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Synthesis and Properties of Oxygen-bridged Aromatic Polyesters Based on Isomeric Naphthalenediols

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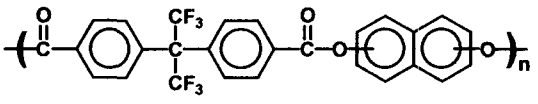
Abstract : Six aromatic polyesters with ether-linkages were prepared from 4,4'-oxybis(benzoic acid) and naphthalenediol (ND) isomers which were 1,4-, 1,5-, 1,6-, 2,3-, 2,6- and 2,7-derivatives. The solution viscosity numbers ranged from 0.23 to 0.65 dL/g. The glass transition temperatures ranged from 142 to 179 °C. The initial decomposition temperatures were all above 400°C, and the residue weights at 600 °C were in the range of 50-64%. Only the polyesters derived from 1,5- and 2,6-NDs, which have a linear linking mode, were found to be semicrystalline and could form thermotropically nematic phase. Multiple melting phenomena and annealing of the polyester derived from 1,5-ND and related polymers are described. The experimental results show that the polyester derived from 1,4-ND of linear shape was amorphous and non-liquid crystalline. Particularly, the polyester derived from 2,3-ND could form a smectic mesophase as banana-shaped molecules, and this is ascribed to the C_{2v} symmetry where highly kinked molecules are packed in the same direction.

Introduction

Wholly aromatic polyesters containing naphthalene groups in the main chain are referred to as high performance polymers because of their excellent thermal and mechanical properties. Numerous efforts have been made to clarify the structure-property relationship of the polyesters of naphthalene derivatives,[1,2] and some structures and compositions have been commercialized successfully. During the past few years, much attention has been paid to aromatic polyesters of naphthalenediol isomers because the range of possible substitution-positions of the hydroxyl groups can provide structural variations in the polymer chains.[3-9]

In a recent study, we have examined the effect of isomeric naphthalene links on the thermal and radiation sensitivity of a series of aromatic polyesters prepared from 4,4'-(hexafluoroisopropylidene)-bis(benzoic acid) and various isomeric naphthalenediols.[10] In addition, it was demonstrated that the hexafluoroisopropylidene-bridged structures could affect the alignment of the naphthalene rings in adjacent polymer chains.



= isomeric naphthylene unit

In this study, we have synthesized six aromatic polyesters from 4,4'-oxybis(benzoic acid) with 1,4-, 1,5-, 1,6-, 2,3-, 2,6- and 2,7-naphthalenediols. The polyesters have been coded as polymer-X,Y,

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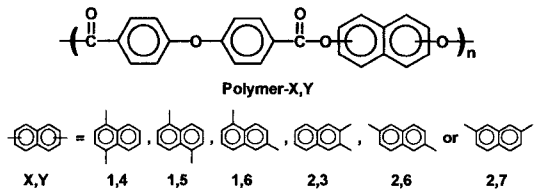


which identifies the relative positions of the two hydroxyl groups on the naphthalene rings. In an effort to study the effect of the oxygen-bridged structure on the arrangement of the isomeric naphthalene moieties in the polymer chains, we have investigated their crystalline, liquid crystalline, and thermal properties.

Experimental

Polycondensation. The naphthalenediols and 4,4'-oxybis(benzoic acid) were purchased from Aldrich Chemical Co. and used as received. Pyridine, 1,1,2,2-tetrachloroethane (TCE), and thionyl chloride were purified by usual methods.[11] The diacid dichloride (30 mmol) prepared from 4,4'-oxybis(benzoic acid) with thionyl chloride, 30 mmol of the naphthalenediol and 50 mL of dry TCE were added to a three-necked flask fitted with a dropping funnel and a nitrogen inlet. The mixture was stirred for about 10 min at ambient temperature. Then, 5 mL of pyridine was slowly added over a 10 min period. The mixture was subsequently stirred for 4 h at 100°C. After cooling, the mixture was poured into methanol with vigorous stirring and the precipitated polymer was subsequently collected by filtration. The polymer was further purified by several repeated washing steps with methanol and water sequentially. The polymer was finally dried at 60°C under vacuum. The overall yield of the polymer was nearly quantitative.

