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Properties of Aromatic Copolyesters Derived from *p*-Hydroxybenzoic Acid, Terephthalic Acid, and Naphthalenediol Isomers

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ABSTRACT: A series of aromatic copolyesters were prepared in the melt from terephthalic acid (TPA), *p*-acetoxybenzoic acid (ABA), and diacetoxynaphthalene (DAN) isomers. The DAN isomers used in this study were the 1,4-, 1,5-, 1,6-, 1,7-, 2,3-, 2,6-, and 2,7-derivatives. All the polymers having the composition (molar ratio) of TPA:DAN:ABA = 1:1:2 are thermotropic, while some of the compositions derived from a lower concentration of ABA are not mesomorphic. All as-polymerized samples, except those prepared from 2,6- and 2,7-DAN, are amorphous. Their glass transition temperatures (T_g) ranged from about 80 to 145 °C, depending on the polymer composition and the structure of the naphthylene unit. The melting temperatures (T_m) of the 2,6-DAN copolymers were about 260 °C, while those of 2,7-DAN copolymers ranged from 190 to 245 °C, depending on the content of the *p*-oxybenzoyl unit. Annealing increased copolymer molecular weights and also the degree of crystallinity of crystallizable compositions. Most of the thermotropic copolymers formed nematic phases, while 1,4- and 1,5-DAN copolymers formed smectic phases.

Introduction

The importance of thermotropic aromatic polyesters as a new class of materials is ever increasing because in their liquid-crystalline state they can be spun or injection molded, leading to oriented fibers or plastics of high strength.[1-4] One of the most distinguishing properties of these polymers is the ease in producing a uniform molecular orientation by the elongation flow experienced during processing or intentionally applied. Such a molecular orientation not only gives rise to high strength but also results in low melt viscosity along the flow direction.

The two representative linear, aromatic polyesters, poly(*p*-phenylene terephthalate) and poly(*p*-hydroxybenzoate), however, are too high melting to be melt processed. Various structural and compositional modifications have produced numerous low-melting homo- and copolyesters that could be readily processed and characterized. Inclusion of flexible spacers or nonlinear structural elements and copolymerization are the most frequently utilized synthetic approaches. The presence of unsymmetrical, bulky substituents on phenylene rings also is very effective in reducing T_m.[5] But many of the resulting polymers no longer possess the desirable properties, such as liquid crystallinity and linearity and rigidity of the chain, which are necessary to attain superior mechanical properties.

In one of our earlier papers[6] we reported the loss of liquid crystallinity by incorporation of nonlinear bis(phenol) structures in the polyesters based on terephthalic acid and 2-chlorohydroquinone. Properties of aromatic polyesters derived from 2-bromo- or 2-nitroterephthalic acid and a series of unsymmetrically substituted hydroquinones also were investigated by us.[7] Structure–property relationships of main-chain, thermotropic polyesters having on alternating sequence of mesogenic units and aliphatic, flexible spacers are subjects of many of our earlier studies.[8-10] In this investigation we prepared a series of aromatic copolyesters at three different molar ratios of terephthalic acid (TPA), *p*-acetoxybenzoic acid (ABA), and diacetoxynaphthalene (DAN) isomers. The DAN isomers included are the 1,4-, 1,5-, 1,6-, 1,7-, 2,3-, 2,6-, and 2,7-derivatives. The molar ratio of TPA and DAN was kept

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Table I
Polymerization Conditions

polymer	temp, °C/time, min/pressure, Torr
1,4	240/60/760 → 260/120/760 → 280/40/260 → 290/55/1
1,5	240/90/760 → 260/120/760 → 280/50/170 → 290/50/1
1,6	260/95/760 → 280/40/360 → 290/20/1
1,7	220/60/760 → 240/60/760 → 260/60/760 → 280/30/760 → 290/40/260 → 290/45/1
2,3	240/90/760 → 260/120/760 → 280/50/210 → 290/60/1
2,6	240/30/760 → 260/90/760 → 280/75/760 → 290/60/100 → 300/60/1 → 310/10/1
2,7	220/30/760 → 240/90/760 → 260/120/760 → 280/40/340 → 290/35/1

Table II
Results of Elemental Analyses of Polyesters

	X,*Y*/2-series		*X*,*Y*/1.5-series		*X*,*Y*/1-series	
X,*Y*	wt % C (72.45)[a]	wt % H (3.42)[a]	wt % C (72.76)[a]	wt % H (3.43)[a]	wt % C (73.17)[a]	wt % H (3.44)[a]
1,4	70.90	3.48	71.90	3.62	70.97	3.44
1,5	70.97	3.52	71.47	3.52	71.06	3.47
1,6	70.98	3.48	72.07	3.53	71.60	3.45
1,7	72.03	3.44	72.20	3.46	70.73	3.46
2,3	72.18	3.45	72.92	3.60	71.58	3.35
2,6	71.64	3.40	72.27	3.61	71.43	3.42
2,7	71.45	3.45	72.38	3.44	70.86	3.43

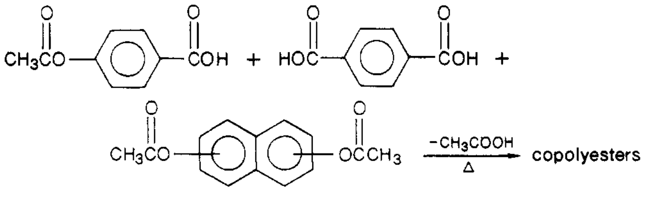
[a] Values in parentheses represent calculated values assuming that actual compositions are the same as those in the feed.

