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Synthesis and Characterization of Regioregularly Ring-Substituted, Liquid Crystalline Aromatic Polyesters

Jung-Il Jin,* Chung-Seok Kang, Il-Hoon Lee, and Yong-Kuk Yun

Department of Chemistry, College of Sciences, Korea University,
1-Anam Dong, Seoul 136-701, Korea

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ABSTRACT: A series of regioregularly ring-substituted aromatic homopolyesters has been synthesized, and their general properties are compared with those of randomly substituted polymers. The newly synthesized polymers are poly(oxy-1,4-phenyleneoxy-2-bromoterephthaloyl), poly(oxy-1,4-phenyleneoxy-2-nitroterephthaloyl), poly(oxy-2,7-naphthalenediyloxy-2-bromoterephthaloyl), and poly(oxy-2-bromo-1,4-phenyleneoxy-2-bromoterephthaloyl). The polymers were prepared via low-temperature solution polymerization of 4-hydroxyphenyl 2-substituted terephthalates, 2-(7-hydroxynaphthyl) terephthalate, or 2-bromo-4-hydroxyphenyl 2-bromoterephthalate, all of which were prepared via multistep synthetic routes. The polymers of regular microchemical structures have much higher melting temperatures and greater degrees of crystallinity than those of irregularly substituted polymers. The glass transition temperature was also found to be dependent on the manner in which the substituents are located. Positional isomerism of the substituents leads to dissimilar structures of the crystalline regions.

Introduction

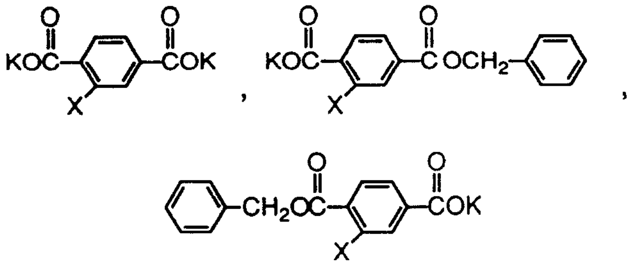
The synthesis and properties of aromatic polyesters have been extensively studied recently following the observation of the excellent physical and mechanical properties of thermotropic aromatic polyesters noted in both academia and industry.[1-10] Some of these materials are presently commercially available; Hoechst-Celanese's Vectra and Amoco's Xydar are representative examples. These compositions are aromatic copolyesters and have many unique processing and mechanical properties resulting from their ability to form molecular order in the melt. Copolymerization and utilization of unsymmetrically substituted monomers are the two most frequently used synthetic approaches in obtaining compositions whose transition temperatures lie in a manageable temperature range either for processing or for characterization.[11] Inclusion of aliphatic spacers has also been studied widely,[11] but aliphatic structures lead to diminished thermal stability and mechanical properties.

Placement of substituents on aromatic rings is very effective in lowering the melting temperatures of aromatic polyesters, especially when the substituents are randomly placed. This can be achieved simply by polymerizing unsymmetrically substituted monomers.[11] For example, polymerization of bromohydroquinone[12] and phenylhydroquinone[9,13] with terephthalic acid produces polymers with T_{ms} of 353 and 340 °C, respectively. These values are much lower than that (610 °C)[13] of the parent poly(oxy-1,4-phenyleneoxyterephthaloyl). Suppression of T_{m} in this case results not only from the steric effect of the substituents but also from their random orientation or positional isomerism along the chain. The latter, in a strict sense, leads to a structure of a random copolymer as depicted in Chart 1, structure A, for the polyester prepared from bromohydroquinone and terephthalic acid. The structural irregularity caused by the positional isomerism of the substituents can certainly be beneficial when one wants to synthesize low-melting polymers. But it is almost impossible to separate the substituent effect from the positional isomerism effect if one is to study how a substituent would affect the properties of the polymer. Therefore, we tried to develop synthetic methods for the preparation of a series of regioregularly ring-substituted aromatic polyesters where positional isomerism of the substituents does not complicate our issue. The structures, names, and abbreviations of the polymers whose synthetic methods and general characterizations are described in this article are shown in Chart 1. RR stands for "regioregular", and H and N stand for hydroquinone and naphthalenediyl, respectively. For the corresponding irregularly substituted polyesters, the prefix IR as in IR-BrH is used instead. Comparison of the properties of these polymers is also described in this report.

Results and Discussion

Synthesis of Monomers and Polymer. The synthesis of all of the present regioregularly ring-substituted (RR) polymers first requires a separate multistep synthetic route to the preparation of the respective monomers. The synthetic routes to RR-BrH, RR-NO$_2$H, and RR-BrN are similar and are shown in Scheme 1.

Substituted terephthalic acid I was refluxed with thionyl chloride, converting I to the corresponding dichloride II, which was then reacted with excess benzyl alcohol to form dibenzyl terephthalate III. This diester was partially hydrolyzed to half-ester IV.[14] Since the alkaline hydrolysis of III produced a mixture of following compounds, selective separation of IV was required:



An aqueous solution of the mixture of the potassium salts was slowly neutralized with dilute hydrochloric acid, and the precipitate formed down to pH 5.0 or those formed between pH 4.0 and 2.5 were collected respectively for the separation of 4-(benzyloxycarbonyl)-3-bromobenzoic acid (IV-Br) and 4-(benzyloxycarbonyl)-3-nitrobenzoic acid

