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# Synthesis and properties of poly(dioxynaphthyleneisophthaloyl)s with various isomeric naphthylene links

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## SUMMARY

By condensation of 1,4-, 1,5-, 1,6-, 2,3-, 2,6-, and 2,7-naphthalenediol (ND) isomers with a isophthaloyl chloride six aromatic polyesters were prepared, and after removal of low molecular weight materials by extraction with acetone their properties were investigated. Effects of the isomerism of the naphthylene units on the properties of the polyesters were discussed. All the polyesters except one derived from 2,7-ND were soluble in a mixed solvent of phenol/*p*-chlorophenol/ 1,1,2,2-tetrachloroethane (TCE). Weight-average molecular weight of the polymer derived from 2,3-ND having the lowest inherent viscosity of 0.10 dL/g was measured to be 12,200 g/mol in TCE by means of a laser light scattering spectrometer. Polydispersity of this sample was determined to be 1.59 by a gel permeation chromatography with *o*-chlorophenol at 100°C. Glass transition temperatures of the polymers ranged from 144 to 195°C, depending on their molecular weight and chain structure. The polyesters derived from 1,6- and 2,3-NDs were amorphous and all the others were crystalline. Melting temperatures ($T_m$) of the polymers range from 341°C to 417 °C and the polymer derived from 2,6-ND showed the highest $T_m$. All the polymers had initial decomposition temperature higher than 400°C and showed residue more than 50 wt% at 600°C.

## INTRODUCTION

Wholly aromatic polyesters with naphthylene units in the main chain have been accepted as high performance polymers for many years[1-5], due to the excellent thermal and mechanical properties. But their properties are known to be greatly dependent on the isomeric structure of the naphthylene units. From the structural point of view it is particularly interesting to study the effect of isomeric naphthylene units on chain structures and properties of the polyesters containing them. It is reasonable to presume that 1,4-naphthylene unit would provide a linear chain structure with an additional benzene ring protruded, while both 1,5- and 2,6-substitutions would lead to more or less crankshaft-like structure and 1,6-, 2,3- and 2,7-substitutions to bent structure. Recently Jin et al.[6-10] have reported studies on synthesis and properties of the rod-like polyesters containing various ND isomers. In their efforts to improve the balance between processibility and performance of these polyesters forming mesophase, it was found that properties of the polymers were greatly influenced by the position of the two hydroxy groups of the monomer NDs. However, on the polyarylate-type polyesters derived from the same ND isomers, little information has been reported.

In this article, a series of polyesters with isomeric main chain structure were prepared by condensation of various ND isomers with isophthaloyl chloride (IPC),

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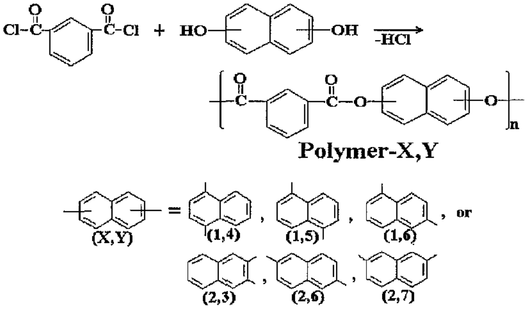

Scheme 1. Synthetic route to polymer-X,Y.

as shown in Scheme 1. Their thermal and crystalline properties were evaluated and discussed with respect to the effects of the isomeric structure of naphthylene units. The NDs used include 1,4-, 1,5-, 1,6-, 2,3-, 2,6-, and 2,7-dihydroxynaphthalene. By introducing kinked isophthaloyl unit into the backbone of the polyarylate-type polymers it was expected to obtain amorphous polyesters with excellent thermal stability and quite high glass transition temperature ($T_g$). For simplicity the polymers are coded as polymer-X,Y where X and Y stand for the relative positions of the two hydroxy groups on the naphthalene ring. For example, polymer-1,4 is the one prepared from 1,4-naphthalenediol and IPC.

## EXPERIMENT

**Chemicals and Polycondensation.** Naphthalenediols (Aldrich Chemical Co.) were recrystallized from mixtures of water and methanol. IPC (Aldrich Chemical Co.) was used directly after opening a paraffin-sealed bottle. Pyridine was purified by a usual method. Dichloromethane (DCM) of anhydrous grade packaged under nitrogen was obtained from Aldrich Chemical Co.. The other reagents were also commercially available and used as received.

A solution of IPC (5 mmole) in 50 mL of DCM was added all at once to solution of an ND (5 mmole) in 25 mL of DCM and 25 mL of pyridine with vigorous stirring under a nitrogen atmosphere at 0°C. The mixture was stirred further for 1 h at 0°C and than overnight at ambient temperature. The mixture was poured into excess *n*-hexane. The precipitate was filtered, washed with boiling water, dilute HCl, water and methanol, and dried at 60°C under vacuum for 1 day. These samples were extracted with acetone in a Soxhlet for 24 h and the insoluble portions were recovered and dried at 100°C in vacuum for 2 days. The IR spectra exhibited absorptions at 1750 $cm^{-1}$ (C=O) and 3100 $cm^{-1}$ (C-H).

