanol and water (5:1 by volume). The yield was 89%, mp 205 °C. This compound was found to be thermotropic and underwent isotropization at 215 °C.

Anal. Calcd for $C_{30}H_{34}O_7$: C, 71.13; H, 6.76. Found: C, 70.82; H, 6.69. IR spectrum (KBr; cm^{-1}): 3650−2350 (acidic O−H stretching), 2924 (aliphatic C−H stretching), 2853 (C−H stretching in ArOCH_2), 1740 and 1700 (C=O stretchings), and 1301, 1239, and 1020 (C−O stretchings). ^{1}H NMR spectrum (DMSO-d_6, δ, ppm): 1.2−1.5 (m, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$) 1.6−1.8 (m, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 4.0 (t, 2H, $HOC_6H_4C_6H_4OCH_2-$), 4.1 (t, 2H, ArOCH_2-), 6.8−7.5 (m, 8H, $HOC_6H_4C_6H_4O-$), 7.6−7.8 (m, 3H, ArH), 9.4 (s, 1H, $HOC_6H_4C_6H_4-$), and 12.8−13.2 (broad, 2H, acid OH).

Synthesis of Polymers

Since the both polymers (P-PDTA and P-BDTA) were prepared in the same manner, only a detailed procedure for the synthesis of P-PDTA is given: Purified thionyl chloride[21] (2.50 g; 2.0×10^{-2} mol) was slowly mixed with 20 mL of dry pyridine,[23] and the mixture was stirred at room temperature for 30 min. To this solution was added 4.0 g (9.3 mmol) of PDTA (**6**) dissolved in 30 mL of dry pyridine. The mixture, after being stirred at room temperature for 30 min, was heated to and maintained at 80 °C for 15 h. After being cooled to room temperature, the reaction mixture was poured into 200 mL of 5 M HCl. The precipitate obtained was redissolved in 50 mL of pyridine. The insoluble were removed by filtration. The filtrate was acidified again using 10 M HCl. The precipitate formed was washed thoroughly with distilled water and dried at 60 °C in a vacuum oven. The product was subjected to Soxhlet extraction for 3 days using methanol. The polymer yield was 2.55 g (67%).

Anal. Calcd for $C_{264}H_{310}O_{67}$ (for DP = 16.9): C, 69.61; H, 6.86. Found: C, 69.01; H, 6.77. IR spectrum (KBr; cm^{-1}): 3600−2300 (acidic O−H stretching), 3071 (aromatic C−H stretching), 2925 (aliphatic C−H stretching), 2854 (C−H stretching in ArOCH_2), 1732 (ester C=O stretching), 1689 (acid C=O stretching) and 1290, 1234, 1108, and 1045 (C−O stretchings). ^{1}H NMR spectrum (DMSO-d_6; δ, ppm): 1.0−1.5 (m, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$) 1.5−1.8 (m, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 3.7−4.3 (m, 4H, −OAr$CH_2-$ and ArOCH_2), 6.7−7.25 (m, 4H, −O*Ar*O−), and 7.5−7.8 (m, 3H, $-C_6H_3<$).

The second polymer, P-BDTA, was prepared and purified in the same manner. The polymer yield was 61%.

Anal. Calcd for $C_{930}H_{992}O_{18}$ (for DP = 30.8): C, 73.75; H, 6.60. Found: C, 73.32; H, 6.54. IR spectrum (KBr; cm^{-1}): 3600−2300 (acidic O−H stretching), 3037 (aromatic C−H stretching), 2934 (aliphatic C−H stretching), 2854 (C−H stretching in ArOCH_2), 1733 (ester C=O stretching), 1693 (acid C=O stretching), and 1293, 1241, 1190, and 1043 (C−O stretchings). ^{1}H NMR spectrum (DMSO-d_6, δ, ppm): 0.8−1.5 (m, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$) 1.5−1.8 (m, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 3.6−4.2 (m, 4H, $-OC_6H_4C_6H_4OCH_2-$ and ArOCH_2), 6.6−8.0 (m, 11H, $-OC_6H_4C_6H_4-$ and $-C_6H_3<$).

Esterification of Terminal Groups of P-PDTA and P-BDTA. The two polymers were first acetylated in order to convert the phenolic hydroxy groups into the acetate ester groups. And then the carboxylic terminal groups were esterified with methanol. Since the exact same reaction procedures

were employed for the synthesis of esterified polymers [P-PDTA(ester) and P-BDTA(ester)] from P-PDTA and P-BDTA, a detailed description is only given for the esterification of P-PDTA.

P-PDTA (0.5 g) was dissolved in a mixture of 20 mL of dry THF[24] and 1 mL of dry pyridine. At 0 °C, to this solution was introduced dropwise 1 mL of acetyl chloride using a syringe. The mixture was stirred for 20 h under a dry nitrogen atmosphere. The reaction mixture was poured into a large excess of distilled water. The oily layer was separated and dissolved in 10 mL of pyridine. The pyridine solution was poured into 100 mL of 5 M HCl. The precipitate was collected on a filter, washed thoroughly with distilled water, and dried in a vacuum oven at 60 °C. The recovered yield was 0.45 g. The acetylated polymer (0.35 g), thus obtained, was dissolved in 10 mL of purified thionyl chloride. The solution was refluxed for 3 h under a dry nitrogen atmosphere, and the excess thionyl chloride was distilled off. The residue was dissolved in 10 mL of dry THF. To this solution was added dropwise under a dry nitrogen atmosphere a mixture of 1 mL of anhydrous methanol, 1 mL of dry pyridine and 5 mL of dry THF. The mixture was stirred for 20 h and then poured into 100 mL of distilled water containing 5 mL of 10 M HCl. The precipitate was collected on a filter and washed with distilled water. The polymer, after being dried, was dissolved in 5 mL of chloroform and precipitated again by mixing the solution with excess *n*-hexane. The amount of polymer recovered was 0.27 g. The overall recovered yield for the two steps was 69%. The corresponding value for P-BDTA was 62%.