Table III
Properties of *X*,*Y*/2-Series Polyesters

	as-polymerized samples							annealed samples						
X,*Y*	η_{inh}[a]	T_g, °C	T_f,[b] °C	T_m, °C	ΔH_m, kJ/mol	DC,[c] %	LC[d] phase	T_a,[e] °C	η_{inh}[a]	T_g, °C	T_{k-k},[f] °C	T_m, °C	ΔH_m, kJ/mol	DC,[c] %
1,4	0.61	94	168			0	S	190	1.32	96		214	1.1	7
1,5	0.62	87	189			0	S	190	1.36	90				0
1,6	0.57	124	202			0	N	170	ins	135		197	1.3	9
1,7	0.63	144	212			0	N	190	ins	156				0
2,3	1.03	108	167			0	N	135	ins	110				0
2,6	1.50	82		259	1.6	16	N	190	ins	87	224	260	2.4	36
2,7	0.73	106		191	0.5	10	N	170	1.13	113		197	1.9	26

[a] Inherent viscosities of the 1,4-, 1,5-, 1,6-, 1,7-, and 2,7-copolyesters were measured at 40 °C by using 0.1 g/100 mL solutions in a *p*-chlorophenol/phenol/TCE = 40:25:35 (w/w/w) mixture and those of the 2,3- and 2,6-copolymers at 25 °C at a concentration of 0.1 g/100 mL in a pentafluorophenol/*p*-chlorophenol/chloroform = 30:30:40 (v/v/v) mixture. [b] Flow temperature. [c] Degree of crystallinity. [d] Liquid crystal phase; N stands for a nematic phase and S for a smectic phase. [e] Annealing temperature. [f] Temperature for crystal–crystal transition.

constant at 1:1, but the molar ratio of ABA's to those of the two other monomers was varied from 1:1 to 2:1.



For the sake of convenience, the symbol *X*,*Y*/*Z* is used to describe the composition derived from *X*,*Y*-DAN at the molar ratio of TPA:DAN:ABA = 1:1:*Z*. For example, the symbol 2,6/2 describes the 2,6-DAN copolyester prepared at the feed of TPA:2,6-DAN:ABA = 1:1:2. Thermal properties and liquid crystallinity of the polymers were studied by use of differential scanning calorimetry (DSC), polarized microscopy, and X-ray analysis. The effect of annealing on molecular weight, thermal properties, and solid-state properties also was investigated.

Experimental Section

Synthesis of Polymers. All of the polyesters were prepared as melts. Since the synthetic procedures for all of the polymers were about the same, only a representative example, for the preparation of the 2,6/2 polymer, is given. Monomeric 2,6-DAN and ABA copolymer precursors were prepared respectively by reacting 2,6-naphthalenediol (Aldrich Chemical Co.) and *p*-hydroxybenzoic acid (Aldrich Chemical Co.) with an excess of acetic anhydride. 2,6-DAN was recrystallized from an 8:2 (v/v) mixture of chloroform and methanol and ABA from *p*-xylene. TPA (1.33 g, 0.80 × 10^{-2} mol, Aldrich), 2,6-DAN (1.95 g, 0.80 × 10^{-2} mol), and ABA (2.88 g, 1.6 × 10^{-2} mol) were placed in a polymerization tube. This mixture was heated first for 30 min at 240 °C, then for 90 min at 260 °C, and then for 75 min at 280 °C under a steady stream of N_2 gas. During this period continuous generation of acetic acid was observed. The temperature of the reaction mixture was raised to and maintained at 290 °C for 60 min under a reduced pressure of 100 Torr. Finally, the mixture was heated for 60 min at 300 °C and 10 min at 310 °C at the pressure of 1 Torr. The polymer formed was cooled to room temperature and recovered. Table I summarizes polymerization conditions employed for the preparation of each polymer.

Characterization. Elemental analyses were performed by the Microanalytical Laboratory of the University of Massachusetts and the Analytical Laboratory of the Korea Institute of Chemical Technology; see Table II. Inherent viscosities of the copolymers were measured on solutions of 0.1 g/dL in the solvents specified in Table III. The thermal behavior was studied under a N_2 atmosphere on a Du Pont 910 DSC and a Perkin-Elmer TGS-2 at a heating rate of 10 °C/min. The temperature at which the melt started to flow was taken as T_f. T_f's were determined on a Fisher-Johns melting point apparatus. The optical texture and thermal behavior of the melts also were examined on a hot stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux).

The approximate degree of crystallinity was estimated from the crystalline and the amorphous reflection areas in the wide-angle X-ray diffractogram obtained on a JEOL JDX-8D instrument using nickel-filtered Cu Kα radiation. The scan speed was

Table IV
Properties of As-Polymerized Samples of *X*,*Y*/1.5- and *X*,*Y*/1-Series Copolyesters[a]

	X,*Y*/1.5-series						*X*,*Y*/1-series					
X,*Y*	η_{inh}	T_g, °C	T_f, °C	T_m, °C	DC, %	LC phase	η_{inh}	T_g, °C	T_f, °C	T_m, °C	DC, %	LC phase
1,4	0.61	99	216		0	S	0.90	98	178		0	S
1,5	0.76	92	230		0	S	0.83	95	182		0	S
1,6	0.39	130	224		0	no	ins	109	190		0	no
1,7	0.23	146	260		0	N	0.58	138	194		0	no
2,3	1.52	118	206		0	N	1.25	117	172		0	N
2,6	2.03	108		258	35	N	1.20	85		263	14	N
2,7	0.80	124	220		0	N	0.82	114		245	12	N

[a] See Table III for definitions of parameters.

