Articles

Synthesis and Liquid Crystalline Properties of Hyperbranched Aromatic Polyesters Consisting of Azoxybenzene Mesogens and Polymethylene Spacers[†]

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Received February 27, 2002

A new series of hyperbranched aromatic polyesters containing azoxybenzene mesogens and polymethylene spacers were prepared by polymerizing AB_2 type monomers that have the isophthaloyl dicarboxylic acid terminal at one end and the *p*-oxyphenol terminal at the other end. The monomers contain a built-in azoxybenzene mesogen that is linked to the terminal groups through polymethylene spacers. The polyesters prepared were characterized by solution viscosity, differential scanning calorimetry, X-ray diffractometry and polarizing microscopy. All of the polyesters were found to be thermotropic (nematic). Their glass-transition temperatures and mesophase temperature ranges were very sensitive to the length of the two spacers existing in the repeating unit. The degree of branching of one of the polyesters was determined by the NMR spectroscopy and found to be 0.56.

Key Words : Hyperbranched LCPs, Aromatic polyesters, Built-in mesogen, Degree of branching

Introduction

The most important structural requirement for a polymer to be liquid crystalline is the rigid rodlike molecular shape or to contain long enough rigid structural units, *i.e.*, mesogenic units, along the backbone. They may contain so-called flexible spacers such as polymethylene, polyoxyethylene, and oligosiloxyl groups. These polymers are commonly called main chain liquid crystalline polymers (LCPs).[1-7] In contrast, the side chain LCPs[8-13] contain the mesogenic units in the side branches or as pendants. Many papers[1-7] have been published during the past quarter of a century on the structure-property relationships of main chain LCPs. Thanks to those research efforts, the structure-property relationship of the main chain and side chain LCPs are rather well established.

Recently, hyperbranched polymers are attracting a great deal of interest among polymer scientists due to their interesting structural features[14-18] and also to their possible future applications.[19-25] They are readily prepared by polymerizing AB_x ($x \geq 2$) type of monomers. Earlier, Percec *et al.*[26-33] reported LC behavior of hyperbranched aromatic polyethers containing flexible spacers. They claimed that the spacers undergo conformational changes in such a way that the dendritic architecture of the polymer molecules is transformed into more compact, branched collinear shape. The structure of the mesogenic units in the polymers was benzylphenyl or benzylbiphenyl ether that can also undergoes conformational adjustment by rotation around the single

bond connecting the two phenylene units.

We[34,35] previously reported LC properties of two different types of hyperbranched aromatic polyesters as graphically represented below:

In polymer 1[34] the connecting or branching points are located at the aromatic ester type mesogenic units whereas in polymer 2[35] they are located at the polymethylene flexible spacers. We found that polymer 1 was thermotropic only
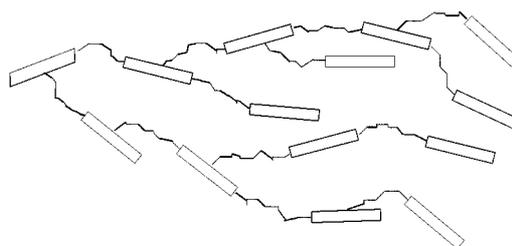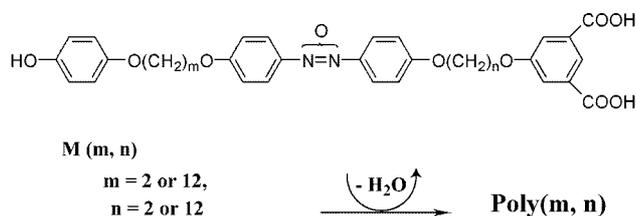

Polymer 1
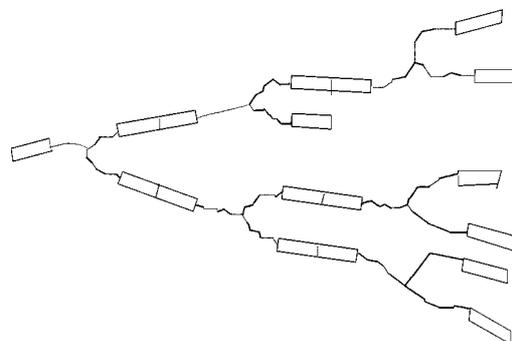
Polymer 2

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when the terminal carboxylic acid groups are kept as such. They lost their LC properties upon esterifying the acid end groups. This indicates that hydrogen bond formation between the carboxylic acid terminal groups is the driving force to the formation of the mesophase. On the other hand, polymer 2 was found to be thermotropic regardless whether the terminal groups remained unreacted or were esterified. Therefore, it was concluded that in polymer 2 a very highly degree of conformational freedom of the spacers create the opportunity for the mesogenic units to form LC domains. In the both polymers, the aromatic ester mesogenic groups

M (m, n)

m = 2 or 12,
n = 2 or 12

$- H_2O$

Poly(m, n)

were formed only by reactions between the carboxylic and hydroxyl terminal groups in the monomers.