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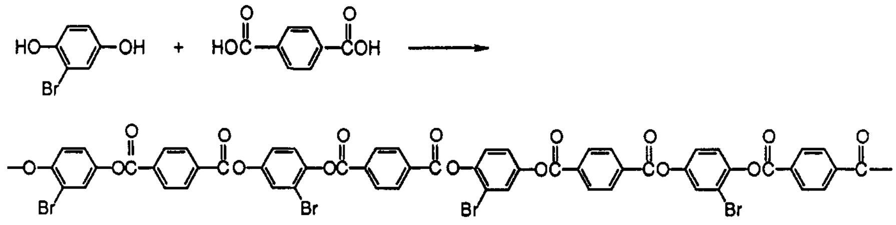
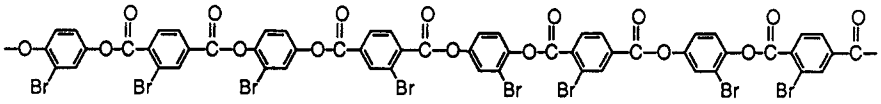
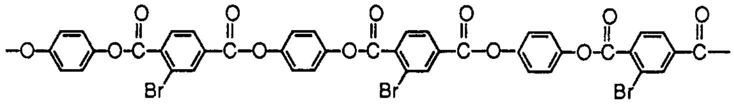
Chart 1



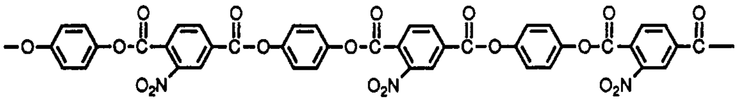
A



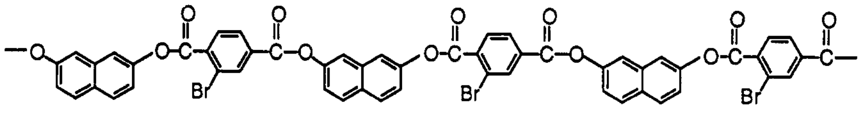
B



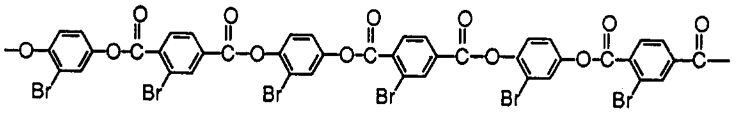
poly(oxy-1,4-phenyleneoxy-2-bromoterephthaloyl), RR-BrH



poly(oxy-1,4-phenyleneoxy-2-nitroterephthaloyl), RR-NO2H



poly(oxy-2,7-naphthalenediyloxy-2-bromoterephthaloyl), RR-BrN



poly(oxy-2-bromo-1,4-phenyleneoxy-2-bromoterephthaloyl), RR-BrBr

(IV-NO_2). Both half-esters could be purified by recrystallization. Their structures could be confirmed by elemental analysis and also by spectroscopy as described in the Experimental Section.

The benzylated half-esters, after being transformed into acid chlorides, were reacted with a large excess of hydroquinone or 2,7-naphthalenediol to make the precursors V. Finally, the diad type monomers, IV, could be prepared by removing the benzyl protecting group from V through selective hydrolysis at room temperature.[15] The structures of the three monomers thus prepared, VI-BrH, VI-NO_2H, and VI-BrN, were confirmed by elemental as well as spectroscopic analyses.

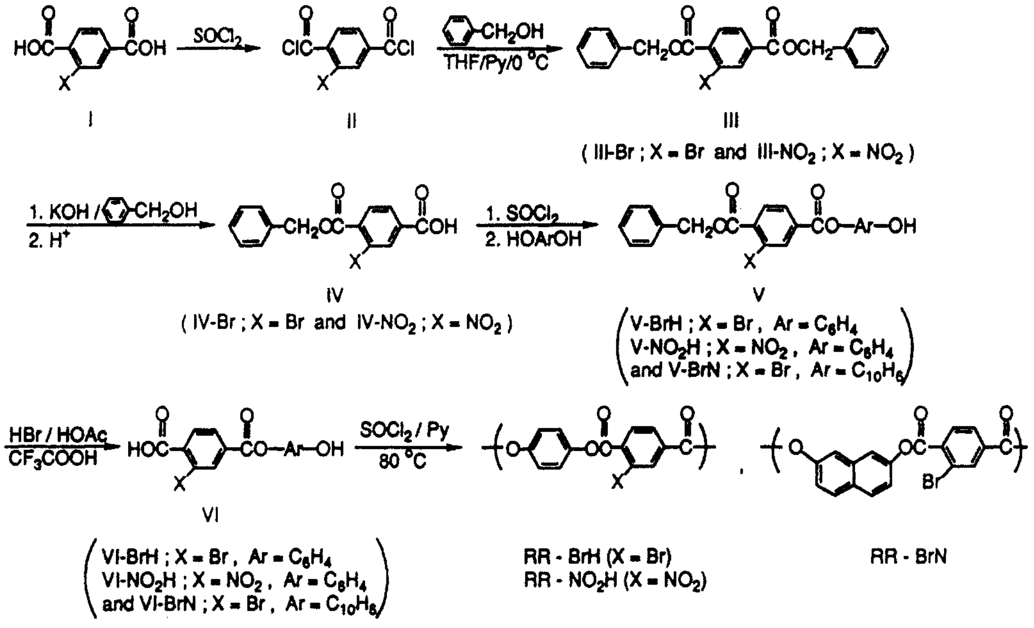
Synthesis of RR-BrBr, which contains bromine substituents on both phenylene rings in the repeating unit, requires a different synthetic route and is shown in Scheme 2.

Compound VII was brominated to obtain VIII. Since bromination can occur also at the position meta to the free hydroxy group as well as, to a lesser extent, on the phenyl ring of the benzyl group, the yield was rather low (40%). The reaction of the acid chloride derived from IV-Br with VIII in the presence of pyridine produced IX in good yield. The both benzyl protecting groups of IX were removed by hydrogenolysis using 1,4-cyclopentadiene as a hydrogen source and Pd–C as a catalyst.[16] The monomer X thus prepared was purified by repeated recrystallization from a mixture of dioxane and toluene (16/84 v/v).