IR spectrum (KBr; cm^{-1}): 3070 (aromatic C−H stretching), 2928 (aliphatic C−H stretching), 2850 (C−H stretching in ArOCH_2−), and 1728 (C═O stretching). ^{1}H NMR spectrum ($CDCl_3$; δ, ppm): 1.2−1.6 (m, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 1.75−1.95 (m, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 3.8−4.2 (m, 7H, OCH_3, ArOCH_2− and OArOCH_2−), 6.9−6.7 (m, 4H, $-OC_6H_4O-$), and 7.6−8.0 (m, 3H, $>C_6H_3-$).

The spectral data of the esterified polymer of P-BDTA prepared in the same manner are given below:

IR spectrum (KBr; cm^{-1}): 3046 (aromatic C−H stretching), 2932 (aliphatic C−H stretching), 2850 (C−H stretching in $ArOCH_2-$), and 1730 (C═O stretching). ^{1}H NMR spectrum ($CDCl_3$; δ, ppm): 0.8−1.6 (m, 12H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 1.7−1.95 (m, 4H, $-OCH_2CH_2(CH_2)_6CH_2CH_2O-$), 3.7−4.2 (m, 7H, OCH_3, $-OC_6H_4C_6H_4OCH_2-$ and $>C_6H_3OCH_2-$), and 7.7−8.2 (m, 11H, $-OC_6H_4C_6H_4O-$ and $>C_6H_3-$).

Determination of Molecular Weights of P-PDTA and P-BDTA. The molecular weights of P-PDTA and P-BDTA were determined by the potentiometric titration. As a representative example, the titration method utilized for the determination of the molecular weight of P-PDTA is given below.

P-PDTA (4.40×10^{-2} g) was dissolved in 5 mL of pyridine in a 50 mL volumetric flask. Distilled water was mixed with the solution up to the mark. The solution was titrated with a standardized solution of tetrabutylammonium hydroxide (6.48×10^{-2} M) using a pH meter equipped with a glass electrode and a calomel electrode. The inflection point on the mV−mL curve was taken as the end point. The volume of the tetrabutylammonium hydroxide solution required was 2.082 mL. A blank test was run for the pyridine solution absent of the polymer. The blank test required 0.098 mL of the hydroxide solution. Using these data the molecular weight of the polymer can be calculated. And the values obtained are $\overline{M}_n = 6970$ and $\overline{DP} = 16.9$. The values for P-BDTA determined in the same manner were $\overline{M}_n = 15\,050$ and $\overline{DP} = 30.8$.

Identification and Characterization of Intermediates and Polymers. IR and ^{1}H NMR spectra were obtained on a Bomem MB-series FT-IR instrument and on a Bruker AM 300 NMR spectrometer, respectively. Elemental analyses were performed using an Eager 200 elemental analyzer by the Organic Research Institute of Sogang University, Seoul, Korea. Thermal properties of the polymers were examined on a differential scanning calorimeter (Mettler DSC 821^e) at the heating and cooling rate of 10 °C/min under a nitrogen atmosphere. The inflection points on the DSC curves were taken as the glass transition temperatures (T_g's). Indium was employed as the reference. The molecular weights of the esterified polymers, i.e., P-PDTA(ester) and P-BDTA(ester), were determined against polystyrene standards using a Waters GPC with a refractive index detector. Chloroform was used as the eluent. Optical textures of polymer melts were observed on a cross-polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP-82HT).

Measurement of the Degree of Branching[25−27] by NMR. One-dimensional ^{13}C NMR spectra were acquired with a Bruker DPX 300 instrument (Bruker Analytische Messtechnik GmbH, Germany) with a 2.7 μs pulse length (30° flip) and an 8 s pulse repetition delay. For quantitative analysis by means of peak integrals, the inverse gated decoupling method[28] was employed. Acquisition numbers were 9k for P-PDTA and 14k for P-BDTA. For peak assignment, DEPT (distortionless insensitive nuclei enhanced by polarization transfer),[28] homonuclear (H−H)-COSY (correlation spectroscopy),[28] HMQC (heteronuclear multiple quantum correlation spectroscopy),[28] and HMBC (heteronuclear multiple bond correlation spectroscopy)[28] spectra acquired on a Bruker DMX 600 instrument (Bruker Analytische Messtechnik GmbH, Germany) and chemical shift values[29] of carbon peaks in one-dimensional spectra were used. The NMR solvent used was CD_2Cl_2 for P-PDTA(ester) and P-BDTA(ester) and a mixed (7−8 to 1 (v/v)) solvent of $SOCl_2$ and CD_2Cl_2 for P-PDTA and P-BDTA, respectively.