In the present investigation, we tried to synthesize a series of hyperbranched polyesters consisting of azoxybenzene mesogens and polymethylene spacers. Differently from polymers 1 and 2, the mesogenic structure was built in the monomers which underwent polyesterification to form polymers. The structures of monomers are given below:

This paper discusses the synthetic details and LC properties of monomers and polymers therefrom. M and Poly stand for monomers and polymers, respectively. The letters m and n present the number of methylene units in the spacers.

Experimental Section

Synthesis of Monomers. Since the synthetic procedure for the preparation of the three monomers is the same, only the details for the synthesis of **M (12, 12)** is given. The synthetic route is shown in Scheme 1.

Dimethyl 5-(12-bromododecyloxy)isophthalate, **2**. 1,12-Dibromododecane (46.0 g; 0.140 mol) was dissolved in 300 mL of acetone containing 7.5 g (0.054 mol) of potassium carbonate and 0.174 g (5.4 × 10^{-4} mol) of tetrabutylammonium bromide. While the solution was being refluxed, dimethyl 3-hydroxyisophthalate (3.8 g; 0.018 mol) in 20 mL of acetone was added to the solution over a period of one hour. The whole mixture was refluxed for 24 hrs. The salts formed and remaining K$_2$CO$_3$ were removed by filtration. The volume of the filtrate was reduced to about 200 mL by distilling out acetone under a reduces pressure, to which excess methanol was added precipitating the yellowish product. The product was thoroughly washed with methanol and dried under vacuum. The yield was 6.8 g (83%), mp 65 $^{\circ}$C.

Anal. Calcd for C$_{22}$H$_{33}$BrO$_5$: C 57.77 H 7.27. Found C 57.80 H 7.32. IR spectrum (KBr; cm^{-1}): 2916 (aliphatic C-H stretching), 1728 (ester C=O stretching), 1593 (aromatic C-C

stretching), 1242 (C-O stretching). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 1.29-1.47 (m, 16H, -CH$_2$CH$_2$CH$_2$-), 1.78-1.88 (m, 4H, -OCH$_2$CH$_2$- & BrCH$_2$CH$_2$-), 3.41 (t, 2H, BrCH$_2$-), 3.94 (s, 6H, ArCOOCH$_3$), 4.04 (t, 2H, -OCH$_2$-), 7.74-7.75 (d, 2H, ArH), 8.26 (s, 1H, ArH)

Mono-[12-(3,5-Bis(methoxycarbonyl)phenoxy)dodecyl] ether of 4,4'-azoxydiphenol, 4. 4,4'-Azoxyphenol[36] (**3**, 12.3 g; 0.053 mol) was dissolved in 300 mL of acetone containing 5.7 g (0.041 mol) of K$_2$CO$_3$ and 0.7 g (2 × 10^{-3} mol) of tetrabutylammonium bromide. While the mixture was being refluxed, 4.5 g (9.8 × 10^{-3} mol) of **2** dissolved in 20 mL of acetone was added dropwise over a period of one hour. After removing the insolubles by filtration, acetone in the mixture was removed by distillation under a reduced pressure. The residue was thoroughly washed with methanol. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane (1:2 by vol.) as an eluent. The product yield was 3.6 g (60%), mp 128 $^{\circ}$C.

Anal. Calcd for C$_{34}$H$_{42}$N$_2$O$_8$: C 67.31 H 6.98 N 4.62. Found C 67.20 H 6.91 N 4.72. IR spectrum (KBr; cm^{-1}): 3425 (O-H stretching), 2924 (aliphatic C-H stretching), 2852 (C-H stretching of ArOCH$_2$), 1720 (ester C=O stretching), 1595 (aromatic C-C stretching), 1257, 1043 (C-O stretching). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 1.30-1.80 (m, 20H, -CH$_2$CH$_2$CH$_2$-), 3.94 (s, 6H, ArCOOCH$_3$), 4.02 (t, 2H, -OCH$_2$-), 6.92-8.25 (m, 11H, ArH)

12-Bromododecyl 12-[3,5-bis(methoxycarbonyl)phenoxy]-dodecyl ether of 4,4'-azoxyphenol, 5. In order to prepare **5**, 1,12-dibromododecane was reacted with **4** following the same procedure as in the case of preparation of **2**. After the solvent was removed from the reaction mixture using a rotavap, the residue was dissolved in a small quantity of dichloromethane. The solution was poured into excess hexane. The precipitate was collected on a filter and washed thoroughly with hexane. The product yield was 71%, mp 89 $^{\circ}$C.