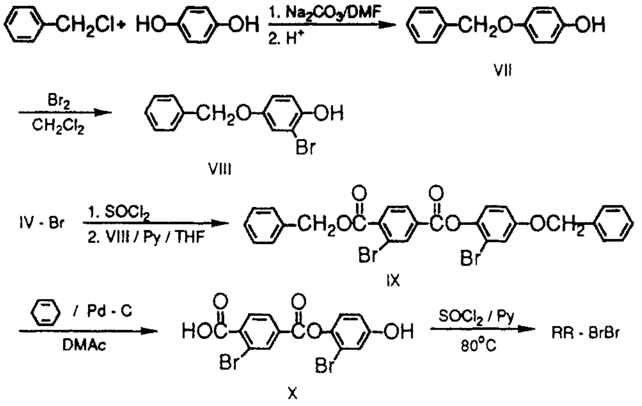
Since the monomers VI and X contain an ester group, we had to utilize a mild polymerization condition to preserve the ester group during polymerization. Earlier,[17,18] we found that the use of thionyl chloride in pyridine solution as a condensing agent at 80 °C was satisfactory for the preparation of ordered-sequence aromatic copolyesters, where also maintenance of the sequence order set in ester type dimeric or trimeric monomers was required. Therefore, direct polycondensation of the monomers VI and X using the thionyl chloride/pyridine pair was again adopted in the present work.

In contrast, the irregularly substituted polymers were prepared from the dihydroxy and dicarboxylic monomers by either solution or melt polymerization as shown in Scheme 3. Although some of these polymers were reported earlier,[12,19] all of them were prepared anew and their properties were compared with those of the RR series. All of the polymers were subjected to Soxhlet extraction with ethanol for 3 days before drying. Yields of recovered RR- and IR-series polymers are given in Table 1.

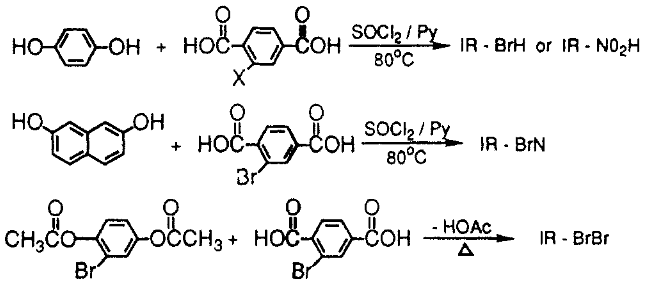
Scheme 1. Synthetic Route to RR-BrH, RR-NO$_2$H, and RR-BrN



Scheme 2. Synthetic Route to RR-BrBr



Scheme 3. Synthetic Methods of IR-Series Polyesters



General Properties. As alluded to above regarding the microchemical structures of ring-substituted aromatic polyesters, the position of substituents can be either regioregular or random. The former polymers can be taken as true homopolymers, whereas the latter polymers, in a strict sense, should be regarded as random copolymers if orientation of the substituents is taken into account. Therefore, comparison of the properties of the RR series with those of the IR series is expected to provide us with a new insight into how such orientational isomerism influences the general properties of the polymers such as glass transition temperature (T_g), melting point (T_m), and crystallization tendency. It is our belief that this work is the very first attempt to raise this particular issue in aromatic polyesters.

Suter et al.[20] studied theoretical aspects of constitutional isomerism of polycondensates derived from nonsymmetrical monomers. They[21,22] also reported the dependence of some of the solution properties on the constitutional isomerism in aramids, which are lyotropic. They found Flory's theory[23] based on the lattice concept can be satisfactorily applied to the nematic polymer solutions and that the dependence of the onset of the nematic phase on the degree of polymerization did not greatly depend on the constitutional order of the polymers. This must be due to the fact that the polyamides they studied have extended-chain rigid rodlike molecular characteristics in solution and, thus, their axial ratio does not rely much on the regularity in the placement of ring substituents. Therefore, it is also very interesting to compare the influence of positional isomerism on the mesophase-forming ability of aromatic polyesters in the melt. Recently, Ueda et al.[24] reported the synthesis of ordered polyamides by direct polycondensation of a symmetric monomer with a nonsymmetric monomer using a phosphonate activating agent.

The data given in Table 1 compare the general properties of the regioregularly substituted polyesters (RR series) with those of the corresponding randomly substituted polymers (IR series). All of the polymers are not soluble in such common solvents as chloroform, 1,1,2,2-tetrachloroethane (TCE), and TCE/phenol mixtures but are soluble in pentafluorophenol, trifluoromethanesulfonic acid, and mixed solvents containing *p*-chlorophenol. A concentration of 0.1 g/dL was employed for the solution viscosity measurement, because the polymer solubilities were rather poor even in the mixed solvents indicated in the footnote of Table 1. We could not measure the solution viscosity of RR-NO$_2$H because of the polymer's extremely poor solubility. The solution viscosity numbers range from 0.72 to 2.60 for the RR series and from 0.43 to 2.15 for the IR series.

The glass transition temperature (T_gs) of the polymers could be determined from the heating DSC curves; see Figure 1 and Table 1. It is noted that the T_g values of RR-BrN and IR-BrN are 135 and 139 °C, respectively, and that they are higher than those of others. As far as the difference between the T_g values of the RR and IR series is concerned, we can divide the present polymers into two different groups; in the first group, the T_g values of the RR and IR series are about the same as in RR-BrH (78 °C) vs IR-BrH (77 °C) and RR-BrN (135 °C) vs IR-BrN (139 °C), whereas in the second group, they differ significantly depending on the regioregularity of the substituent placement as in RR-NO$_2$H (92 °C) vs IR-NO$_2$H

Table 1. Synthetic Results and Properties of Polymers

polymer	yield,[a] %	η_{inh}, dL/g	T_g,[f] °C	T_m,[g] °C	T_i,[g] °C	DC,[h] %
RR-BrH	88	0.72[b]	78	365	dec.	38 (46; 250 °C/1 h)
IR-BrH	90	0.43[b]	77	286	dec.	26 (37; 250 °C/1 h)
RR-BrN	90	1.09[c]	135	312	333	34 (40; 200 °C/1 h)
IR-BrN	87	0.52[d]	139	223	no LC	19 (33; 150 °C/1 h)
RR-NO_2H	74	insol[d]	92	345	dec.	11 (15; 180 °C/5 h)
IR-NO_2H	77	1.01[e]	77	220	dec.	10 (12; 115 °C/5 h)
RR-BrBr	89	2.60[c]	110	284	333	~3 (~4; 220 °C/2.5 h)
IR-BrBr	94	2.15[c]	88	211	348	~2 (~3; 150 °C/2.5 h)