Results and Discussion

Synthesis and Liquid Crystalline Properties of the Two Monomers, 6 and 7. The two monomers, compounds **6** and **7**, were prepared following the synthetic route shown in Scheme 1. Compound **1**, prepared from 2,5-dimethylanisole, was esterified to **2** simply by reacting it at room temperature with a mixture of methanol and thionyl chloride. The diester **2**, was refluxed with excess 1,10-dibromodecane in acetone in the presence of potassium carbonate and a small amount of potassium iodide to produce **3**. Compound **3** was then reacted with excess hydroquinone in the presence of potassium carbonate to produce the dimethyl ester (**4**) of the desired monomer. The diester was hydrolyzed to the potassium salt, which was then converted to the acidic form **6** simply by acidifying the solution. The biphenyl analogue, **7**, also was prepared in the exact same manner. The structures of all of the intermediates and the final monomers were confirmed by elemental analysis and IR and NMR spectra. Thin-layer chromatography and high-pressure liquid chromatography also were utilized to ensure the purity of the compounds obtained in each step.

The two monomers, **6** and **7**, revealed a peculiar thermal transition behavior as shown by the DSC thermograms in Figure 2. Both compounds reveal two endothermic peaks on the DSC thermograms on heating the samples. They show only one exothermic peak on cooling. When their thermal behavior was examined on a hot stage attached on a polarizing microscope, they melted into anisotropic melts, most probably nematic according to the optical textures observed, followed by isotropization at higher temperatures. The two temperatures coincide with the temperatures where the two endothermic peaks appeared on the DSC thermograms. But when the isotropic melts were cooled, they did not crystallize but vitrified in their mesophases. In other words, nematic glasses were obtained on cooling the isotropic melts, which again agrees with their cooling DSC thermograms, which show only one exothermic peak corresponding to the isotropic phase → mesophase transition. Since compounds **6** and **7** do not contain mesogenic groups, it is conjectured that formation of

Table 1. General Properties of Polymers[a]

polymer	η_{inh},[b] dL/g	T_g, °C	T_i, °C	T_D^i, °C	LC[c]	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\overline{DP}$
P-PDTA	0.36	83	142	300	nematic	6 970[d]			16.9
P-BDTA	0.30	70	208	260	nematic	15 050[d]			30.8
P-PDTA (ester)	0.24	20		310	non LC	5 900[e]	18 500	3.1	14.3
P-BDTA (ester)	0.23	26		325	non LC	14 000[e]	48 100	3.4	28.7

[a] T_g, T_i, T_D^i represent the glass, isotropization, and initial decomposition temperature. [b] Inherent viscosity values were obtained for 0.2 g/dL solution in NMP at 30 ± 0.1 °C. [c] Liquid crystallinity [d] All values were obtained by potentiometric titration of the terminal carboxylic acid groups. [e] All values were obtained by GPC.

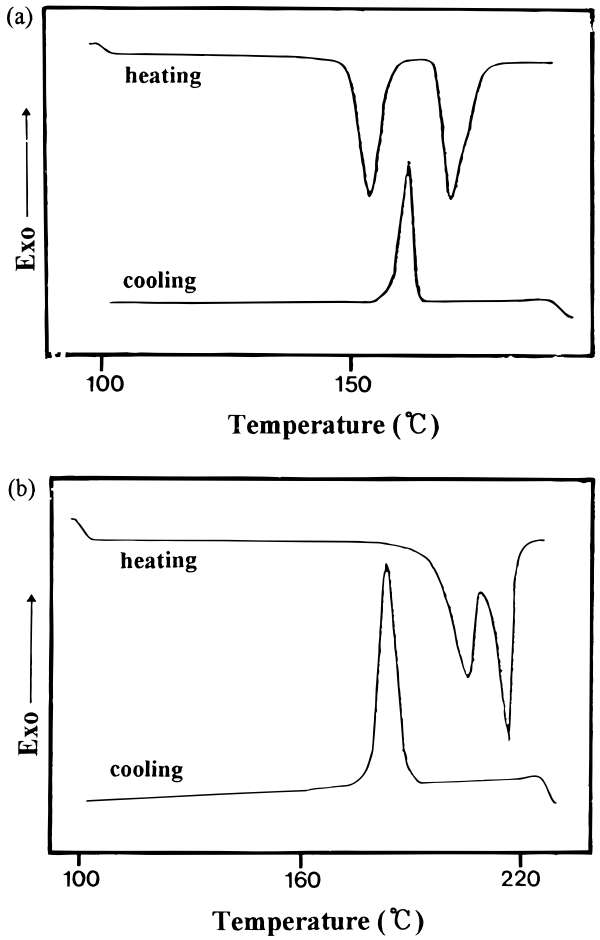


Figure 2. DSC thermograms of PDTA and BDTA.

intermolecular hydrogen bonds resulting in the formation of cyclic dimers between carboxylic acid groups leads to long rigid structures that are expected to enable them to form mesophases. It has been well established[30] that some of carboxylic acids, in particular, those carrying alkyl or alkoxy groups, are able to form liquid crystalline phases in melts.

It is also very possible that the phenolic groups in the monomers are also involved in hydrogen bonding, but probably to a lesser extent than the carboxylic acid groups. Anyway, hydrogen bonding appears to have such a crucial role in the stabilization of the mesophases that heats (ΔH_i) of isotropization of the compounds are very high, even higher than their heats (ΔH_m) of melting. Usually, ΔH_i ranges only from 1 to 5% of the ΔH_m value for ordinary liquid crystalline compounds[31] that do not form hydrogen bonds in their liquid crystalline phases. The stabilization of the mesophase by the hydrogen bonds is also reflected by the fact that the mesophases are rather resistant toward crystallization into crystalline solids and remain vitrified even at room temperature when they were cooled.