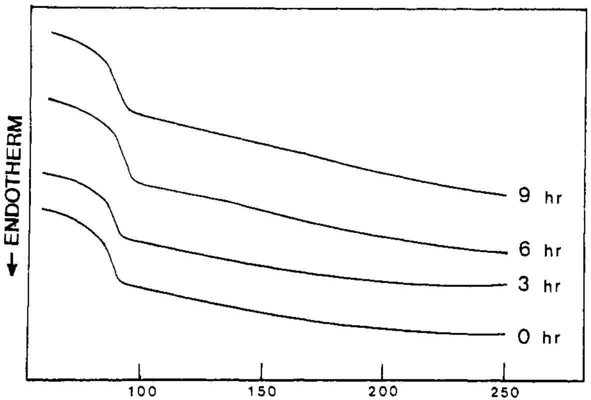


Figure 1. DSC thermograms of the 1,5/2-polymer before and after annealing. The annealing temperature was 170 °C.

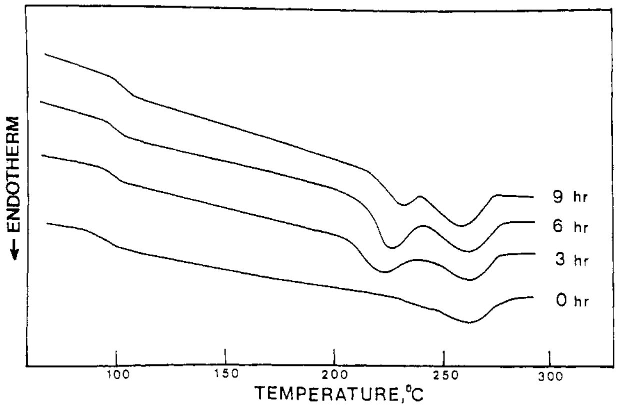


Figure 2. DSC thermograms of the 2,6/2-polymer before and after annealing. The annealing temperature was 190 °C.

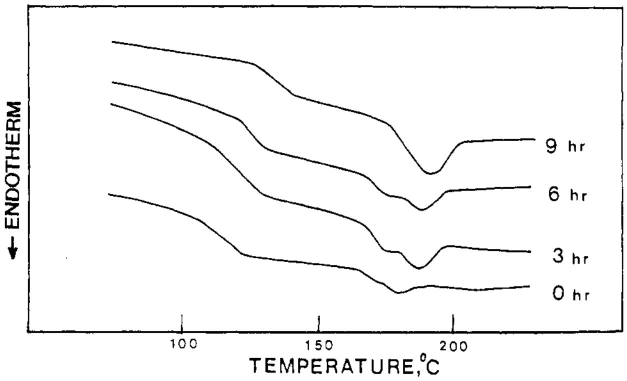


Figure 3. DSC thermograms of the 2,7/2-polymer before and after annealing. The annealing temperature was 190 °C.

4 deg/min. Quenched samples for X-ray analyses were prepared by immersing the polymer melts in a dry ice/acetone bath. Annealings were conducted in a vacuum oven (1 Torr) preheated to a desired temperature. Afterward, the annealed samples were slowly cooled to room temperature (ca. 10 °C/min) in the vacuum oven.

Results and Discussion

General Properties. The results of elemental analyses (Table II) are in good agreement with calculated values, suggesting that the actual compositions of the copolyesters are very close to those of the feed. None of the polymers are soluble in common solvents and, therefore, a mixed solvent of either 2,3,4,5,6-pentafluorophenol/*p*-chlorophenol/chloroform or *p*-chlorophenol/phenol/1,1,2,2-tetrachloroethane had to be used for the measurement of solution viscosities. Table III describes which solvent mixtures and the ratios that were employed for each polymer. Since the solubilities of all the polymers were rather low even in those solvent mixtures, a concentration of 0.1 g/dL was employed for the solution viscosity measurement. The solution viscosity numbers are reasonably high (0.6–2.0) with the exception of those for the 1,6/1.5 and 1,7/1.5 polymers. In general, solution viscosity numbers of annealed samples were significantly higher (Table III) than those of their as-polymerized precursors. Several of the polymers even became insoluble on annealing, probably due to their increased molecular weights and enhanced degree of crystallinity; this will be discussed later.