[a] After ethanol extraction for 3 days. [b–e] Measured at 30 °C on 0.1 g/dL solution in (*b*) pentafluorophenol, (*c*) pentafluorophenol/*p*-chlorophenol/CHCl = 30/30/40 (v/v/v), (*d*) p-chlorophenol/phenol/1,1,2,2-tetrachloroethane (TCE) = 40/25/35 (w/w/w), or (*e*) *p*-nitrophenol/*p*-chlorophenol/TCE = 6/50/44 (w/w/w). [f] Temperature where initial slope change was observed on DSC thermogram. [g] Temperature where the peak minimum position of endotherm is located on DSC thermogram. [h] Approximate degree of crystallinity estimated from the diffraction areas on WAXD.

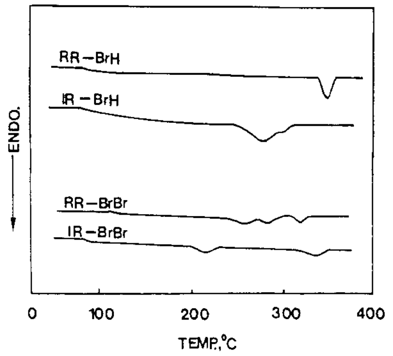


Figure 1. DSC thermograms obtained in the first heating scan of RR- and IR-BrH and RR- and IR-BrBr polyesters under an N_2 atmosphere (heating rate: 10 °C/min).

(77 °C) and RR-BrBr (110 °C) vs IR-BrBr (88 °C). It, however, should be noted that a part of the difference in the T_g values of the second group might have been derived from the higher molecular weights of the regioregularly substituted polymers, although molecular weights of RR-BrBr and IR-BrBr appear to be high enough to neglect the effect of molecular weight on their T_g values. The T_g values of all of these substituted polyesters are far lower than that (267 °C) of poly(*p*-phenylene terephthalate),[25] which indicates that the substituted polyesters' free volumes are much higher than the free volume of poly(*p*-phenylene terephthalate).

All of the present polyesters, independent of regioregularity in the placement of substituents, are crystalline and show clear melting endotherms on DSC analysis; see Figure 1 and the T_m data given in Table 1. It is obvious that the T_m values depend strongly on the regioregularity of the substituents, the number of substituents in the repeating unit, and the structure of the diol moieties. First, the difference between the T_m values of the RR and IR series ranges from 73 °C for the BrBr pair to 125 °C for the NO_2H pair, with those of the RR series being higher than those of the IR series. A part of this difference could result from the fact that some of the RR polymers' solution viscosities are significantly higher than those of the corresponding IR polymers. A comparison of the T_m values of RR-BrBr and IR-BrBr, however, convinces us that the higher T_m values of the RR series mainly originate from regioregularity in the placement of the substituents. The T_m values of RR-BrBr and IR-BrBr are 284 and 211 °C, respectively, and, thus, the difference amounts to 73 °C. These two polymers have rather high solution viscosities (2.60 dL/g for RR-BrBr and 2.15 dL/g for IR-BrBr), and it is expected that the difference in their T_m values is mainly the result of the difference in regioregularity of the substituents' placement. Moreover, IR-NO_2H has a reasonably high (1.01 dL/g) solution viscosity, but its melting temperature (220 °C) is far lower than that (345 °C) of RR-NO_2H. Therefore, there is no doubt that the regioregularly substituted polymers have significantly higher T_m values than their IR counterparts. Although information on the chain conformations of these polyesters in the solid state is lacking, it is clear that regioregular placement of the substituents leads to a more efficient chain packing, which would, in turn, result in higher T_m values for the RR series.

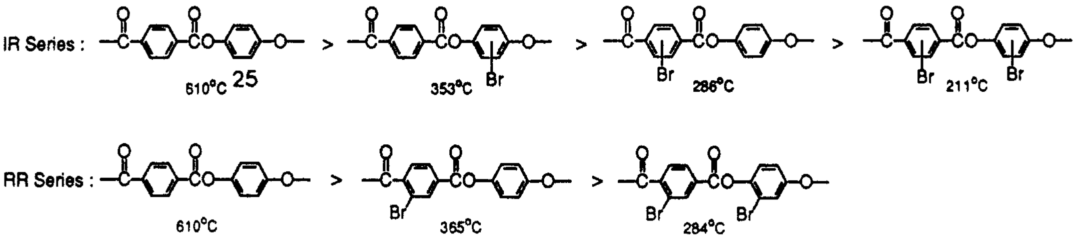
The second interesting comparison of the T_m values can be found in the way the T_m values of the present polyesters depend on the position and number of substituents in the repeating unit. The T_m value decreases in the order shown in Chart 2. In the two series in Chart 2, we observe that the T_m value decreases with increasing number of substituents in the repeating unit. However, monosubstitution in the repeating unit, regardless of the position of the bromine substituent in either the terephthaloyl or phenylene structure, dramatically reduces the T_m value. The introduction of the second substituent in the second benzene ring of the repeating unit, however, decreases the T_m values to a much smaller extent, when compared with those of monosubstituted polymers.

Lastly, the T_m values of the polyesters containing the 2,7-naphthalenediyl structure are much lower than those containing the 1,4-phenylene structure as compared in the RR-BrH (365 °C) vs RR-BrN (312 °C) and IR-BrH (286 °C) vs IR-BrN (223 °C) pairs. We believe that this can be ascribed partly to the bent structure of the 2,7-naphthalenediyl unit and partly to the lower content of the polar ester group per unit length of the main chain.