Anal. Calcd for C$_{46}$H$_{65}$BrN$_2$O$_8$: C 64.70 H 7.67 N 3.28. Found C 64.55 H 7.58 N 3.37. IR spectrum (KBr; cm^{-1}): 2920 (aliphatic C-H stretching), 2850 (C-H stretching of ArOCH$_2$), 1726 (ester C=O stretching), 1597 (aromatic C-C stretching), 1256, 1045 (C-O stretching). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 1.29-1.83 (m, 40H, -CH$_2$CH$_2$CH$_2$-), 3.41 (t, 2H, BrCH$_2$-), 3.94 (s, 6H, ArCOOCH$_3$), 4.03 (m, 6H, -OCH$_2$-), 6.92-8.25 (m, 11H, ArH).

12-(4-Hydroxyphenoxy)dodecyl 12-[3,5-bis(methoxy-carbonyl)phenoxy]dodecyl ether of 4,4'-azoxydiphenyl, 6. Hydroquinone was reacted in acetone with **5** in the presence of K$_2$CO$_3$ and tetrabutylammonium bromide. The reaction condition was exactly same as the one employed in the synthesis of **5**. At the end of the reaction, salts formed and remaining K$_2$CO$_3$ were removed by filtration from the reaction mixture. And then acetone was distilled out by a rotavap. The crude product was extracted from the residue using methylene chloride. Methylene chloride was distilled out again using a rotavap. The residue was subjected to purification by column chromatography on silca gel. A mixture of dichloromethane and methanol (50:1 by vol.) was

used as an eluent. The product yield was 53%, mp 120 $^\circ$C.

Anal. Calcd for $C_{52}H_{70}N_2O_{10}$: C 70.72 H 7.99 N 3.17. Found C 70.80 H 8.04 N 3.11. IR spectrum (KBr; cm^{-1}): 3468 (O-H stretching), 2920 (aliphatic C-H stretching), 2852 (C-H stretching of ArOCH_2), 1726 (ester C=O stretching), 1597 (aromatic C-C stretching), 1252, 1043 (C-O stretching). ^{1}H-NMR spectrum (CDCl$_3$, δ, ppm): 1.30-1.81 (m, 40H, -CH$_2$$CH_2CH_2$-), 3.89-4.03 (m, 8H, -O$CH_2$-), 3.94 (s, 6H, ArCOO$CH_3$), 6.76-8.25 (m, 15H, Ar$H$).

12-(4-Hydroxyphenoxy)dodecyl 12-[3,5-bis(carboxy)-phenoxy]dodecyl ether of 4,4'-azoxydiphenol, M (12, 12). Compound **6** (0.77 g; 8.7×10^{-4} mol) was dissolved in 100 mL of ethanol containing 0.15 g (0.3×10^{-2} mol) of KOH. The mixture was refluxed for 5 h. The reaction mixture was poured into excess water. And then the solution was acidified to pH 2 by adding 1M HCl. The precipitate formed was thoroughly washed with water and dried. The product yield was 0.69 g (93%), mp 153 $^\circ$C.

Anal. Calcd for $C_{50}H_{66}N_2O_{10}$: C 70.23 H 7.78 N 3.28. Found C 70.15 H 7.69 N 3.34. IR spectrum (KBr; cm^{-1}): 3600-2400 (acidic O-H stretching), 3080 (aromatic C-H stretching), 2920 (aliphatic C-H stretching), 2850 (C-H stretching of ArOCH_2-), 1697 (acid C=O stretching), 1595 (aromatic C-C stretching), 1254, 1034 (C-O stretching). ^{1}H-NMR spectrum (TFA-d, δ, ppm): 1.12-1.26 (m, 32H, -CH$_2$CH$_2$$CH_2CH_2CH_2$-), 1.57-1.66 (m, 8H, ArOCH$_2$$CH_2$-), 3.99-4.02 (m, 8H, ArOCH_2-), 6.67-8.29 (m, 15H, ArH).

M (2, 12) and **M (12, 2)** were prepared by the same procedure. Their melting points are 187° and 205 $^\circ$C, respectively. The structures of intermediates and the final monomers were confirmed by elemental and spectroscopic analyses.