The T_g's of the polymers could be precisely determined from heating curves of their DSC analyses (e.g., Figures 1–3). For all of the three series the T_g's (ca. 80–110 °C) of the 1,4-, 1,5-, and 2,6-copolyesters are consistently lower than those (ca. 110–115 °c) of the rest. The relatively low T_g's for the 1,4- and 1,5-DAN compositions can be ascribed to their higher free volumes, generated either by the presence of bulky, fused pendant phenyl rings or by the steplike bent structure of the main chain. For the relatively low T_g's of 2,6-copolyesters compared with, for example, those of 2,3- and 2,7-copolymers, it is postulated that rotation of the naphthylene unit around its two connecting bonds is less restricted in 2,6-polymers than in 2,3- or 2,7-polymers. The latter require major dislocation of the naphthylene structures in order to achieve rotational motion around the two linking bonds, which in turn would necessitate a higher energy input for segmental motions, leading to high T_g values. It is rather well established that reduced internal mobility of polymer chains increases T_g. The same factor also must be a major reason for the 1,6- and 1,7-copolyesters' high T_g's. Although the dependence of T_g on molecular weight (MW) cannot be neglected, we believe that the trend observed in the present polymers is mainly due to their structural character. This can be supported by the fact that the T_g values of annealed and thus of higher MW polymers (Table III) are not much different from those of the as-polymerized samples and revealed the same trend.

Regardless of *p*-oxybenzoate content, all of the as-polymerized samples, with the exception of the 2,6- and 2,7-copolymers, showed no melting endotherms on DSC

Table V
Dependence of Transition Temperatures and Degree of Crystallinity on Annealing Time

annealing time, h	1,5/2-polymer (170 °C)[a]			2,6/2-polymer (190 °C)[b]						2,7/2-polymer (190 °C)[b]					
	η_{inh}	T_g, °C	DC, %	η_{inh}	T_g, °C	T_{k-k}, °C	T_m, °C	ΔH_m, kJ/mol	DC, %	η_{inh}	T_g, °C	T_{k-k}, °C	T_m, °C	ΔH_m, kJ/mol	DC, %
0	0.62	87	0	1.5	82		259	1.6	16	0.73	106		191	0.5	10
3		90	0	ins	87	216	260	2.1	30		113	181	195	1.3	16
6		91	0	ins	87	221	261	2.3	34	0.94	113	183	195	1.5	19
9	1.36	90	0	ins	87	224	260	2.4	36	1.13	113		197	1.9	26

[a] Annealing temperature was 170 °C. [b] Annealing temperature was 190 °C.

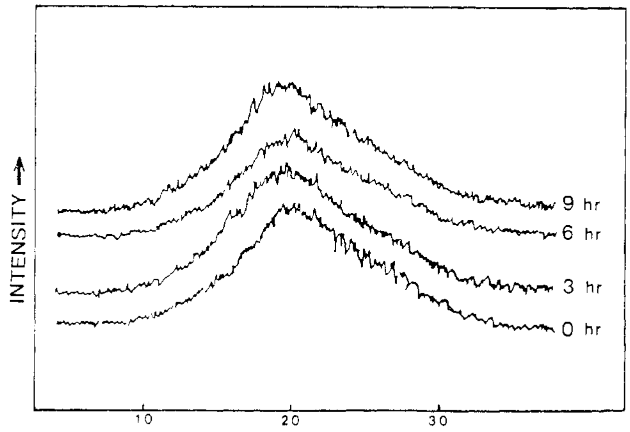


Figure 4. X-ray diffractograms of the 1,5/2-polymer before and after annealing. The annealing temperature was 170 °C.

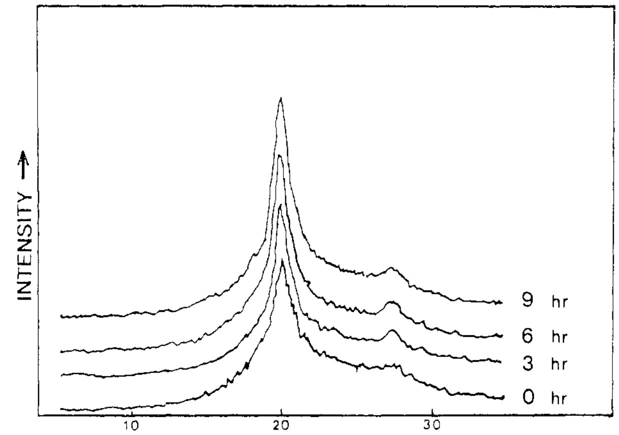


Figure 5. X-ray diffractograms of the 2,6/2-polymer before and after annealing. The annealing temperature was 190 °C.

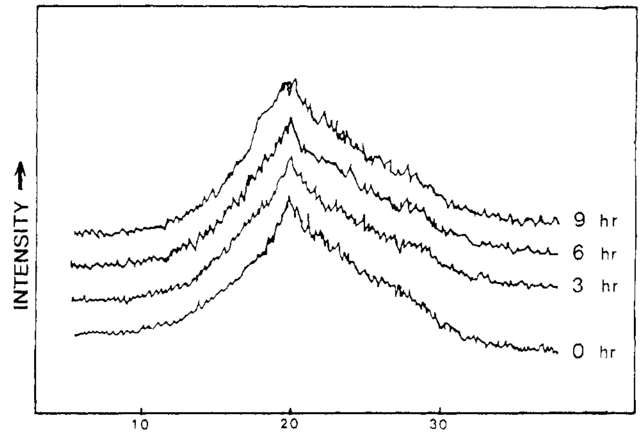


Figure 6. X-ray diffractograms of the 2,7/2-polymer before and after annealing. The annealing temperature was 190 °C.

analysis (Figure 1 and Table III–V). The three compositions of 1,5/2, 1,7/2, and 2,3/2 did not exhibit melting transitions even after annealing (see Figure 1 and Table III). These polymers may be intrinsically amorphous or extremely slow in crystallization. Structural irregularity caused by a random sequence of monomer units, together with the random existence of bent structures, certainly would hinder crystallization. Unlike other isomeric structures, 2,6-naphthylene moieties do not destroy linearity of the polymer main chain; therefore, all the copolymers containing this naphthylene unit are able to form crystalline structures.