**Polymer Characterization.** The inherent viscosity was measured from a 0.2 g/dL solution in a phenol/*p*-chlorophenol/1,1,2,2-tetrachloroethane (TCE) mixture (25/40/35 by wt%) at 30°C. The weight average molecular weight was determined by a home-made light scattering spectrometer operated with the $\lambda_o$ = 632.8 nm line of He-Ne laser. The incident beam as well as the scattered beam was vertically polarized to the scattering plane in this experiment. Benzene was used as the standard reference for computing the Rayleigh ratio of polymer solution ($R_{vv}$) with $R_{vv}^{Bz} = 9.40 \times 10^{-6}$ $cm^{-1}$ at 30°C. The specific refractive index increment (dn/dc) was measured also by a home-made differential refractometer. The polydispersity was determined by a gel permeation chromatography (Waters GPC, Model 150C) at 100°C with *o*-chlorophenol as a eluent and differential refractometer as a detector.

Thermal transition temperatures were determined on a duPont 910 DSC at a heating rate of 20°C/min under a nitrogen atmosphere. $T_m$ values were obtained from the first heating scans and $T_g$ values from the second heating scans. Thermogravimetrical measurements were conducted under a nitrogen atmosphere on a duPont 951 TA at a heating rate of 20°C/min. The optical texture was examined on a heating stage (Leitz 350) attached to a polarizing microscope (Leitz, Laborlux). Wide-angle X-ray diffractograms were obtained in a reflection mode using Ni-filtered Cu $K_\alpha$ radiation on a Rigaku D-Max 1400 X-ray diffractometer. IR spectra (KBr pellets) were taken from a Perkin-Elmer IR spectrometer. Annealing of the polymers was conducted in a standard DSC cell preheated to a desired temperature under a nitrogen atmosphere. After the annealing the sample was rapidly cooled to room temperature.

## RESULTS AND DISCUSSIONS

**Viscosity and Solubility.** Inherent viscosities ($\eta_{inh}$) and polymerization's yields are summarized in Table 1. The yield of the as-polymerized samples was higher than 90 wt%. The $\eta_{inh}$ values of the as-polymerized samples ranged from 0.20 to 0.34 g/dL except for polymer-2,3. The exceptionally low $\eta_{inh}$'s, 0.07 g/dL, of the polymer-2,3 might be ascribable for a steric hindrance of 2,3-ND, because in 2,3-ND two hydroxy groups are positioned too close each other to undergo a facile condensation reaction with the fairly bulky isophthaloyl group. As the $\eta_{inh}$ values of as-polymerized samples indicate not very high molecular weights, these samples were Soxhlet-extracted with acetone for 24 h to thoroughly remove low molecular weight portions. As shown in Table 1, most polymer's residue amount remained after the extraction is hardly dependent on the kind of ND used except for the polymer-2,3. The exceptionally small residue amount of the polymer-2,3 means that some cyclizations took place during the polymerization due to the same reason as its $\eta_{inh}$ value was lowered. The cyclized oligomers could be extracted by acetone,

**Table I. Yields and Viscosities**[a]

| | As-Polymerized | | After Extraction | |
|---|---|---|---|---|
| Polymer Code | Yield (wt%) | $\eta_{inh}$ (dL/g) | Yield (wt%) | $\eta_{inh}$ (dL/g) |
| 1,4 | 89.6 | 0.24 | 98.3 | 0.25 |
| 1,5 | 93.2 | 0.20 | 89.5 | 0.25 |
| 1,6 | 97.2 | 0.34 | 83.7 | 0.38 |
| 2,3[b] | 95.0 | 0.07(5,300) | 46.7 | 0.10(12,200) |
| 2,6 | 96.0 | 0.26 | 95.6 | 0.27 |
| 2,7 | 98.1 | ins. | 93.1 | ins. |

[a]Measured from 0.2 g/dL solution in a mixed solvent of phenol/*p*-chlorophenol/TCE = 25/40/35 (w/w/w) at 30°C. [b]The values shown in the parenthesis are the weight average molecular weight (g/mol) measured by light scattering spectrometry. In the polymer-2,3/TCE system, the value of dn/dc was 0.116 mL/g at 30°C, $\lambda_o$ = 632.8 nm.

and should give only 46.7 wt% residue to the polymer-2,3 after the extraction.