Polymer Characterization. The inherent viscosities were measured in 0.1 g/dL solution at 30°C. IR spectra were obtained on a Jasco-300E FT/IR spectrometer using samples in KBr pellets. On a Bruker AMX FT/NMR spectrometer at 200 MHz, ^{1}H- and ^{13}C-NMR spectra were recorded. The spectra were determined at 25°C in DMSO-d_6 (10 % w/v) with TMS as an internal standard. Thermal analyses were performed on a DuPont TA instrument equipped with a differential scanning calorimeter (DSC 910) and a thermogravimetric analyzer (TGA 951). The DSC and TGA thermograms were obtained at a heating rate of 20°C/min under a nitrogen atmosphere. The T_m values were obtained from the first heating scans and the T_g values were determined from the second heating scans. Thermal treatment of the polymers were conducted in a standard DSC cell preheated to the desired temperature under a nitrogen atmosphere. The optical texture was examined on a heating stage (Mettler FP82H) attached to a polarizing microscope (Zeiss, Jenapol). Wide-angle x-ray diffractograms were obtained in a reflection mode using Cu-Kα radiation on a Jeol JDX-8P x-ray diffractometer.

Result and Discussions

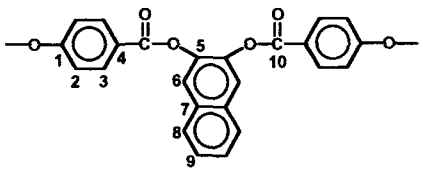
Synthesis and Solubility. All polyesters were synthesized by a solution polymerization method through an acid chloride route. The obtained polyesters were characterized by means of IR- and NMR-spectroscopy and the results were in agreement with expected formulae. A typical IR spectrum for polymer-1,6 showed characteristic absorptions of ester groups at 1739 cm^{-1} due to C=O stretch and at 1242-1062 cm^{-1} due to C-O stretch, and the spectra of the rest polymers showed the same aspect of absorptions. Previously, it has been suggested that polymer-2,3 would form a cyclic polyester in competition with linear one during polymerization due to the adjacent hydroxyl groups on the naphthylene units.[7] However, in this study, the resonance of carboxyl end group appeared at 12.5 ppm in ^{1}H-NMR spectrum of polymer-2,3. In Table I, chemical shifts for ^{13}C-NMR peaks of polymer-2,3 are listed, and the resultant data are in agreement with the expected formula.[12,13]

Table II shows that the solution viscosity numbers range from 0.23 to 0.65 dL/g. The polyesters were soluble either in a mixture of 1,1,2,2-tetrachloroethane (TCE) with phenols or a single TCE solvent. Polymers-1,5 and -2,7 were soluble in a phenol/TCE = 60 : 40 (w/w) mixture solvent. Polymers-1,4 and -2,6 were soluble in a phenol/*p*-chlorophenol/TCE = 25 : 40 : 35 (w/w/w) mixture

Table I. Chemical Shifts and Assignments for ^{13}C NMR Spectrum of Polymer-2,3

Number of Carbon Atom[a]	Observed δ (ppm)	Calculated[b] δ (ppm)
C10	164.3	-
C1	161.1	163.9
C5	142.1	144.8
C7	132.2	133.0
C3	133.6	129.9
C8	128.6	128.4
C9	127.9	126.4
C4	124.8	121.0
C6	122.1	121.0
C2	120.1	115.0

[a]



[b] Calculated by means of additivity rule reported by Lauterbur[12] and used by Jin and Hatada.[13]

Table II. Solution Viscosities and Thermal Properties of Polyesters

Polymer X, Y	$^{a}\eta_{inh}$ (dL/g)	T_g (°C)	$^{b}T_d^i$ (°C)	$^{c}T_d^{mcx}$ (°C)	$^{d}Wt^R$ (%)
1,4[e]	0.31	156	402	459	50
	0.65	172	396	450	54
1,5	0.46	171	418	506	63
1,6	0. 27	179	449	492	64
2,3	0.24	148	412	455	55
2,6	0.26	145	427	530	52
2,7	0.23	142	410	511	57

[a] Inherent viscosities of the polymers-1,4 and -2,6 were measured in a phenol/p-chlorophenol/TCE = 25 : 40 : 35 (w/w/w) mixture. Those of the polymers-1,5 and -2,7 were measured in a phenol/TCE = 60 : 40 (w/w) mixture. A single TCE solvent was used for the polymers-1,6 and -2,3.

[b] Initial decomposition temperature.

[c] Maximum weight loss temperature.

[d] Weight percent of residue at 600 °C.

[e] Two of the polymer-1,4 were prepared in different batch.

solvent. Polymers-1,6 and -2,3 were soluble in a single TCE solvent. The good solubility characteristics of the polymers-1,6 and -2,3 are mainly attributed to the unsymmetrical linking mode of 1,6-naphthylene units and the most bent substitution angle of 2,3-naphthylene units, respectively.