As far as the flow temperatures of the polymers, T_f's, are concerned, generally polymers with higher T_g's show higher T_f values. Some of the nonconforming data are believed to be due in part to inaccuracies in the experimental method used in the determination of T_f values and, in part, to the variation in melt viscosity of the polymers.

Thermal Treatment and Crystallization of Copolyesters. As mentioned earlier, most of the as-polymerized samples did not show melting endotherms on DSC, implying that they are amorphous. Their amorphous nature can be further supported by X-ray diffraction studies (for example, see Figure 4). The 2,6- and 2,7-copolyesters, however, were obtained as semicrystalline materials (see Figures 5 and 6). In order to induce crystallization, all the $X,Y/2$ series polymers were subjected to heat treatment at an annealing temperature, T_a, shown in Tables III and V. These tables compare the degree of crystallinity of each polymer before and after annealing. Figures 1–3 are the DSC thermograms for the three compositions obtained after selected annealing periods. Figures 4–6 show the X-ray diffractograms of the corresponding samples.

According to Figure 1, the 1,5/2-polymer cannot be crystallized, even after prolonged annealing at 170 °C. This suggests that the polymer is amorphous in nature. On the other hand, Figures 2 and 3 of the 2,6/2- and 2,7/2-copolymers, respectively, show that the melting transition peak areas grew with annealing time. In addition, crystal-to-crystal transitions of low-temperature polymorphs or premelt endotherms became much more evident for annealed samples. The endotherm area for T_{k-k} or premelting, however, either was reduced or disappeared with prolonged heat treatment.[11]

The X-ray diffractograms shown in Figures 4–6 for the same annealed polymers provide us with similar information on how the degree of crystallinity progressively increases on annealing (see Table V). As one can see from Figure 5, for example, the shape and positions of diffraction patterns did not change at all on annealing. Instead, only the diffraction intensity increased. This implies that the increase in crystallinity on annealing was not accompanied by any change in crystal structure. Therefore, it can safely be said that under the present annealing condition, i.e., with catalyst absent and at a relatively low temperature, below T_m, the copolyesters did not undergo

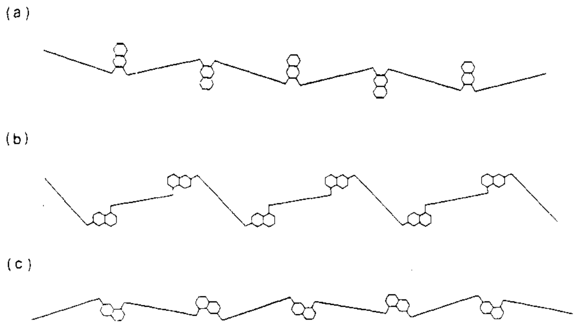


Figure 7. Molecular geometry of the (a) 2,3/1-, (b) 1,6/1-, and (c) 1,7/1-polymers.

any detectable degree of change in monomer sequence. Detailed analysis of X-ray diffractions requires further study.[12,13]

Table V summarizes the change of properties of the 1,5/2-, 2,6/2-, and 2,7/2-copolyesters with annealing time. The thermodynamic parameters and the degree of crystallinity were obtained from DSC and X-ray analyses,[12,13] as described above. The data in Tables III and V lead us to these conclusions on the effect of annealing the polymers: thermal treatment increases (1) molecular weight, (2) T_g and T_m, and (3), as mentioned above, degree of crystallinity of crystallizable polymers. The increase in MW on annealing is in part responsible for the increase in T_g and T_m. The T_g and T_m values, however, approach their asymptotic limits after a relatively short period of annealing, most probably due to the fairly high initial polymer MW's. As described earlier the 1,5/2-, 1,7/2-, and 2,3/2-copolymers remained amorphous even after prolonged annealing.

The increase in crystallinity is most conspicuous for the 2,6/2-copolymer; its degree of crystallinity increased from 16 to 36% when annealed for 9 h at 190 °C.[14] Further annealing produced no further increase in the degree of crystallinity. The results included in Table V show that the value of ΔH_m steadily increases from 1.6 to 2.4 kJ/mol as the degree of crystallinity increases. We did not conduct similar annealing studies for the *X*,*Y*/1.5 and the *X*,*Y*/1 series, but we believed that a similar phenomenon would be observed.

Inoue et al.[15] reported the synthesis and thermal transitions of the 2,6/3-, 2,6/4-, and 2,7/3-copolyesters. The copolymers had melting points (300–325 °C) significantly higher than those (190–260 °C) of the 2,6- and 2,7-copolymers reported here, which contain fewer *p*-oxybenzoyl units. Their T_g's, however, are comparable. Unfortunately, Inoue et al.[15] gave a very limited amount of information on the polymer properties other than T_m's and T_g's. It is impossible to compare our results with theirs.