Synthesis and General Properties of Polymers. The two polymers, P-PDTA and P-BDTA, were prepared by polymerizing the respective monomers, PDTA and BDTA, at 80 °C in a mixed solution of pyridine and thionyl chloride. The combination of thionyl chloride and pyridine was found to be a satisfactory condensing agent[32] in the preparation of aromatic polyesters at relatively low temperatures. The recovered yields of the present polymers, after Soxhlet extraction using methanol over a prolonged period of time, were not very high (ca. 60 and 70%, respectively). It is very probable that a substantial amount of low molecular weight species has been removed during Soxhlet extraction. The structures of polymers could be confirmed by their IR- and ^{1}H NMR spectra, as summarized in the Experimental Section.

General properties of the polymers are shown in Table 1. The number average molecular weights of the polymers determined titrimetrically were 6970 and 15 050, respectively. These values correspond to the number average degrees of polymerization of 16.9 and 30.8 for the respective polymers. The inherent viscosity values of P-PDTA and P-BDTA measured at 30 °C for the 0.2 g/dL solutions in *N*-methylpyrrolidone (NMP) were 0.36 and 0.30 dL/g, respectively. Elemental analysis of both polymers resulted in carbon contents that coincide with those expected for the degree of polymerization determined titrimetrically. The two polymers exhibit excellent solubility in a variety of polar organic solvents such as THF, DMF, DMSO, NMP, and pyridine. When they were dissolved in pyridine, addition of water into the solution failed to precipitate them. Evidently, formation of salts between the carboxylic end groups and pyridine causes this phenomenon. Although tetrabutylammonium hydroxide readily dissolved the polymers in water, sodium hydroxide was found to be less efficient in dissolution. This must be due to tetrabutylammonium counterions, which are known to have a better phase-transfer[33] ability of the hydrophobic part of the molecules than the sodium ion.

Successful esterification of terminal groups of P-PDTA and P-BDTA could be confirmed by the absence of any O−H stretching absorptions in the IR spectra of P-PDTA(ester) and P-BDTA(ester). Esterification of P-PDTA and P-BDTA made the polymers soluble even in chloroform and 1,1,2,2-tetrachloroethane. The number average molecular weights of the two polymers determined by GPC against polystyrene standard are 5900 and 14 000, respectively. These values correspond to $\overline{DP} = 14.3$ and $\overline{DP} = 28.7$, respectively. THF was used as the eluent. The values are lower than those of starting polymers, whose M_n's were determined titrimetrically. It is reasonable to ascribe this observation mainly to the difference in the methods utilized for the determination of the molecular weights of the polymers before and after esterification. We also believe that there is a possibility for a partial breakage of polymer

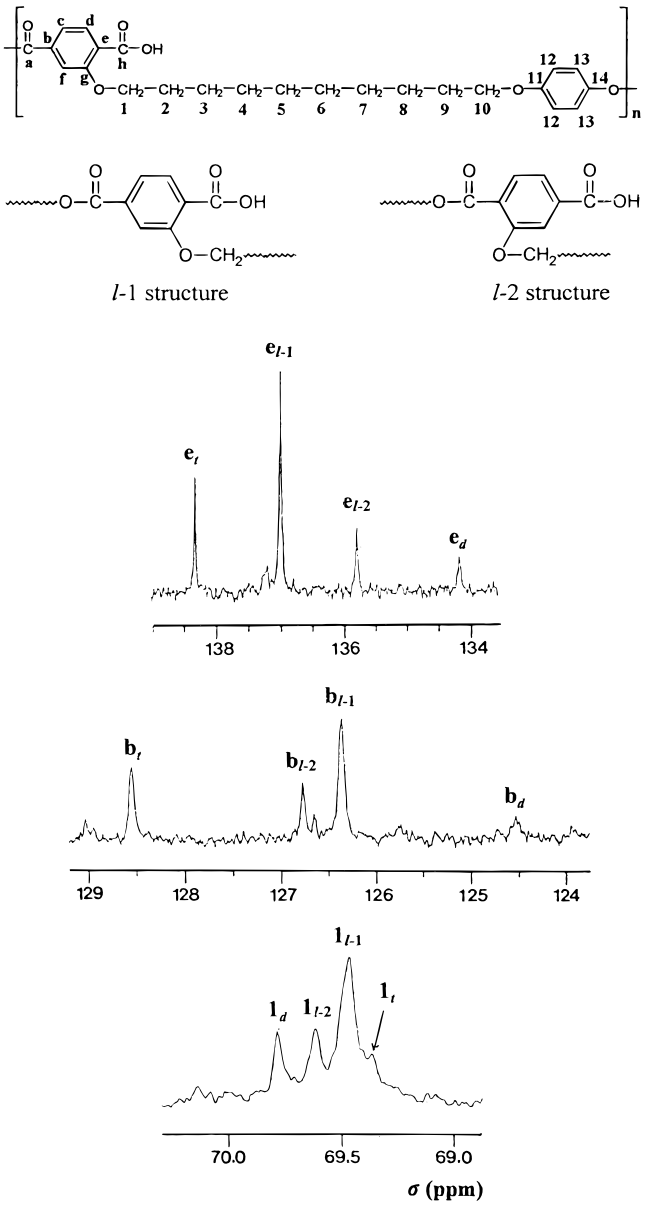


Figure 3. ^{13}C NMR spectra of P-PDTA.

chains during esterification reactions and subsequent separation processes. The inherent viscosity values of the two esterified polymers were 0.24 and 0.23 dL/g in NMP; they are again lower than those of the starting polymers.