Synthesis of Polymers[37]. Since all the polymers were prepared by the same procedure, representative synthetic details are given only for **Poly (12, 12)**.

Poly (12, 12). The monomer **M (12, 12)** (0.57 g; 6.7×10^{-4} mol) dissolved in 8 mL of dry pyridine was slowly added at 0 $^\circ$C to a mixture of 0.2 mL of purified thionyl chloride and 4 mL of dry pyridine. The whole mixture was stirred for 20 minute at room temperature, and then for 10 h at 80 $^\circ$C. At the end of polymerization, the reaction mixture was poured with vigorous stirring into 100 mL of methanol. The precipitate was collected on a thimble and subjected to Soxhlet extraction for 3 days using methanol. Finally, the polymer obtained was dried in a vacuum oven at 50 $^\circ$C. The recovered yield was 0.24 g (55%).

IR spectrum (KBr; cm^{-1}): 3600-2400 (acidic O-H stretching), 3082 (aromatic C-H stretching), 2924 (aliphatic C-H stretching), 2852 (C-H stretching of ArOCH_2-), 1726 (ester C=O stretching), 1697 (acid C=O stretching), 1595 (aromatic C-C stretching), 1252, 1024 (C-O stretching). ^{1}H-NMR spectrum (TFA-d, δ, ppm): 1.20-1.35 (m, 16H, -CH$_2$CH$_2$-CH_2CH$_2$CH$_2$-), 1.72 (m, 4H, ArOCH$_2$$CH_2$-), 3.90-4.42 (m, 8H, ArOCH_2-), 6.98-8.27 (m, 15H, ArH)

Poly (2, 12) and **Poly (12, 2)** was obtained by the same procedure. The recovered yields after purification were 69 and 58%, respectively. Their structures were also confirmed

spectroscopically.

Characterization of Polymers. IR and ^{1}H-NMR spectra of intermediates, monomers, and polymers were obtained respectively on a Bomem MB FT-IR instrument and a Bruker AM 300 NMR spectrometer. The solution viscosity values of the polymers were obtained at 30 $^\circ$C for 0.13 g/dL solution in a mixture of *p*-chlorophenol and 1,1,2,2-tetrachloroethane (v/v = 1/1). Thermal properties of the polymers were studied in a stream of nitrogen atmosphere on a differential scanning calorimeter (Mettler DSC 821^e) at the heating and cooling rate of 5 $^\circ$C/min and also on a thermogravimetric analyzer (Mettler TG 50) at the heating rate of 10° C/min. The inflection points on the DSC and TGA curves were taken respectively as the glass transition temperatures (T_g's) and the initial decomposition temperatures (T_d's), whereas the temperatures of peak minima were taken for isotropization temperatures (T_i's).

The wide-angle X-ray diffractograms (WAXD) of polymers were obtained on an X-ray diffraction system (XRD, MAC Science MXP3A-HF) of the Center for Mineral Resources Research, Korea University. A curved graphite monochromator filtered Cu-Kα line was utilized as the X-ray source. Optical textures of polymer melts were obtained on a cross-polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP-82HT).

Result and Discussion

Synthesis and General Properties of Polymers. All the present hyperbranched were obtained by homopolymerization of the respective monomers utilizing the condensing agent pair of thionyl chloride and pyridine. The use of the combination of thionyl chloride and pyridine was found to be a satisfactory condensing agent pair in the preparation of other hyperbranched LC polyesters earlier by us[34,35] and also in the preparation of other polyesters by Higashi *et al.*.[37] The only inconvenience experienced in the present syntheses was that the three monomers had to be prepared *via* multistep route as shown in Scheme 1. Polymerization of the three monomers proceeded homogeneously. The polymers obtained from the reaction mixtures by precipitation in methanol were subjected to methanol Soxhlet extraction to remove impurities and soluble low molar mass oligomers, which resulted in relatively low recovered yields (55-69%). The final polymers were found to be soluble in trifluoroacetic acid, tetrachloroethane, pyridine, and mixtures of phenol and tetrachloroethane. The solution viscosity values of the polymers are shown in Table 1 and range from 0.57 to 1.70. These values are regarded fairly high, when they are compared with those of other series of hyperbranched aromatic polyesters reported recently by us.[34,35] Although we could not measure their absolute molar mass, it can be safely said that their molar mass are higher than $\overline{M}n = 20,000$ according to the earlier reports by us[34,35] and others[38-40] on the viscosity values and absolute mass of other series of hyperbranched polyesters.