Nature of the Mesophase. All of the *X*,*Y*/2-series formed mesophases above T_m or in fluid melt states, regardless of structure of the naphthylene moiety. Among the *X*,*Y*/1.5- and *X*,*Y*/1-polymers, however, 1,6/1.5-, 1,6/1-, and 1,7/1-copolymers were found not to be liquid crystalline. This implies that when a copolyester chain, on average, consists of two *p*-oxybenzoyl units and one terephthaloyl group, i.e., three consecutive more or less linear monomer structures in its repeating unit, it is able to form a mesophase even when a sharply bent structure such as the 2,3-naphthylene unit is included in the composition. When the content of linear *p*-oxybenzoyl units was reduced, nonmesomorphic compositions resulted from the 1,6- and 1,7-DAN's. At first sight, it may appear hard to believe that the 2,3/1-composition is liquid crystalline while the 1,6/1- and 1,7/1-compositions are not. Comparison of the molecular shape (Figure 7) of one conformer of these polymers, however, dramatically demonstrates that such a 2,3-copolymer chain is much more nearly linear than that of any 1,7-copolymer conformer. This figure also shows that the degree of bending of the 1,6-polymer is significantly more severe than that of the 1,7-polymer. This probably is the reason why the 1,6/1.5-copolymer is not mesomorphic while the 1,7/1.5-copolymer is. Specific chain conformations of the 2,3/1- and 1,7/1-copolymers appear to guarantee about the same degree of linearity in molecular shape (see Figure 7). The fact that the former is liquid crystalline, while the latter is not, however, implies that interlocking effect by the extruding 2,3-naphthylene unit in the former strongly favors mesophase formation.[9] A similar interlocking effect is not anticipated to occur in the 1,7/1-polymer. All these observations strongly emphasize the importance of a polymer chain's linear conformations to impart liquid crystallinity. The straight line portion in Figure 7 corresponds to the (*p*-oxybenzoyl)terephthaloyl structural unit (ca. 13 Å). Perfect linearity was assumed for this unit in order to make the comparison easier. The structures shown in the figure depict a strictly ordered monomer sequence of [(*p*-oxybenzoyl)terephthaloyl]naphthylene, which is not completely representative of random sequences. Nevertheless, we believe that our conclusion based on such an analysis is acceptable.

Table VI
Results of Thermogravimetric Analyses of *X*,*Y*/2-Series Polymers[a]

X,*Y*	T_D^i, °C	T_D^{max}, °C	T_D^{50}, °C	wt^R, %
1,4	460	485	535	39
1,5	450	493	555	35
1,6	420	465	570	39
1,7	430	470	570	38
2,3	440	480	570	41
2,6	490	525	570	38
2,7	445	485	565	37

[a] T_D^i and T_D^{50} are the temperatures at which initial and 50% weight loss, respectively, were observed. T_D^{max} is the temperature at which the maximum rate of weight loss was observed. wt^R stands for the weight percent of residue remaining after the sample was heated to 600 °C.

Typical photomicrographs of optical textures observed through a polarizing microscope for the liquid-crystalline polymer melts are shown in Figure 8. Most of the liquid-crystalline compositions (see Tables III and IV) showed either the so-called polished marble texture or a threaded Schlieren texture (Figure 8a,b) typical of nematogens. Wide-angle X-ray diffraction patterns of the quenched melts of nematic polymers showed broad peaks centered around 2θ = 20–21°, corresponding to spacings of about 4 Å. This represents an average interchain distance. However, surprisingly enough, the 1,4- and 1,5-copolymers formed smectic phases in melts and exhibited smectic optical textures as shown in Figures 8c,d. Figure 8c shows a focal-conic texture and Figure 8d a broken fan texture. Unfortunately we are not able to give any particular reason why only the 1,4- and 1,5-polymers form smectic phases, although molecular models of the two polymer chains suggest a possibility that their chains may be able to form smectic layers through interchain lateral fitting or interlock.

Thermal Stability of Polymers. The thermal stability of the *X*,*Y*/2-polymers in N_2 was studied by DSC and TGA. Table VI summarizes the experimental results. All of the unannealed polymers showed small weight loss (–5%) at around 400 °C (see Figure 9), which results from the loss of acetic acid generated by further polymerization in the melt during TGA scanning. Formation of volatile