The thermal transition behavior of the RR-BrBr examined by DSC analysis is peculiar when compared with that of other polymers (Figure 1). The DSC thermogram of RR-BrBr exhibits three major endotherms whose minimum points are located at 257, 284, and 333 °C, respectively. As will be described later, the last endotherm corresponds to isotropization. According to the observation made on a hot-stage attached to the polarizing microscope, this polymer melts at 284 °C. But we do not observe any obvious changes at 257 °C. Therefore, the second endotherm corresponds to a melting transition, whereas the first one probably corresponds to a solid-to-solid transition.

As demonstrated by others[26,27] and us,[28] it is very possible that ester interchanges in regular polymers occur at high temperatures leading to scrambling of the microstructure of the original polymers. Therefore, all the transition temperatures reported in Table 1 were obtained from the first-heating DSC thermograms (Figure 1). Although end-capping can slow down significantly the interchange reactions,[29] we have not yet tried to do so. However, according to our earlier observations[17,28] with other ordered-sequence aromatic copolyesters and also to our preliminary study of ^{13}C-NMR spectra of RR-BrN samples heated at 315 °C, the microstructures remain stable approximately up to 20–30 min at 300–315 °C. Therefore, it is believed that the possible ester interchange during

Chart 2



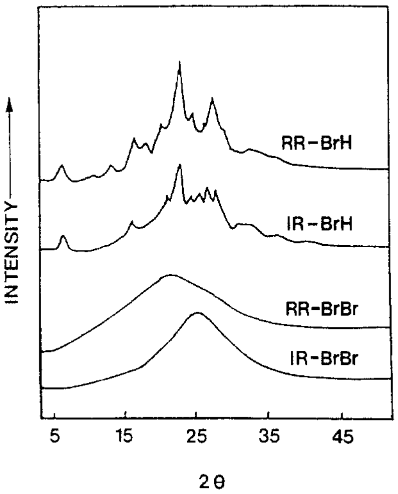


Figure 2. Wide-angle X-ray diffractograms of polyesters.

DSC analyses should be negligible, and, thus, the thermal data reported should be the real values or very close to them for the virgin samples.

X-ray Analysis of Solid Polymers. As mentioned above, all of the as-polymerized samples showed melting endotherms on the DSC thermograms, indicating that they are semicrystalline. Their crystalline nature can be further supported by their wide-angle X-ray diffractograms shown in Figure 2, although both RR-BrBr and IR-BrBr exhibit extremely low degrees of crystallinity. With the exception of RR-BrBr and IR-BrBr, the rest show rather sharp diffraction peaks. The approximate degrees of crystallinity estimated from the crystalline and the amorphous reflection areas in the diffractograms[30,31] of the as-polymerized samples are given in Table 1.

Comparison of the X-ray diffractograms and the degrees of crystallinity of the present polymers emphasizes the following three distinct features: (1) Details of the X-ray diffractograms of the RR series are much different from those of the corresponding IR series, suggesting that the two series have dissimilar crystal structures. (2) When the repeating unit contains only one relatively small substituent as in RR-BrH, IR-BrH, RR-BrN, and IR-BrN, the degree of crystallinity (DC) is high. At the same time the DC values of regioregularly substituted polymers seem to be higher. (3) When either the size of the substituent is large as in RR-NO$_2$ and IR-NO$_2$ or the repeating unit contains two substituents, one each on the two aromatic rings, the degree of crystallinity becomes lower. Moreover, RR-BrBr shows about the same amorphous diffraction as IR-BrBr does. This observation emphasizes the importance of size, number, and regioregular placement of substituents in controlling the structure of the solid state and the degree of crystallinity of the substituted aromatic polyester.

Table 1 shows how the degree of crystallinity increases on heat treatment of the as-polymerized samples. We did not try to optimize the annealing conditions to attain the highest obtainable degree of crystallinity. All of the polymers reveal an increase in DC on annealing. The extent of the increase, however, depends much on the size and the number of substituents in the repeating unit. The DC values of the monosubstituted compositions containing bromine, regardless of whether they are regioregularly or irregularly substituted, are enhanced substantially on annealing. On the other hand, the values of the nitro-substituted compositions, i.e., RR- and IR-NO$_2$H, increase on annealing only to a slight extent. This implies that the larger size of the nitro group hinders crystallization. A similar phenomenon is observed for RR- and IR-BrBr, because the presence of the two bromine substituents in the repeating unit diminishes the crystallizing tendency of the polymers.

Nature of Mesophase. The optical texture of the polymer melts were examined on a hot-stage attached to a polarizing microscope. Since the T_{m}s of RR-BrH and RR-BrN are high, their optical textures were observed for the quenched melts that were prepared by heating the polymers to 380 and 330 °C, respectively, and quenched in liquid nitrogen. The textures of the rest were observed directly on a hot stage. According to the optical textures, all but IR-BrN formed mesophases in the melt. Surprisingly enough, the IR-BrN melt is not birefringent when observed through a polarizing microscope, suggesting that the composition is not thermotropic, whereas its regioregular counterpart RR-BrN is mesomorphic. Although it is not easy to propose a simple supposition to explain this distinction, this is the first example in which regioregularity or positional isomerism in substituent placement governs the mesophase-forming ability in the aromatic polyesters. The molecular weight of IR-BrN appears to be substantially lower than that of RR-BrN as reflected by their solution viscosity values, which could have influenced the mesophase-forming ability of these polymers. It, however, is not yet clear how molecular weight would influence these polymers' abilities to form mesophases, and this aspect requires further study. The isotropization temperatures (T_{i}) of RR-BrH, IR-BrH, RR-NO$_2$H, and IR-NO$_2$H could not be determined because they underwent thermal decomposition before reaching T_{i}. The T_{i} values of RR-BrN, RR-BrBr, and IR-BrBr, however, could be detected by DSC analysis (Table 1) and they are found to be rather low, which can be ascribed to the presence of two bromine substituents in the repeating unit increasing interchain distance in the melt. Moreover, the naphthalene moieties present in RR-BrN can destabilize the mesophase because of their role to form slightly bent segments along the chain. It is also noted that the mesophase temperature range ($\Delta T = T_{\mathrm{i}} - T_{\mathrm{m}}$) for RR-BrBr is substantially narrower (49 °C) than that (137 °C) of the IR counterpart. This is mainly due to the much elevated T_{m} for the former in spite of the fact that the T_{i}s for RR- and IR-BrBr are almost same.