Measurement of the Degree of Branching by NMR[25−27]. The NMR spectra of P-PDTA(ester) and P-BDTA(ester) were used as references for the peak assignment of P-PDTA and P-BDTA spectra, respectively. Peak assignment are summarized in Figures 3 and 4. The peak assignments are based on the peak positions of the monomers **6** and **7** and their *p*-ethoxyphenol esters. Some peak integrals were observed to be off about 15% from ideal values. Unfortunately, all peaks could not be assigned clearly and some peaks were overlapped. Thus, only the aliphatic carbon peaks were used for the calculation of the degree of branching (DB). The carbon peaks of P-PDTA used for calculation of DB are summarized in Table 2. Likewise, the carbon peaks of P-BDTA are summarized in Table 3. From the data for the aliphatic carbon 1 and the definition of DB by

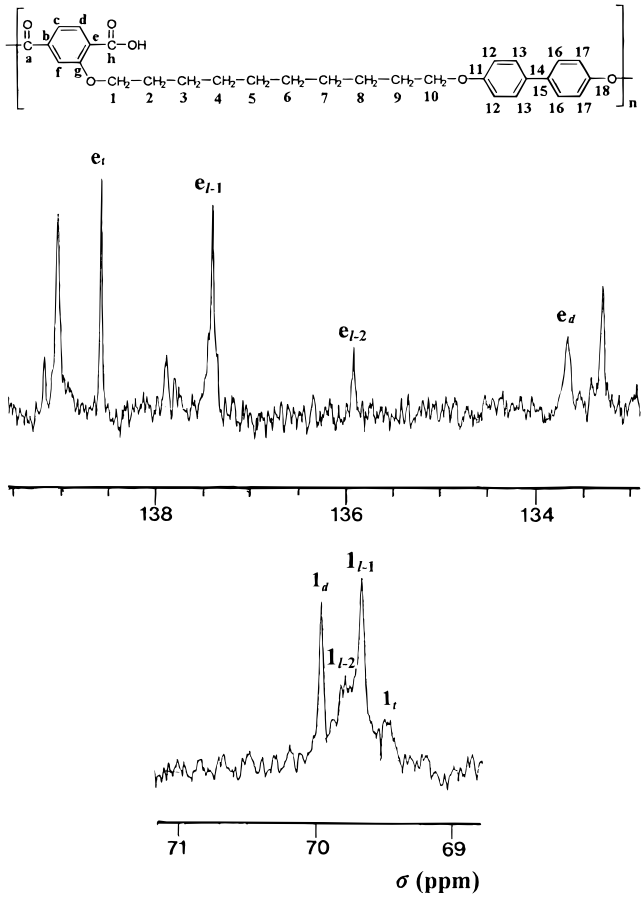


Figure 4. ^{13}C NMR spectra of P-BDTA.

Table 2. Carbon-13 Resonance Peaks of P-PDTA Used for Calculation of the Degree of Branching[a]

carbon site	chemical shift (ppm)	integral	DB (%)
e_t	138.3	0.21	
e_d	134.3	0.12	
e_{l-1}	137	0.58	
e_{l-2}	135.8	0.16	
b_t	128.6	0.23	
b_d	124.6	0.15	
b_{l-1}	126.4	0.42	
b_{l-2}	126.8	0.22	
1_t	69.35	0.22	
1_d	69.77	0.18	37 ± 10
1_{l-1}	69.45	0.40	
1_{l-2}	69.60	0.21	

[a] For notation of peaks, refer to Figure 3. Subscript *t*, *d*, *l*-1, and *l*-2 were added to the notation for P−PDPA to denote carbon sites in terminal, branched, linear 1, and linear 2 units, respectively.

$$\mathrm{DB} = \frac{2D}{2D + L}$$

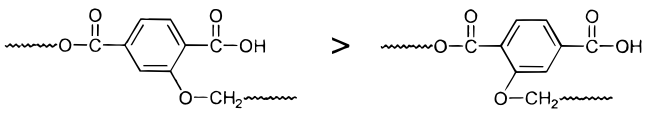
where D and L are the fractions of dendritic and linealy incorporated monomer units, respectively, we obtain degrees of branching of 37 ± 10% and 43 ± 10% for P-PDTA and P-BDTA, respectively. Among the three carbon atoms of e, b, and 1 subjected to NMR analysis, only the aliphatic carbon atoms 1 in both P-PDTA and P-BDTA appear to provide us with more reliable results: terminal (*t*) and dendritic (*d*) units reveal almost the same probabilities, not far from 0.25, and linear units ($1_{l-1} + 1_{l-2}$) have a probability close to 0.5, both of which are predicted by theoretical considerations.[26] However, it should be noted that the DB values thus obtained are

Table 3. Carbon-13 Resonance Peaks of P-BDTA Used for Calculation of the Degree of Branching[a]

carbon site	chemical shift (ppm)	integral	DB (%)
e_t	138.6	0.23	
e_d	133.7	0.28	53 ± 10
e_{l-1}	137.4	0.38	
e_{l-2}	135.9	0.11	
1_t	69.50	0.20	
1_d	69.97	0.22	43 ± 10
1_{l-1}	69.67	0.36	
1_{l-2}	69.80	0.22	