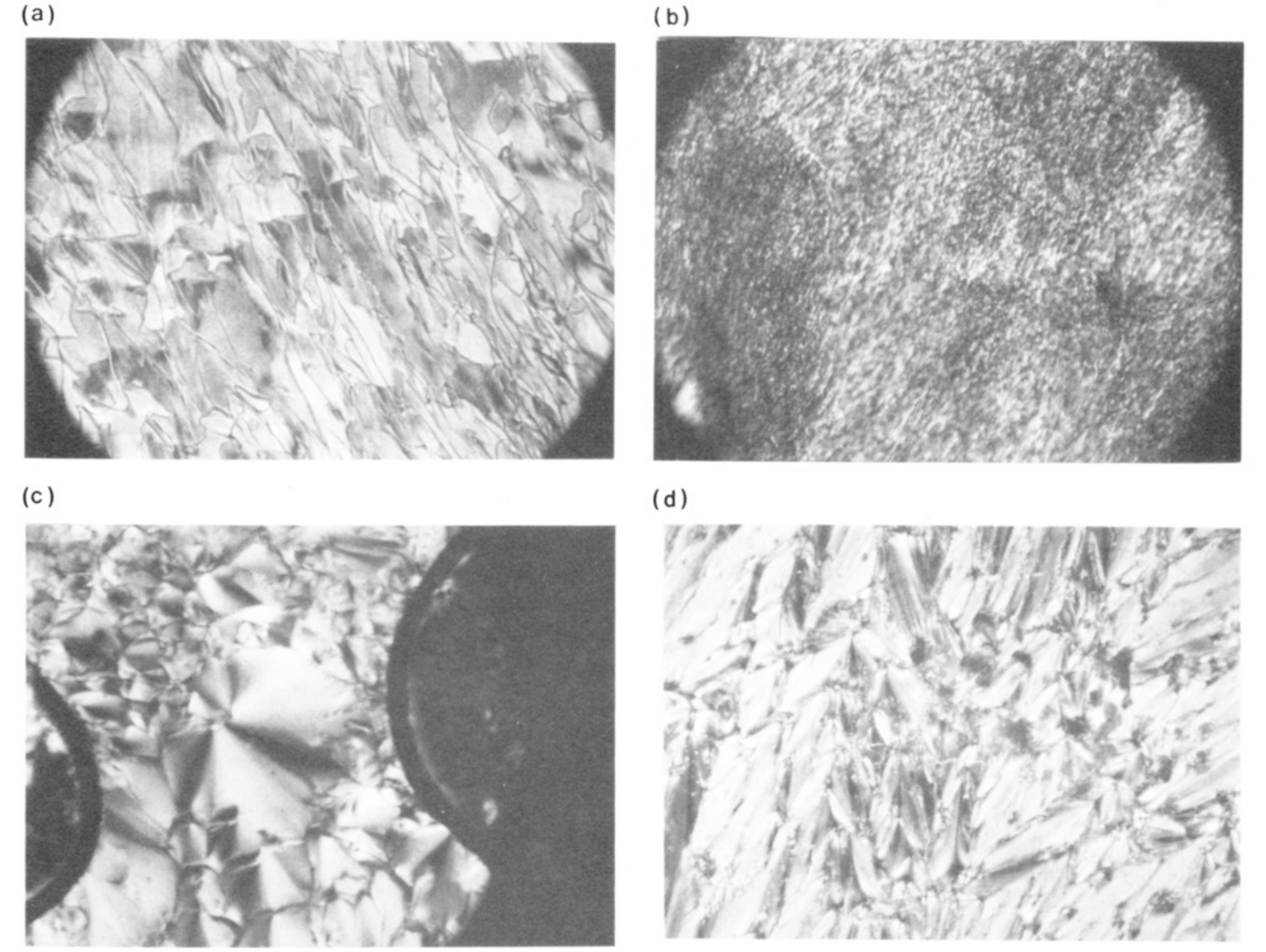


Figure 8. Photomicrographs (a) taken for the 2,6/2-polymer at 273 °C, (b) taken for the 2,7/2-polymer at 251 °C, (c) taken for the 1,5/2-polymer at 250 °C, and (d) taken for the 1,4/1-polymer at 273 °C (magnification 130×).

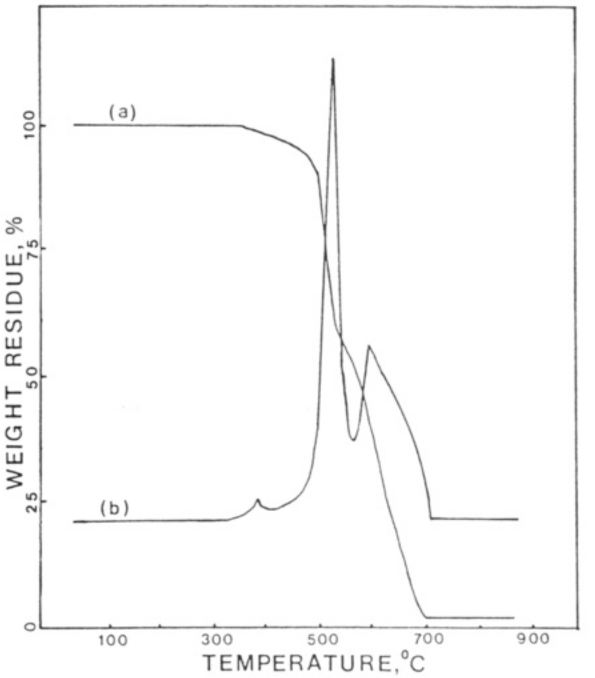


Figure 9. Thermogravimetric analysis (a) and differential thermogravimetry (b) thermograms of the 2,6/2-polymer.

degradation products was observed at 420–490 °C ($T_D{}^i$ in Table VI), depending on the polymer structure. The 2,6/2-polymer exhibited the highest $T_D{}^i$, 490 °C. The temperatures at which the maximum rates of weight loss were observed, $T_D{}^{max}$, obtained from the differential thermogravimetry curve (e.g., curve b in Figure 9), ranged from 465 to 525 °C. Again, the 2,6/2-copolymer showed the highest $T_D{}^{max}$ at 525 °C. $T_D{}^{50}$, the temperature where 50% weight loss was observed, and wt^R, the weight of residues at 600 °C, were about the same for all of the polymers. A comparison of only $T_D{}^i$ and $T_D{}^{max}$ values leads to the conclusion that the 2,6-copolyester is the most thermally stable, although all of the polymers show fairly good thermal stabilities.