Glass Transition and Thermal Stability. Thermal transitions for the polyesters were examined by DSC measurement. The glass transition of the polymers could be clearly defined on DSC thermograms at the second heating cycles, as shown in Figure 1. In Table II, the glass transition temperatures (T_g) were determined to be in the range from 142 to 179°C. On the one hand, the highest T_g value for the polymer-1,6 can be accounted for by steric hindrance due to a bulky 1,6-naphthylene unit with unsymmetrical linking mode toward benzoyloxy units. On the other hand, a fairly strong interaction between adjacent naphthalene rings probably gives rise to nearly identical T_gs in all of the remaining polymers. According to the general rule between molecular weight and T_g, higher T_g values for polymers-1,4 and -1,5 are ascribed to their higher molecular weight.

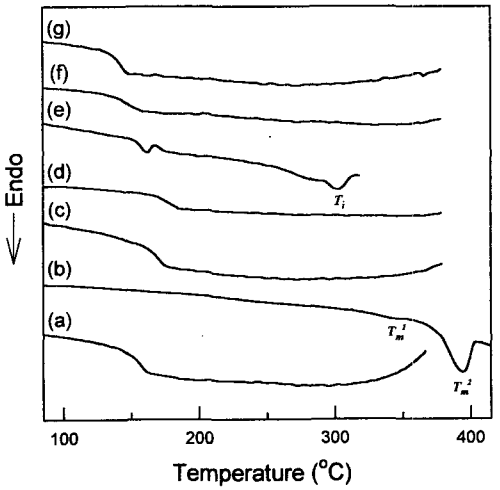


Figure 1. DSC thermograms of polymers-X,Y: (a) polymer-1,4 (2nd heat); (b) polymer-1,5 (1st heat); (c) polymer-1,5 (2nd heat); (d) polymer-1,6 (2nd heat); (e) polymer-2,3 (1st heat); (g) polymer-2,6 (2nd heat); (h) polymer-2,7 (2nd heat).

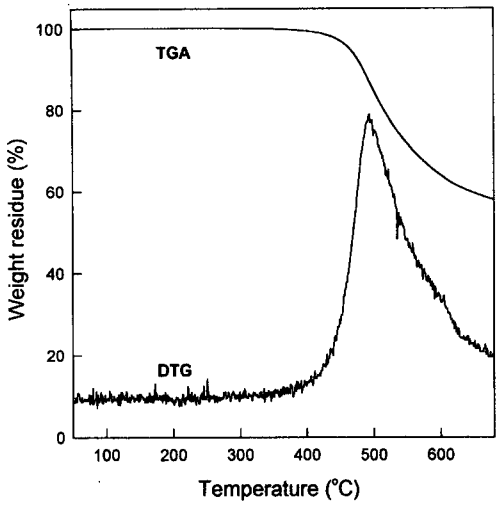


Figure 2. A typical TGA thermogram for polymer-1,6 and its derivative thermogravimetry (DTG) curve.

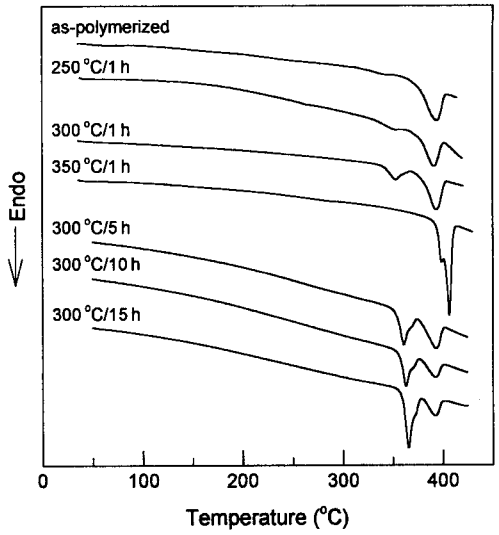


Figure 3. DSC thermograms for polymer-1,5 before and after annealing at each temperature for the different periods shown on the curves.

The thermal stabilities of the polymers in a N_2 atmosphere were studied by TGA, and the results are included in Table II. Representative TGA and DTG curves are displayed in Figure 2. In Table II, the polyesters show residue weights at 600°C in the range of 50-64%. The temperatures at initial decomposition (T_d^i) of the polymers were above 400°C, and their temperatures at maxium rate of decomposition (T_d^{max}) were in excess of 450°C. A comparison of the T_d^i and T_d^{max} values with those of other aromatic polyesters[14] highlights the good thermal stabilities of these naphthalene-containing polymers, even for the polymer-1,4, which is the least thermally stable. Comparing two 1,4-polymers having different molecular weight, T_g increases as molecular weight increases while the thermal stability is relatively unaffected. Steric hindrance arising from an additional benzene ring protruding from the 1,4-naphthylene units leads polymer-1,4 to be less thermally stable than remaining polymers. In our earlier report on the polyesters prepared from 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) and the equivalent isomeric naphthalenediols, the same tendency was observed.[10] However, it may need further study to understand the observation completely, namely that the polymer derived from 1,4-naphthalenediol was the least thermally stable among all the polyesters.