The optical textures of the liquid crystalline compositions were not well-defined and, therefore, conclusive identification of their mesophases could not be made. Most of the liquid crystalline compositions revealed either the so-called polished marble texture or a threaded schlieren texture typical of nematogens. In contrast, the optical textures of the nitro-substituted polymers, i.e., RR-NO_2H and IR-NO_2H, were not well-defined, and, therefore, conclusive identification of their mosophases could not be made. Wide-angle X-ray diffraction patterns of the present polymer melts quenched in liquid nitrogen commonly showed a broad peak centered around 2θ of 18–23° corresponding to spacings of ~4–5 Å, which represents an average interchain spacing in liquid crystalline phases.

Experimental Section

Synthesis of Monomers. 4-(Benzyloxycarbonyl)-3-bromobenzoic Acid (IV-Br). Dibenzyl 2-bromoterephthalate (38.07 g, 8.95×10^{-2} mol) prepared from 2-bromoterephthalic acid and benzyl alcohol was dissolved in 150 mL of benzyl alcohol, and the solution was heated to and maintained at 60 °C. To this solution was added dropwise a benzyl alcohol (50 mL) solution containing 5.023 g (8.95×10^{-2} mol) of dissolved potassium hydroxide.[14] The whole mixture was stirred an additional hour at 60 °C and the solution was then poured into 1.8 L of dry diethyl ether. The precipitate obtained was thoroughly washed with ether and dried in a vacuum oven. The mixture of potassium salts [potassium 4-(benzyloxycarbonyl)-3-bromobenzoate and potassium 4-(benzyloxycarbonyl)-2-bromobenzoate] was dissolved in 1 L of deionized distilled water. The solution was slowly acidified to pH 5.0 with 0.1 M HCl. The precipitate formed was collected and washed with an HCl solution of pH 5.0. The precipitate was redissolved in 0.1 M Na_2CO_3, and the solution was retitrated with 0.1 M HCl to pH 5.0. The precipitate was collected again, redissolved in 0.1 M Na_2CO_3 solution, and then retitrated with 0.1 M HCl. This procedure was repeated once more and the final precipitate was dried at 50 °C in a vacuum oven. The solid product thus obtained was recrystallized from CCl_4. The yield was 19.8 g (66%), mp 111 °C. IR (KBr): 3500–2400 (acid O–H stretch), 3050 (aromatic C–H stretch), 1709 and 1720 (C=O stretch), 1230–1150 cm^{-1} (ether C–O stretch). ^{1}H-NMR (acetone-d_6): δ 5.33 (s, 4H, CH_2), 7.32 (s, 5H, phenyl in benzyl), 7.82–8.37 (m, 3H, bromoterephthaloyl). Anal. Calcd for $C_{15}H_{11}BrO_4$: C, 53.75; H, 3.31; Br, 23.84. Found: C, 53.46; H, 3.31; Br, 24.05.

Benzyl 4-Hydroxyphenyl 2-Bromoterephthalate (V-BrH). Compound IV-Br (5.00 g, 1.49×10^{-2} mol) was refluxed with 50 mL of purified thionyl chloride[2] for 4 h. After excess thionyl chloride was removed by distillation under reduced pressure, the acid chloride formed was dissolved in 50 mL of dry THF. This solution was added dropwise with stirring under a nitrogen atmosphere to a chilled (0 °C) THF (50 mL) solution containing 16.31 g (0.149 mol) of hydroquinone and 3.54 g of pyridine. The mixture was allowed to warm up to and stirred for 6 h at room temperature. The mixture was stirred an additional 2 h at 60 °C. THF was removed from the mixture using a rotatory evaporator. The residue was thoroughly washed with 0.1 M HCl, distilled water, 5% $NaHCO_3$ solution, and finally again with distilled water. The dry crude product was recrystallized from CCl_4. The product yield was 4.84 g (76%), mp 79 °C. IR (KBr): 3300 (O–H stretch), 1755 and 1810 (C=O stretch), 1250–1160 cm^{-1} (ether C–O stretch). ^{1}H-NMR ($CDCl_3$): δ 7.87–8.80 (m, 3H, bromoterephthaloyl), 7.33 (s, 5H, phenyl), 6.90 (q, 4H, hydroquinone), 5.34 (s, 2H, CH_2). Anal. Calcd for $C_{21}H_{15}BrO_5$: C, 59.03; H, 3.55; Br, 18.70. Found: C, 58.77; H, 3.54; Br, 18.92.

4-((4-Hydroxyphenyl)oxycarbonyl)-2-bromobenzoic Acid (VI-BrH). Compound V-Br (3.08 g, 7.20×10^{-3} mol) was dissolved in 50 mL of trifluoroacetic acid, to which solution was added dropwise at room temperature 2.8 mL of HBr (30 wt % in HOAc).[15] After the mixture was stirred for 3 h at room temperature, it was poured into cold distilled water. The precipitate, after being washed with distilled water, was dissolved in 1.0 M $NaHCO_3$, and the insoluble material was removed by filtration. The final compound was reprecipitated by addition of 0.1 M HCl to the filtrate. The product was thoroughly washed with distilled water and dried at 60 °C in a vacuum oven. The yield was 1.92 g (79%), mp 234 °C. IR (KBr): 3280 (O–H stretch), 3400–2400 (acid O–H stretch), 1740 and 1810 (C=O stretch), 1260–1180 cm^{-1} (ether C–O stretch). ^{1}H-NMR (acetone-d_6): δ 8.0–8.56 (m, 3H, bromoterephthaloyl), 7.6 (broad, 1H, OH), 7.16 (q, 4H, hydroquinone). Anal. Calcd for $C_{14}H_9BrO_5$: C, 49.87; H, 2.70; Br, 23.70. Found: C, 49.85; H, 2.72; Br, 23.64.