The three polymers are amorphous at room temperature as
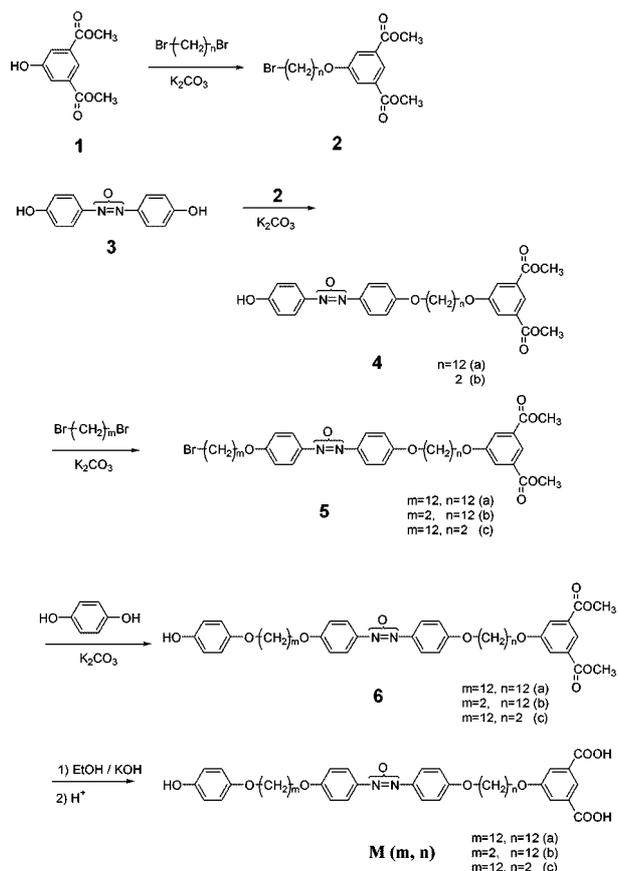
Scheme 1. Synthetic route to monomers.

Table 1. General Properties of **Poly (m, n)s**

Polymer	η_{inh},dL/g[a]	T_g, ^oC[b]	T_i, ^oC[b]	T_d, ^oC[c]	LC
Poly (12, 12)	0.57	91	130 (126-149)[d]	279	Nematic
Poly (2, 12)	1.47	109	141 (138-160)[d]	277	Nematic
Poly (12, 2)	1.70	96	112 (107-128)[d]	296	Nematic

[a]Inherent viscosities were measured at 30 ± 0.1 ^oC on 0.13 g/dL in a mixed solvent of *p*-chlorophenol/1,1,2,2-tetrachloroethane (v/v = 1:1). [b]Transition temperature ranges estimated from the DSC thermograms of the 1st heating cycle at the heating rate of 5 ^oC/min are so broad that the numbers are to be taken only as approximate value. [c]Estimated from the TGA at the heating rate of 10 ^oC/min. [d]Values in the parenthesis estimated from optical microscope on a hot stage at the heating rate of 5 ^oC/min.

shown by their wide-angle X-ray diffractrometry. They commonly show a broad halo centered around $2\theta = 19^o$ (d= 4.7 Å) corresponding to interchain distance. Table 1 tablulates the T_g (see also Figure 1) and T_d values of the polymers. The T_g transitions were more clearly observed on the heating DSC curves than on the cooling curves. The T_g values depend greatly not only on the length (m and n) of the two spacers and also on their combinations. Comparing the T_g values, we can draw two generalizations even with the limited number of data: 1) The combination of longest spacers, *i.e.*, m and n, results in the lowest value (91 ^oC) of T_g for **Poly (12, 12)** among the present three polymers and 2) the spacer (spacer-m) length (m) between the mesogenic unit and the hydroquinone moiety is significantly more effective
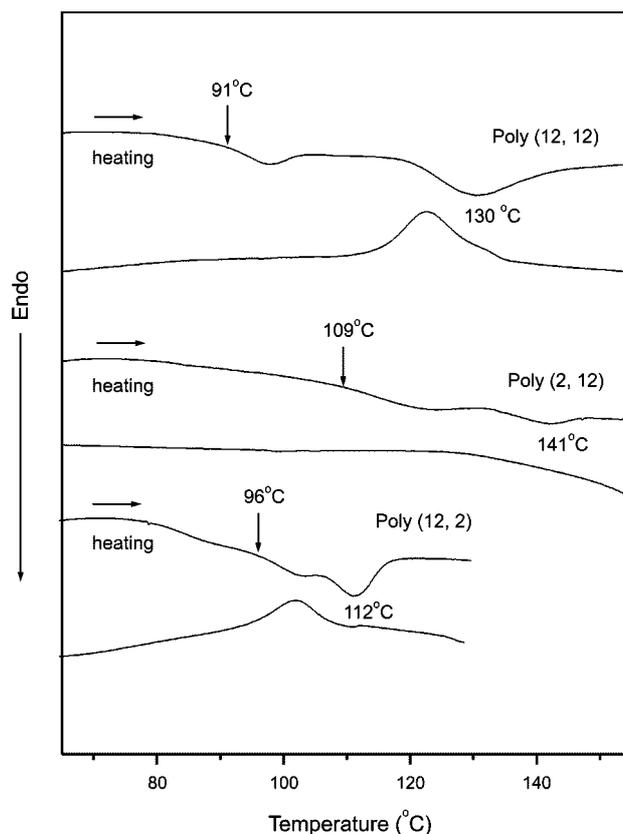