[a] For notation of peaks, refer to Figure 4. Subscript *t*, *d*, *l*-1, and *l*-2 were added to the notation for P-BDTA to denote carbon sites in terminal, branched, linear 1, and linear 2 units, respectively.

only approximate ones since the present polymers were not prepared from exactly AB_2 type monomers. The DB values[34,35] reported for hyperbranched aromatic polyesters are about 50%. Our values appear significantly lower than those values reported for AB_2 polymers by others. This can be explained by the fact that not only are the two carboxylic acid groups in the PDTA and BDTA monomers inequivalent but also one of them is less reactive than the other because of electronic and steric effects of the alkoxy spacer substituent attached onto the phenylene ring. From the data given in Tables 2 and 3 and the spectra shown in Figures 3 and 4, we are able to note that the integrated values of the NMR peaks of e_{l-1}, b_{l-1}, and 1_{l-1} are significantly greater than those of e_{l-2}, b_{l-2}, and 1_{l-2}. This means that the linear structure 1 is much more abundant in the produced polymers than the linear structure 2.



l-1 structure *l*-2 structure

According to the integrated values, the concentration of linear structure 1 is about twice that of linear structure 2. In other words, the carboxylic acid group ortho to the branching alkoxy spacer substituent is much less reactive than the one meta to the branching substituent. This can be ascribed to the electron-donating character of the branching alkoxy substituent as well as to the steric hindrance exerted by the substituent. The combined effects will lead to a lower degree of branching when compared to other AB_2 type systems[34–38] where the two B functional groups are equivalent in reactivity and steric effect is not as severe as in the present systems.

Thermal and Liquid Crystalline Properties of Polymers. As the DSC thermograms (Figure 5) of the present polymers show, P-PDTA and P-BDTA reveal two endothermic transitions on the heating DSC curves. The first peaks correspond to glass transitions and the second ones to mesophase → isotropic phase transitions. Since the polymers are amorphous, they do not show any melting transition. This sequence of phase transitions was confirmed by the observation of the changes in their optical textures during heating of the polymers on a polarizing microscope. These transitions were reversible: the reverse transitions occurred on cooling the isotropic melts. The T_g values of P-PDTA and P-BDTA found by DSC analysis are 83 °C and 70 °C, respectively. The T_g values, however, drop down to 20 °C and 26 °C, respectively, when carboxylic acid groups

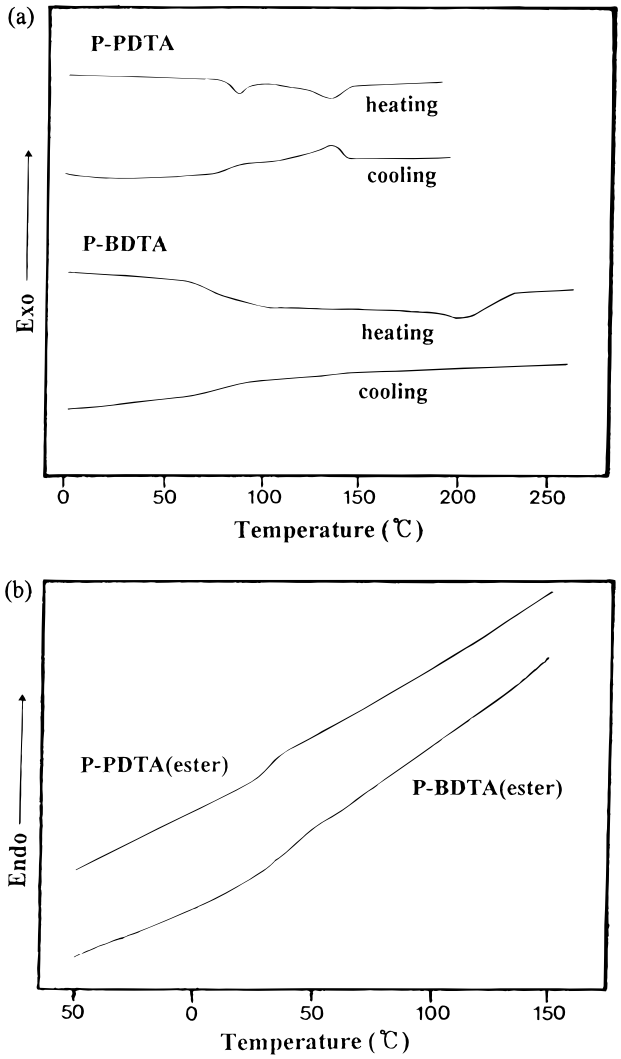


Figure 5. DSC thermograms of (a) P-PDTA and P-BDTA and (b) P-PDTA(ester) and P-BDTA(ester).

of the original polymers are converted to methyl esters (Table 1). This phenomenon strongly reflects the fact that hydrogen bonding between the carboxylic acid end groups enhances the rigidity of the polymer chains, resulting in elevated T_g's. In fact, formation of cyclic dimers by hydrogen bonding between the carboxylic acid terminals in P-PDTA and P-BDTA appears to be the driving force for them to be thermotropic, nematic (Figures 6 and 7). Since all of the carboxylic acid terminals are on an aromatic structure, such hydrogen bondings will generate enough long and rigid structures to promote the formation of a mesophase (see formulas below).[30] But esterification of carboxylic acid terminals makes such hydrogen bondings impossible, with a result that the polymers become non liquid crystalline. This is rather surprising in light of the fact that even esterified polymers, i.e., P-PDTA(ester) and P-BDTA-(ester), should contain triad as well as diad para-linked aromatic ester type mesogenic units, but they are not liquid crystalline. The reason for this observation can be ascribed to the branched structure of the triad mesogenic unit; all of the central phenylene rings of the triad ester structures are connected to another mesogenic unit of the same structure through the decamethylene spacer. Therefore, formation of ordered domains by the collective interactions of mesogenic units is expected to be rather difficult due to competition