Benzyl 2-(7-Hydroxynaphthyl) 2-Bromoterephthalate (V-BrN). This compound was prepared using the same procedure as the one employed for the synthesis of V-BrH. 2,7-Naphthalenediol, however, was used in place of hydroquinone. The crude oily product became solid upon washing repeatedly with 1.0 M HCl and then finally with distilled water. The product was recrystallized from CCl_4. The yield was 75.8%, mp 163 °C. IR (KBr): 3510 (O–H stretch), 1750 (C=O stretch), 1260–1140 cm^{-1} (ether C–O stretch). ^{1}H-NMR (acetone-d_6): δ 5.4 (s, 2H, CH_2), 7.24–8.52 (m, 14H, Ar), 8.9 (broad, 1H, OH). Anal. Calcd for $C_{25}H_{17}BrO_5$: C, 62.90; H, 3.60; Br, 16.74. Found: C, 62.49; H, 3.61; Br, 16.54.

4-((2-(7-Hydroxynaphthyl))oxycarbonyl)-2-bromobenzoic Acid (VI-BrN). Compound V-BrN (8.274 g, 1.733×10^{-2} mol) was dissolved in a mixture of trifluoroacetic acid and dichloromethane (1:1 v/v), to which was added dropwise 6.9 mL of HBr (30 wt % in HOAc). The mixture was stirred for 3 h at room temperature. The reaction mixture was poured into ice cold water. The precipitate formed was collected on a filter and washed with distilled water. The crude product was dissolved in 1 M $NaHCO_3$, and the insoluble material was removed from the solution by filtration. The filtrate was acidified with 0.1 M HCl, precipitating out the product, which was thoroughly washed with distilled water and dried. The product yield was 6.54 g (97.5%), mp 237 °C. IR (KBr): 3280 (O–H stretch), 3200–2400 (acid O–H stretch), 1720 and 1710 (C=O stretch), and 1260–1180 cm^{-1} (ether C–O stretch). ^{1}H-NMR (acetone-d_6): δ 7.30–8.60 (m, 9H, Ar), 8.92 (broad, 1H, OH). Anal. Calcd for $C_{18}H_9BrO_5$: C, 55.83; H, 2.87; Br, 20.64. Found: C, 56.02; H, 2.96; Br, 19.94.

4-(Benzyloxycarbonyl)-2-nitrobenzoic Acid (IV-NO_2). Dibenzyl 2-nitroterephthalate (80.0 g, 0.204 mol) prepared from 2-nitroterephthalic acid and benzyl alcohol was partially hydrolyzed in benzyl alcohol by KOH to a mixture of monobenzylic compounds via the same procedure as described above in the synthesis of IV-Br. The potassium salt mixture was dissolved in 1 L of distilled water, and only the precipitate formed between pH 4.0 and 2.5 was collected and washed with distilled water. The crude product was recrystallized from a mixture of chloroform and *n*-hexane (7/3 v/v). The product yield was 16.05 g (36.7%), mp 121 °C. IR (KBr): 3300–2400 (acid O–H stretch), 1740 and 1710 (C=O stretch), 1547 and 1373 (N=O stretch), 1250–1180 cm^{-1} (ether C–O stretch). ^{1}H-NMR (DMSO-d_6): δ 7.85–8.37 (m, 3H, nitrophenyl), 7.39 (s, 5H, phenyl), 5.48 (s, 2H, CH_2). Anal. Calcd for $C_{15}H_{11}NO_6$: C, 59.80; H, 3.68; N, 4.65. Found: C, 59.75; H, 3.64; N, 4.52.

Benzyl 4-Hydroxyphenyl 2-Nitroterephthalate (V-NO_2H). This compound was prepared from compound IV-NO_2 and hydroquinone following the exact same procedure as described above in the synthesis of compound V-BrH. The crude product was recrystallized from CCl_4. The yield was 71%, mp 97 °C. IR (KBr): 3487 (O–H stretch), 1755 and 1709 (C=O stretch), 1540 and 1346 (N=O stretch), 1250 cm^{-1} (ether C–O stretch). ^{1}H-NMR ($CDCl_3$): δ 7.87–8.80 (m, 3H, nitroterephthaloyl), 7.40 (s, 5H, phenyl), 6.90 (q, 4H, hydroquinone), 5.34 (s, 2H, CH_2). Anal. Calcd for $C_{21}H_{15}NO_7$: C, 64.12; H, 3.84; N, 3.56. Found: C, 64.07; H, 3.84; N, 3.50.

4-((4-Hydroxyphenyl)oxycarbonyl)-3-nitrobenzoic Acid (VI-NO_2H). Compound V-NO_2H (5.150 g, 0.131 mol) was dissolved in 30 mL of trifluoroacetic acid, to which solution was added dropwise at room temperature 7.06 g of HBr (30 wt % in acetic acid). After 3 h of reaction, 50 mL of chloroform was mixed with the reaction mixture. Then the mixture was poured into 200 mL of chloroform. The precipitate formed was collected on a filter and washed thoroughly with distilled water. The product yield was 2.934 g (73.9%), mp 219 °C. IR (KBr): 3300 (O–H stretch), 3500–2400 (acid O–H stretch), 1744 and 1712 (C=O stretch), 1505 and 1346 cm^{-1} (N=O stretch). ^{1}H-NMR (acetone-d_6): δ 8.0–8.56 (m, 3H, nitroterephthaloyl), 7.92 (broad, 1H, OH), 7.16 (q, 4H, hydroquinone). Anal. Calcd for $C_{14}H_9NO_7$: C, 55.46; H, 2.99; N, 4.62. Found: C, 55.40; H, 3.12; N, 4.59.