Figure 1. DSC thermograms of **Poly (m, n)s**.

in lowering the T_g value than the length (n) of the other spacer (spacer-n) existing between the mesogenic unit and the dicarboxylic, *i.e.*, isophthalic acid moiety. As one can see from Table 1, the T_g value (96 ^oC) of **Poly (12, 2)** is much lower than that (109 ^oC) of **Poly (2, 12)**. The first phenomenon is very well in accord with what is expected. In contrast, the second observation is rather surprising and makes us raise some dubiety on the reason why the two spacers influence the T_g so differently. We, however, can find the answer rather easily by a close examination of the structures of the monomers and polymers.

As stated above, the present monomers are of an AB_2 type in which the spacer-m is linked to the structural unit of A whereas the spacer-n to the B structural unit. When the present monomers are polymerized to the corresponding hyperbranched structures, most of the terminals will be the isophthalate moieties or B-termini that are directly linked to the spacer-n's. In other words, more of the spacer-m than the spacer-n will be placed in the middle parts of the branched backbones. Therefore, the T_g values of the polymers will be governed by the spacer-m more than by the spacer-n.

The T_d values of the present polymers are not much different from each other and they range from 27 to 296 ^oC. This is ascribed to the common presence of the azoxy group which is the thermally least stable structural unit existing along the backbone.

Liquid Crystalline Properties of Polymers. As the DSC thermograms (Figure 1) of the present polyesters show, they

(a)

(b)
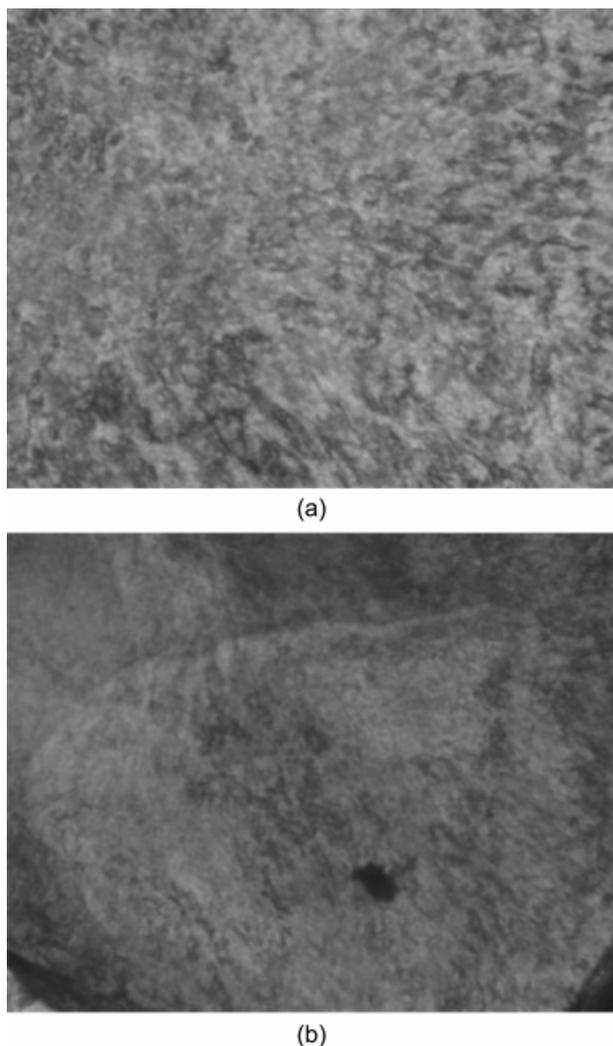
Figure 2. Optical photomicrographs of **Poly (12, 12)** at 118 °C and **Poly (12, 2)** at 105 °C (magnification 400X).