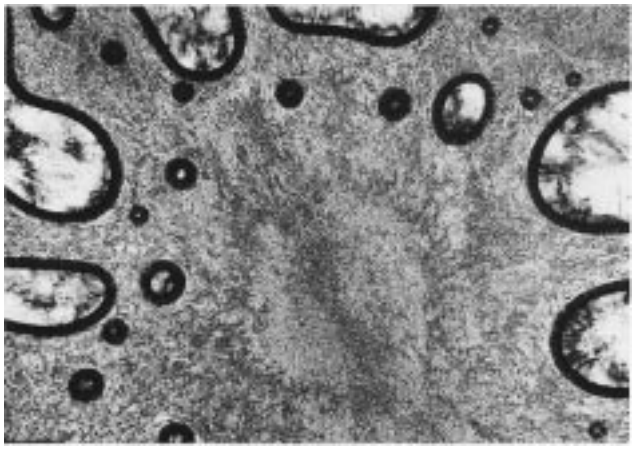


Figure 6. Photomicrograph of P-PDTA taken at 123.8 °C (magnification 200×).

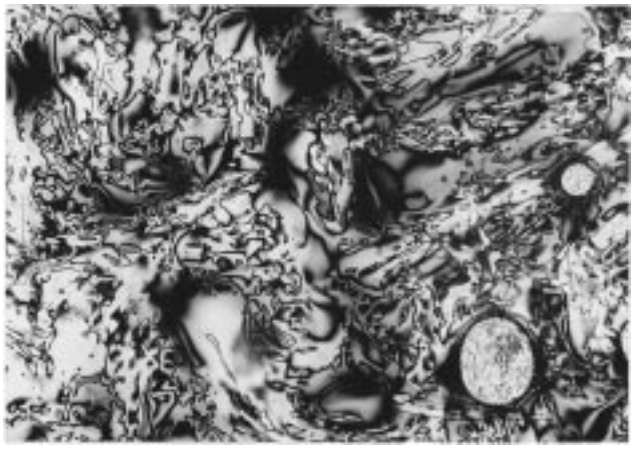
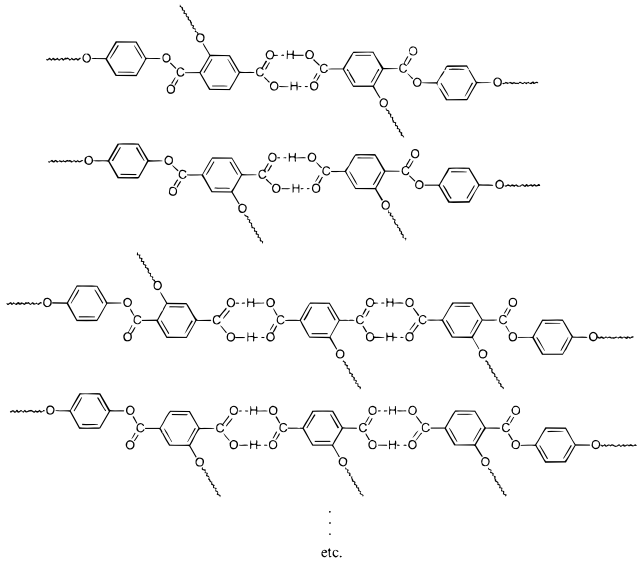


Figure 7. Photomicrograph of P-BDTA taken at 207 °C (magnification 200×).

among the mosogenic units tied to each other. Earlier, Percec et al.[13,14] reported that hyperbranched aromatic polyethers containing polymethylene spacers could form mesophases. They claimed that this could be possible through conformational isomerism of the spacers that favors the formation of parallel alignment of mesogens leading to mesophasic ordering.



But it is evident that the similar explanation may not be applicable to the present polymers. There is one major structural difference between the present polymers and Percec's polymers. The present polymers have branching points located at the middle of mesogenic units, whereas in Percec's polymers the branching spacers are attached to the flexible spacers in the main chain. Evidently, the latter structure can accommodate more readily conformational isomerism of the spacers, leading to a parallel alignment of mesogens. Recently, we[39] have reported that decamethylene spacers connecting the main chain consisting of aromatic esters and side group mesogenic units are in the extended conformation even in the mesophase. It appears that conformation of polymethylene spacers strongly depends on whether they are attached to a rigid structure or to a flexible structure. When the flexible spacers are present in both the main chain and branch structures, hyperbranched aromatic polyesters seem to be able to form mesophases more readily.[17]

The mesophase → isotropic phase transition, i.e., isotropization, occurs at 142 °C for P-PDTA; that is far lower than the isotropization temperature (T_i: 208 °C) of P-BDTA. Such a big difference in T_i values can be explained by the fact that the mesogenic units in P-BDTA are longer than those of P-PDTA because the former contain the longer, 4,4′-biphenol moiety whereas the latters contain the shorter, hydroquinone moiety. Moreover, formation of hydrogen bonds between the carboxylic acid terminals would generate far longer rigid units in P-BDTA than in P-PDTA. Such a structural difference between the two polymers must be a major factor for the difference in their T_i values.