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Registry No. (TPA)(ABA)(1,4-DAN) (copolymer), 113735-38-9; (TPA)(ABA)(1,5-DAN) (copolymer), 113735-39-0; (TPA)(ABA)(1,6-DAN) (copolymer), 116701-85-0; (TPA)(ABA)(1,7-DAN) (copolymer), 116701-86-1; (TPA)(ABA)(2,3-DAN) (copolymer), 116701-87-2; (TPA)(ABA)(2,6-DAN) (copolymer), 70799-59-6; (TPA)(ABA)(2,7-DAN) (copolymer), 101550-31-6.

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Curing Mechanism and Thermal Properties of Epoxy–Imidazole Systems

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ABSTRACT: The role of imidazoles in the curing of epoxy resins and their effects on the thermal properties of the network were investigated. Fourier transform infrared spectroscopy and differential scanning calorimetry were used to identify and analyze the individual reactions occurring during the cure of the diglycidyl ether of bisphenol A with various 1-unsubstituted imidazoles (2-ethyl-4-methylimidazole and imidazole) and 1-substituted imidazoles (1,2-dimethylimidazole and 1-methylimidazole). Two types of etherification reactions were found to occur in 1-unsubstituted imidazoles. These etherification reactions, which occur at imidazole concentrations of 25.0 mol % or less, are characterized by a rapid increase in the glass transition temperature. The curing mechanism and the glass transition temperature were shown to be strongly dependent on the concentration and on the reactivity of the imidazole.

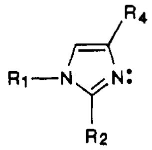
Introduction

Imidazoles are used as hardeners in a variety of commercial epoxy resin systems. They are added to epoxy–anhydride systems to initiate the esterification reaction and to epoxy–cresol systems to catalyze selectively the epoxy–phenolic hydroxyl reaction. Imidazoles also catalyze the homopolymerization of epoxy compounds. The cured product exhibits excellent chemical stability and high heat resistance and, consequently, is used in the electronics industry as a molding and sealing material.[1] However, despite the widespread commercial use of imidazoles, little is known about their role in the curing process.

In previous work[2-8] on epoxy/imidazole systems, the reaction between phenyl glycidyl ether (PGE) and imidazoles was investigated. The formation of epoxy/imidazole adducts was shown to be the first step in the curing process. It was proposed that both nitrogens were involved in forming adducts; consequently, the imidazole became permanently incorporated into the polymer network.[2,3] Barton and Shepard[3] and Dearlove[4] concluded that the formation of both 1:1 and 2:1 epoxy/imidazole adducts resulted from the opening of the epoxide ring by basic "pyridine-type" nitrogens. The 2:1 adduct, which contains the nucleophilic alkoxide ion, was believed to be the catalyst that initiated the polymerization process.

Considerable research has been conducted on the adduct reaction between PGE and various imidazoles which occurs at high catalyst concentrations; however, the etherification reaction that occurs at low catalyst concentrations has not been extensively explored. These etherification reactions cross-link the epoxy resins and determine the final properties of the network. Initial studies[5,9] on a cross-linking epoxy resin cured at low imidazole concentrations, specifically the diglycidyl ether of the bisphenol A (DGEBA)/2-ethyl-4-methylimidazole (EMI-24) system, revealed a complex curing mechanism. Figure 1 shows the proposed reaction mechanism for DGEBA based on previous PGE adduct reaction studies.[3] There are four possible reactions: two adduct reactions and two etherification reactions.

Table I
Chemical Structure of Imidazoles Used to Cure DGEBA



	designation	R_1	R_2	R_4
2-ethyl-4-methylimidazole	EMI-24	H	C_2H_5	CH_3
1,2-dimethylimidazole	DMI-12	CH_3	CH_3	H
1-methylimidazole	MI-1	CH_3	H	H
imidazole	IMDZ	H	H	H

The objective of this work was to identify the different reactions occurring in DGEBA/imidazole systems and to analyze their effect on the thermal properties of the network. Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were used to monitor the curing reactions and to evaluate the resin properties during the cure. Four model imidazoles with different reactivities and selectivities were used to differentiate the curing reactions.

Experimental Section

High-purity DGEBA (X-22) was supplied by the Shell Development Co. The epoxide equivalent weight, determined by titration, was 170 g/mol epoxide. The imidazoles, with purities ranging from 98 to 99%, were obtained from Chemical Dynamics Corporation. The four imidazoles used in this study are shown in Table I. Samples with different imidazole concentrations were prepared by dissolving both components in methyl ethyl ketone (MEK). The homogeneous sample was recovered by solvent flashing followed by crystallization.

Isothermal and temperature ramp studies were performed using a Mettler DSC-30 equipped with a low-temperature cell. Isothermal studies were performed by rapidly ramping (100 °C/min) the sample from 0 °C to the isothermal temperature, holding for various periods of time, and quenching to −50 °C. The sample was then scanned to 300 °C at 10 °C/min to determine the glass transition temperature (T_g) and the residual heat of reaction; the conversion was calculated by assuming that all the reactions have similar heats of reaction. Temperature ramp (dynamic) studies were performed at various heating rates and over a temperature range of 0 to 300 °C. The temperature corresponding to the onset of the endothermic deflection of the base line was taken to be

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