Melting and Crystallinity. In Figure 1, only DSC thermogram of polymer-1,5 reveals melting endotherm at 391°C, while only that of polymer-2,3 shows isotropization endotherm at 303°C instead of melting. However, the absence of melting in their DSC thermograms does not mean that the polymers are all amorphous because for the polymers, whose naphthalene units maintain a linear shape, thermal decomposition would be occurred before they reached their high melting temperatures. In order to make this point more clear, we annealed polymers-1,4, -1,5 and -2,6 for 15 h at 300°C. After annealing, polymer-2,6 could induce a polymorph near to the applied annealing temperature. However, even after annealing, polymer-1,4 did not show any melting, and only showed a slight increase in T_g, suggesting that it is intrinsically amorphous or extremely slow to crystallize. Before annealing, polymer-1,5 showed two DSC melting endotherms; these are a first weak peak at 340°C (T_m^1) and a second more intense one at 391°C (T_m^2). Figure 3 shows how the DSC thermograms of polymer-1,5 change with annealing temperature and time. A first transition becomes more distinct when annealed at 250°C (below T_m^1) and at 300°C (near but below T_m^1). On annealing at 350°C (between T_m^1 and

Table III. Dependence of Transition Temperatures for Polymer-1,5 on Annealing Conditions

Annealing Temperature (°C)/Annealing Time (h)	$^{a}T_m^{1}$(°C)	ΔH_m^{1}(J/g)	$^{a}T_m^{2}$(°C)	ΔH_m^{2}(J/g)	$^{b}\Delta H_t$(J/g)
As-polymerized	340	1.6	391	35.6	37
250/ 1	338	5.4	391	31.5	37
300/ 1	352	9.3	391	28.5	38
350/ 1	397	2.5	405	40.6	43
300/ 5	359	20.1	391	20.2	40
300/10	362	26.9	391	16.7	44
300/15	364	30.1	391	12.1	42

[a] Transition temperatures of first or second endothermic transition.
[b] Total enthalpy changes for T_m^{1} and T_m^{2} transitions.

T_m^{2}), the two transitions nearly merge into a single higher temperature transition. When the polymer was annealed at 300°C for an annealing period extended from 1 to 15 h, the relative magnitude of the first transition increases while that for the second transition decreases. Table III summarized the melting temperatures and enthalpy changes (ΔH) determined from the thermograms shown in the figure. This table shows that as the polymer was thermally treated up to 350°C, T_m^{1} increased from 340 to 397°C, and T_m^{2} remained constant approximately at 400°C. The table also shows that the total heat of melting ($\Delta H_t = \Delta H_m^{1} + \Delta H_m^{2}$) increases with annealing temperature and time. Annealing at 350°C for 1 h induced the most intense, highest temperature polymorph.

It has been reported that the polyesters of 1,5-naphthalenediol with 2-bromoterephthalic acid[6] and poly(2-hydroxy-6-naphthoic acid)[1] displayed similar melting phenomena to the polymer-1,5 in this study. While polymorphism could explain the dual transitions observed for the polymer-1,5, in the same manner as the polyester of 2-bromoterephthalic acid examined previously,[6,14] the possibility that the first is characterized as a crystal-to-plastic crystal (or smectic) transition and the second as a plastic crystal-to-nematic transition should not be discounted since two the temperature values are very comparable with those found for poly(HNA).

As shown in Figure 4, only x-ray diffractogram of polymer-2,6 shows intense peaks with a degree of crystallinity of 41%. By x-ray diffraction analysis, polymer-1,5 shows low degree of crystallinity,

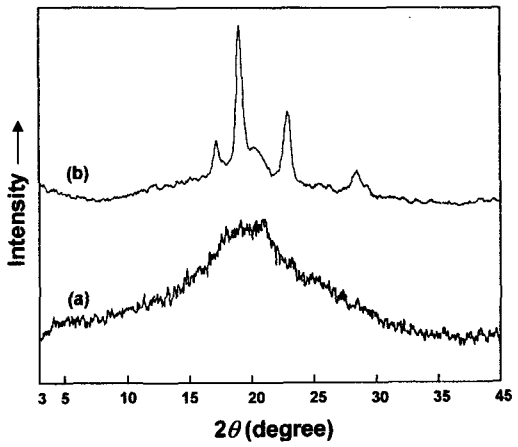


Figure 4. Wide-angle x-ray diffractograms of as-polymerized samples: (a) polymer-2,3; (b) polymer-2,6.

while the remaining polymers showed only amorphous patterns. These x-ray results are in accordance with DSC and annealing data already described.