reveal two transitions: one at a lower temperature for glass transition and the other at a higher temperature for isotropization. Since the polymers are amorphous as described in the previous section, they did not exhibit any melting transition. Observation of the polymers on the polarizing microscope also could confirm the sequence of phase transitions. DSC analysis and polarizing microscopic observations proved the reversibility of the transitions. Figure 2 shows the optical textures of **Poly (12, 12)** and **Poly (12, 2)**, both of which reveal so-called polished marble texture typical of nematic liquid crystals. The polymer melts became birefringent above the T_g's, but the nature of the mesophase was not definitive due to unclear optical textures initially formed. Therefore, we had to age the melts for a prolonged period time, very often even 24 h, at the intended temperatures before the much better optical textures were developed revealing more clearly the nature of the mesophases.

Figure 3 compares WAXD's of **Poly (2, 12)** obtained at three different temperatures of (a) below T_g, (b) the LC phase, and (c) above T_i. The diffractograms show a subtle dependence on temperature or the phase of the polymer. For
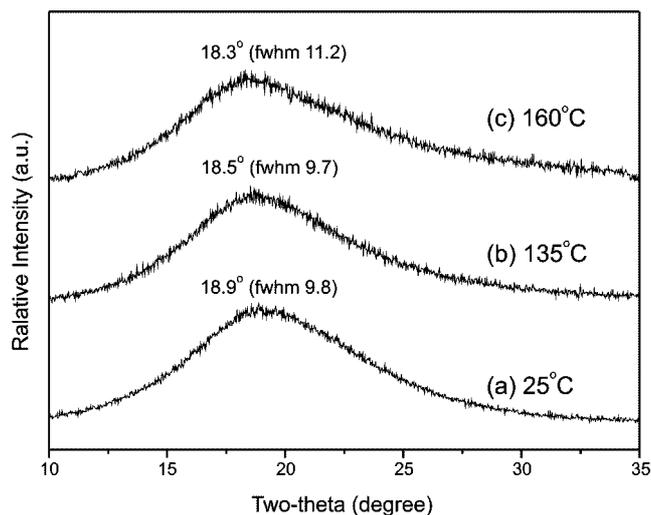

Figure 3. Wide-angle X-ray diffractograms of **Poly (2, 12)** at (a) 25 °C, (b) 135 °C, and (c) 160 °C.

the amorphous phase below T_g, it exhibits the maximum at $2\theta = 18.9°$ (d = 4.7 Å) with an fwhm (full-width at the half maximum) of 9.8°. When the temperature was raised to 135 °C, far above its T_g (109 °C) and in the temperature range of the nematic phase, the maximum 2θ angle slightly moved to small angle region but the fwhm decreased a little bit to 9.7° indicating an increased molecular ordering. Further increase of the temperature to 160 °C, *i.e.*, into the isotropic phase, caused a slight move of the diffraction peak toward increased spacing side ($2\theta = 18.3°$; d = 4.8 Å) accompanied by substantial increase in the fwhm to 11.2°. This indicates that there exist increased molecular motions and chaotic orientations in the isotropic phase when compared to the LC phase.

As far as the isotropization temperatures (T_i's) of the present polymers are concerned, they show a very interesting dependence on the length of spacer-m and spacer-n. The spacer-m's, as discussed above, are incorporated into branched backbones, whereas the spacer-n's will be located either in the branching points or at the termini. Therefore, the shorter the spacer-m, the more rigid the linear portions of the molecule become. On the other hand, longer spacer-n at the branching points will allow a higher degree of conformational freedom which would permit for the polymers' branched architecture to assume domains of elongated collinear shape facilitating the formation of nematic orientation of mesogens. A combination of the two factors would result in the highest T_i value (141 °C) for **Poly (2, 12)**, and the lowest value (112 °C) for **Poly (12, 2)**.