Thermal stability of the polymers was examined on a thermogravimetic analyzer under a nitrogen atmosphere and with IR spectra of the residue. Their TGA thermograms revealed a common feature; an initial weight loss (10−13%) at 300−350 °C followed by a major weight loss at about 400 °C. The first weight loss appears to be originated from the involvement of terminal groups in further polymerization and also a partial decarboxylation, and the second major weight loss is from chain breakages. Turner et al.[35] reported earlier a similar observation for hyperbranched aromatic polyesters. In fact, decarboxylation appears to be the major reason for the initial weight loss especially for P-PDTA and P-BDTA. The IR spectra of the residue of the two polymers obtained after being heated to 370 and 390 °C, respectively, for P-PDTA and P-BDTA, show a very weak carboxyl absorption at 2400−3600 cm^{-1}.

Conclusion

Two new hyperbranched aromatic polyesters having oxydecamethyleneoxy branching points on the central units of aromatic triad units and their ester-terminated counterparts were synthesized, and their LC properties were studied. Only the polymers having terminal carboxylic acid groups are able to form nematic phases. Hydrogen-bond formation between the terminal carboxylic acid groups leading to cyclic dimers appears to be a major driving force for the polymers to be thermotropic. This reasoning is supported by the fact that, when the terminal carboxylic acid groups are esterified, the polymers lose thermotropic characters. The hydrogen bond effect is also clearly reflected by significantly higher T_g values for the polymers with terminal carboxylic acid groups than those of esterified terminal groups. Degrees of branching of the polymers accessed

by ^{13}C NMR spectroscopy are lower than those of other hyperbranched polymers. This is explaned by the inequivalence of the two carboxylic acid groups in the present monomers caused by a strong steric effect by the alkoxy branch group ortho to one of two acid groups.

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References and Notes

(1) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(2) Newkome, G. R., Ed. *Advances in Dendritic Macromolecules*; JAI: Greenwich, 1994; Vol. 1.
(3) Pesak, D. J.; Moore, J. S.; Wheat, T. E. *Macromolecules* **1997**, *30*, 6467.
(4) Kambouris, P.; Hawker, C. J. *J. Chem. Soc., Perkin Trans 1* **1993**, 2717.
(5) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079.
(6) Fréchet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 1399.
(7) Aoi, K.; Itho, K.; Okada, M. *Macromolecules* **1995**, *28*, 5391.
(8) Knapen, J. W. J.; Van der Made, A. W.; De Wilde, J. C.; Van Leuwen, P. W. N. M.; Wijkens, P.; Van Koten, G. *Nature* **1994**, *372*, 659.
(9) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, *118*, 3978.
(10) Cherestes, A.; Engel, R. *Polymer* **1994**, *35*, 3343.
(11) Mak, C. C.; Chow, H.-F. *Macromolecules* **1997**, *30*, 1228.
(12) Newkome, G. R.; Baker, G. R.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, Germany, 1996.
(13) Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843.
(14) Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441.
(15) Percec, V.; Cho, C. G.; Pugh, C.; Tomazos, D. *Macromolecules* **1992**, *25*, 1164.
(16) Percec, V.; Chu, P.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1995**, *117*, 11441.
(17) Bauer, S.; Fischer, H.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1589.
(18) Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.
(19) Kim, Y. H. *Adv. Mater.* **1992**, *4*, 764.
(20) Collier, J.; Chisher, G. B. *Br. J. Pharmacol.* **1956**, *11*, 20.
(21) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1988; p 356.
(22) Buckhard, C. A.; Burnett, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 341.
(23) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1988; pp 267−268.
(24) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1988; p 284.
(25) Hölter, D.; Frey, H. *Acta Polym.* **1997**, *48*, 298.
(26) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.
(27) Beginn, U.; Drohmann, C.; Möller, M. *Macromolecules* **1997**, *30*, 4112.
(28) Breitmaier, E. *Structure Elucidation by NMR in Organic Chemistry: A Practical Guide*; John Wiley & Sons: New York, 1993.
(29) (a) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: Weinheim, Germany, 1987; p 255. (b) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 197.
(30) (a) Gray, G. W.; Jones, B. *J. Chem. Soc.* **1954**, 675. (b) Kato, T.; Kihara, H.; Kumar, U.; Uryu, T.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1644. (c) Kato, T.; Fréchet, J. M. J. *Macromol. Symp.* **1995**, *98*, 311.
(31) Barral, E. M.; Johnson, J. K. In *Liquid Crystals and Plastic Crystals*; Gray, G. W., Winsor, P. W., Eds.; Ellis Horwood: London, 1974; Vols. 1 and 2.
(32) Higashi, F. In *New Method for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum Press: New York, 1992; p 221.
(33) Boileau, S. In *New Method for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum Press: New York, 1992; p 179.
(34) Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, *26*, 4617.
(35) Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, *27*, 1611.
(36) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079.
(37) Hawker, C. J.; Chu, F. *Macromolecules* **1996**, *29*, 4370.
(38) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
(39) Piao, X. L.; Kim, J.-S.; Yun, Y.-K.; Jin, J.-I.; Hong, S.-K. *Macromolecules* **1997**, *30*, 2294.

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