Mesomorphic Property. Based on the optical textures observed for melts of the polymers using a polarizing microscope, only polymers-1,5 and -2,3 were found to be liquid crystalline (see Figure 5). Although polymer-2,6 should also be liquid crystalline, because the polymer was decomposed before the polymer reached its mesophase, we could not observe its birefringence in the melt. The rest of the polyesters in this study are not liquid crystalline. When polymer-1,5 was quickly heated above the 390 °C transition, sheared and rapidly cooled to ambient temperature, it dis-

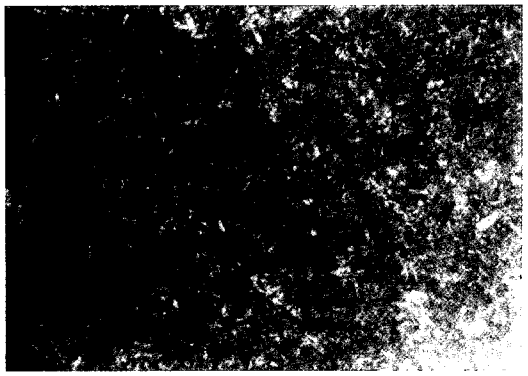
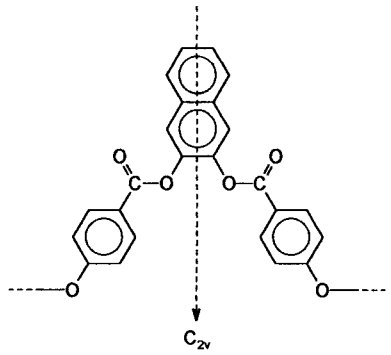


Figure 5. Polarizing micrograph of polymer-2,3 taken at 211 °C (Magnification 250×).

played a nematic marble-texture. The isotropization transition of polymer-1,5 could not be determined because thermal decomposition occurred before the isotropic point was reached. Polymer-2,3, whose isotropic transition could be defined in its DSC curve, could also form a mesophase in the melt, while the polymer contains highly bent naphthylene linking mode in its chain.

In an earlier study, it was described that the presence of the relatively long spacer through its flexibility or conformational adjustment certainly helps to mitigate the effect of the nonlinear structural element, and helps to maintain as much of a linear molecular structure as possible.[6] More recently, it has been demonstrated that the banana-shaped mesogens with C_{2v} molecular symmetry could form smectic mesophases in spite of their angled molecular structures.[16,17] Especially, we believe that the analogues molecular structure to these banana-shaped molecules could account for the mesomorphic nature of the polymer-2,3 in this study. At present, more detailed study about this point is in progress, and will be reported elsewhere.



Conclusions

The solubility of polyesters based on isomeric naphthalenediols was fairly improved by introduction of oxygen bridges into polymer's backbone. All the polymers, except for polymer-1,6, were approximately alike in T_gs due to strong interaction between adjacent fused aromatic rings. In spite of its lower molecular weight polymer-1,6 exhibited the highest T_g among the polymers, since the bulky 1,6-naphthylene unit could provide an additional protruding benzene ring due to its unsymmetrical linking mode. In general, only the polyesters having a linear chain shape were semicrystalline and thermotropically liquid crystalline. It is noteworthy that the polymer-1,4 having linear 1,4-ND units appears to be amorphous, and the polymer-2,3 having angled 2,3-ND units is able to form a mesophase in the melt. However, at present it is not easy to explain that the polymer-1,4 with the linear linkage is amorphous. For the polymer-2,3 we believe that conformational adjustment arising from the flexible oxygen bridges and C_{2v} symmetry of such a highly angled molecular arrangement certainly helps formation of a mesophase. In this study, it is suggested that the polymorphism of the polymer-1,5 is ascribed to formation of plastic crystal. Because the polyesters contain both bulky naphthalene units associated entropy factors, and strong ester units associated enthalpy factors, we can propose the plastic crystal structure in which one of the units has motional freedom while the other unit provides a three-dimensional framework.

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