Degree of Branching. We determined the degree of branching of **Poly (12, 2)** by using ¹H-NMR spectroscopy. In order to determine the degree of branching the following
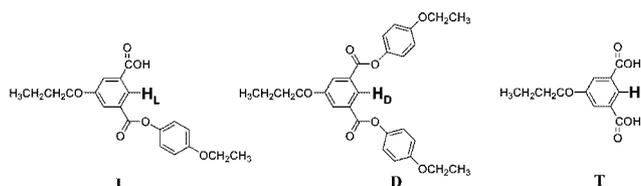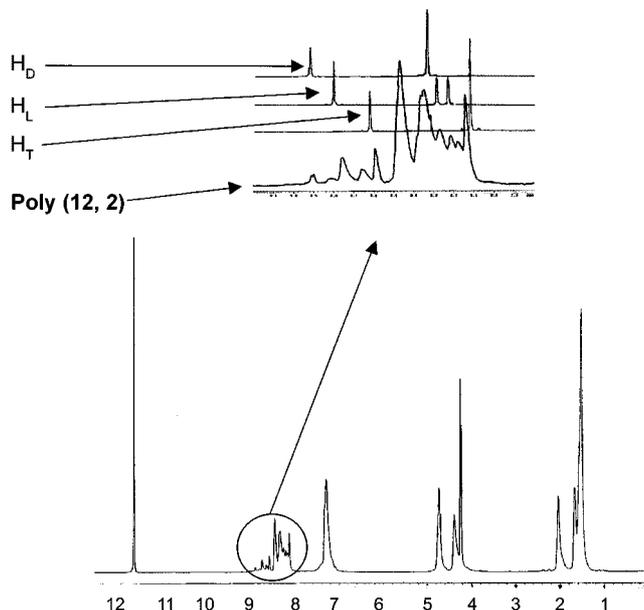
Figure 4. ^{1}H-NMR Spectra of **Poly (12, 2)** and their model compounds in TFA-d.

model compounds were prepared that respectively correspond to linear (L), dendritic (D), and terminal (T) units.

And aromatic protons in the polymers were quantitatively analyzed as shown in Figure 4. The degree of branching (DB) was estimated using the following equation[41]:

$$DB = \frac{D \text{ units} + T \text{ units}}{D \text{ units} + T \text{ units} + L \text{ units}}$$

The NMR peak assignments and integration ratios are given in Table 2. From the data we obtained the DB value of 0.56. This value is not far from the theoretically predicted value of 0.5 for very high molar mass polymers. Turner *et al.*[42,43] and Sunder *et al.*[44] earlier prepared hyperbranched polyesters that they reported had DB values of 0.50-0.59. Therefore, it is concluded **Poly (12, 2)** possesses a hyperbranched structure. Even though, we did not determine the DB values for other two polymers there is no reason not to believe that they also are hyperbranched.

Melt Viscosity Qualitative Observations. While discussing above about the LC optical textures, it was mentioned that the polymer melts had to be aged long before we could obtain well-developed textures. This implies that the melt viscosities of the present polymers' are rather high. We,

Table 2. Proton Resonance Peaks of **Poly (12, 2)** and Their Model Compounds Used for Calculation of the Degree of Branching

	Proton site	Chemical shift (ppm)	integral	DB
Model compounds	H_L	8.80		
	H_D	8.91		
	H_T	8.62		
Poly (12, 2)	L units	8.76-8.81	5.03	
	D units	8.90-8.91	1.00	0.56
	T units	8.59-8.66	5.35	

indeed, felt that the present polymers melt viscosities are much higher than those of conventional, linear aromatic LC polyesters.[45-47] The melts exhibited a high resistance to flow. When we used a spatula to move around the glass cover slips on the melts placed on microscopic slides, we had to apply a force just short of breaking the cover slip to move the melt around. This is taken as an indication that uniaxial molecular alignment including the mesogenic units and spacers is not easily attained due to the hyperbranched molecular architecture. It, therefore, may be possible that anisotropy in physical properties is much less for hyperbranched LC polyesters than for the conventional linear LC polyesters. This aspect has yet to be studied systematically in future.

Conclusion

As a part of our continuing effort to establish the structure-LC properties of hyperbranched polyesters, we have prepared and studied their LC properties of a new series of hyperbranched polymers that consist of the azoxybenzene type mesogenic units and polymethylene spacers. The aromatic ester group, formed by the polymerization of the monomers formed branching points. In the case of the hyperbranched aromatic LC polyesters previously reported by us,[34,35] the mesogenic units of aromatic ester type were formed as the two terminal units of the monomers were involved in polymerization. The present investigation together with our earlier works clearly demonstrates that even hyperbranched molecular architectures can lead to liquid crystallinity. But it is required for the spacers to render enough chain flexibility or easy conformational adjustment so that the polymers can form LC domains. However, this investigation confirms our previous claim that the presence of flexible spacers is not a sufficient, but a necessary condition for a hyperbranched polymer containing mesogenic units to be liquid crystalline. An additional structural requirement is that only flexible spacers, but not mesogenic units, should be involved in branching points.

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