4-(Benzyloxy)-2-bromophenol (VIII). 4-(Benzyloxy)phenol[33] (5.0 g, 2.49×10^{-2} mol) prepared from benzyl chloride and hydroquinone was dissolved in 50 mL of methylene chloride. To this solution was added dropwise at room temperature a solution of methylene chloride (10 mL) containing 1.28 mL of bromine. After being stirred for 1.5 h at room temperature, the mixture was poured into distilled water. The precipitate was collected and recrystallized from *n*-hexane. The product yield was 2.78 g (40%), mp 72 °C. IR (KBr): 3300 (O–H stretch), 1250–1180 cm^{-1} (ether C–O stretch). ^1H-NMR (acetone-d_6): δ 5.02 (s, 2H, CH_2), 6.83–7.45 (m, 8H, aromatic), 8.21 (s, 1H, OH). Anal. Calcd for $C_{13}H_{11}BrO_2$: C, 59.33; H, 4.22; Br, 30.37. Found: C, 60.21; H, 4.30; Br, 29.76.

Benzyl 4-(Benzyloxy)-2-bromophenyl 2-Bromoterephthalate (IX). Compound IV-Br (8.0 g, 2.39 × 10^{-2} mol) was refluxed in 80 mL of thionyl chloride for 4 h, and the excess thionyl chloride was distilled off. The acid chloride formed was dissolved in 50 mL of dry THF. A solution of compound VIII (6.67 g, 2.39 × 10^{-2} mol) dissolved in a mixture of dry pyridine (20 mL) and THF (40 mL) was added dropwise with stirring to the ice-cold THF solution of this acid chloride. The mixture was stirred at room temperature for 12 h and finally at 60 °C for 1 h. The solvent was removed using a rotatory evaporator. The oily residue was washed with 0.1 M HCl, and the precipitate formed was washed with 0.1 M $NaHCO_3$ and finally with distilled water. The crude product was recrystallized from ethanol. The product yield was 11.5 g (80.7%), mp 105–106 °C. IR (KBr): 3060 (Ar C–H stretch), 1680 and 1710 (C=O stretch), 1280–1160 cm^{-1} (ether C–O stretch). ^1H-NMR (acetone-d_6): δ 5.12 (s, 2H, OCH_2), 5.41 (s, 2H, CH_2OCO), 7.11–8.42 (m, 16H, Ar). Anal. Calcd for $C_{28}H_{20}Br_2O_5$: C, 56.39; H, 3.39; Br, 26.80. Found: C, 56.43; H, 3.39; Br, 26.57.

4-((2-Bromo-4-hydroxyphenyl)oxycarbonyl)-2-bromobenzoic Acid (X). Compound IX (3.0 g, 5.0 × 10^{-3} mol) was dissolved in 40 mL of *N,N*-dimethylacetamide, to which solution 6 g of Pd–C (10%) was added. 1,4-Cyclohexadiene (4.7 mL) was then added dropwise to the ice-chilled solution of compound IX.[16] The mixture was stirred at room temperature for 4 h. The insoluble material was removed by filtration, and the filtrate was poured into 1 L of distilled water. The precipitate was collected and the crude product was recrystallized from a mixture of dioxane and toluene (16/84 v/v). The yield was 1.28 g (61.5%), mp 250 °C. IR (KBr): 2320–2400 (acid O–H stretch), 3300 (C–H stretch), 1705–1660 (C=O stretch), 1300–1150 cm^{-1} (ether C–O stretch). ^1H-NMR (acetone-d_6): δ 6.78–7.49 (m, 3H, hydroquinone), 8.17 (s, 3H, terephthaloyl), 5.82 (broad, 1H, OH). Anal. Calcd for $C_{14}H_8Br_2O_4$: C, 40.41; H, 1.94; Br, 38.40. Found: C, 40.06; H, 1.92; Br, 37.84.

Synthesis of Polymers. All of the RR-series polymers were prepared by homopolycondensation of the respective monomers, i.e., VI-BrH, VI-BrN, VI-NO_2H, and X, at 80 °C for 12 h in a mixture of thionyl chloride and pyridine. The detailed procedure can be found elsewhere.[34] At the end of the polymerization, the mixture was poured into methanol. The polymer precipitate was purified by extraction with ethanol for 3 days using a Soxhlet extractor. The irregularly substituted polymers of IR-BrH, IR-BrN, and IR-NO_2H were prepared at 80 °C similarly from an equimolar mixture of bromo- or nitro-substituted terephthalic acid and hydroquinone in the presence of the condensing agent of thionyl chloride/pyridine.

IR-BrBr, however, was obtained by melt polymerization of bromoterephthalic acid and 2-bromo-1,4-diacetoxybenzene: 2-Bromoterephthalic acid (3.34 g, 1.22 × 10^{-2} mol) and 2-bromo-1,4-diacetoxybenzene (3.34 g, 1.22 × 10^{-2} mol) were placed in a polymerization tube. The tube was immersed into a salt bath at 250 °C. The reaction mixture was stirred at 250 °C for 40 min and at 270 °C for 25 min under a nitrogen atmosphere. Then the pressure in the tube was reduced to 0.6 Torr, and the temperature of the salt bath was increased to and maintained at 290 °C for 5 min. Finally, polymerization was further conducted at 300 °C for 10 min. The product obtained was powdered and was subjected to Soxhlet extraction with ethanol for 3 days. The polymer yield was 4.56 g (94%).

Identification and Characterization of Intermediates and Polymers. Melting points were determined either with a Fisher-Johns melting point apparatus or on an differential scanning calorimeter (DSC). ^1H-NMR spectra were recorded on a Bruker AM300 spectrometer and IR spectra on a Mattson Alpha Centauri FT-IR instrument. The polymers' solution viscosity values were measured at 30 °C using a Cannon-Ubbelhode type viscometer. Thermal properties were studied under an N_2 atmosphere on a DuPont 910 or 2000 DSC at a heating rate of 10 °C/min. The DSC thermograms shown in Figure 1 were obtained in the first heating cycle of the DSC scan. Indium was used as a reference for temperature calibration. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa instrument using Ni-filtered Cu Kα radiation. The approximate degree of crystallinity was estimated from the crystalline and the amorphous reflection areas in the diffractomgram.[30,31]

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