All the polymers except polymer-2,7 were soluble in a mixed solvent, phenol/p-chlorophenol/TCE, even after the acetone extraction. The polymer-2,7 was only soluble in strong acid such as $H_2SO_4$, but it was accompanied by degradation. The as-polymerized sample of polymer-2,3 was freely soluble even in a single TCE solvent. The improved solubility of this sample could be caused by its low molecular weight character on one hand and by its unique chain structure on the other hand. Thus, its weight-average molecular weight was determined by laser-light scattering method in TCE, and the value of 5,300 g/mol was obtained. Even after removal of 53.3 wt% acetone-soluble portion this sample was still freely soluble in TCE, though its molecular weight had increased to 12,200 g/mol. This extracted polymer-2,3 was further characterized by gel permeation chromatography with *o*-chlorophenol as a eluent at 100°C. The number-average molecular weight was 7,700 g/mol and hence the polydispersity 1.59. Since the molecular weight of this polymer-2,3 is still fairly low even after extracted with acetone, it can not be clearly concluded yet whether the exceptionally high solubility of the polymer-2,3 results from its unique chain structure or from its low molecular weight character.

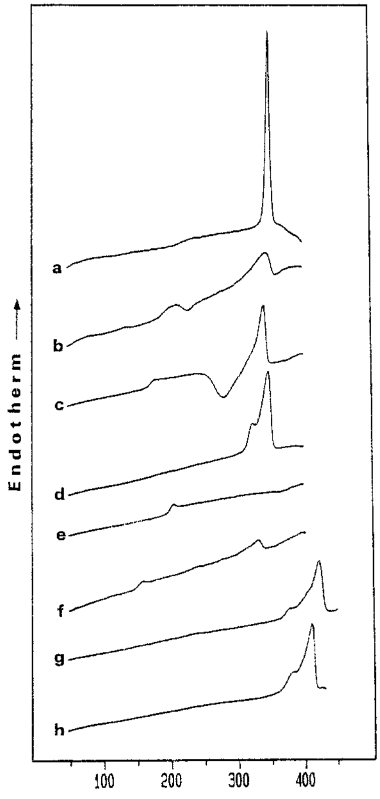

**Figure 1.** DSC Thermograms of the polymers; (a) polymer-1,4, annealed at 310°C for 60 min, (b) polymer-1,4, 1st scan, (c) polymer-1,5, 2nd scan, (d) polymer-1,5, 1st scan, (e) polymer-1,6, 2nd scan, (f) polymer-2,3, 2nd scan, (g) polymer-2,6, 1st scan, and (h) polymer-2,7, 1st scan.

**Table II. Transition Temperatures and Enthalpies**

| Polymer Code | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (KJ/mol) |
|---|---|---|---|
| 1,4[a] | 175(205) | 344(348) | 7.3(15) |
| 1,5 | 168 | 341 | 15 |
| 1,6 | 195 | *c* | *c* |
| 2,3[b] | 144 | *c* | *c* |
| 2,6 | 171 | 417 | 14 |
| 2,7 | 166 | 408 | 15 |

[a] The values in parentheses were obtained from the samples which were annealed at 310°C for 60 min. [b] This sample seemed to show a isotropic transition at 329°C. [c] Not observed because the polymer was amorphous.

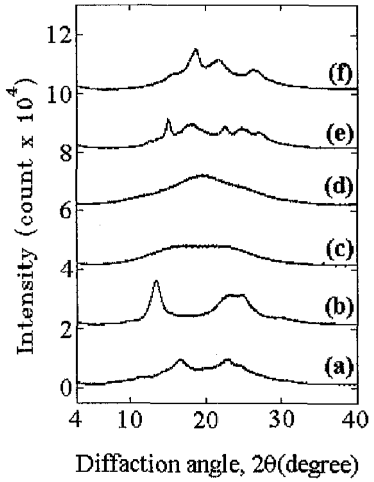

**Figure 2.** X-ray diffraction patterns observed; (a) polymer-1,4, (b) polymer-1,5 (c) polymer-1,6, (d) polymer-2,3, (e) polymer-2,6, and (f) polymer-2,7.

After the extraction with acetone the effects of isomerism of naphthylene unit on thermal and crystalline properties, and chain structures of the polymers were investigated, and the detailed discussion about this follows in the next section.

**Thermal Transition.** The $T_g$s of the polymers could be clearly assigned in the second DSC scans as representatively shown in Figure 1 for some samples. Table II shows first that the $T_g$ values of polymers-1,6 and -2,3 are considerably high and low compared to others, indicating that it might be ascribed rather to their molecular weight character than to their unique chain structure. The $T_g$'s of the rest four polymers is about 170°C. Considering the dependence of $T_g$'s upon molecular weight, it should be complicated to draw a relationship between the chain structure and $T_g$. Nevertheless, we have believed that the $T_g$ of these polymers would be governed more dominantly by the highly bent structure of isophthaloyl group than by naphthylene groups. In addition, a fairly strong interchain attraction between aromatic rings existing on the neighbor chains could also play a role in determining the $T_g$. This attraction should lead to only negligible difference in $T_g$s', which woule be determined more dominantly by the content of the aromatic rings than by the isomeric structure of themselves. In an earlier study[7,8] it has been reported that a greater effect of isomeric substitution is observed more in $T_m$ than in $T_g$.

Figure 1 shows also that the polymers-1,4, -1,5, -2,6, and -2,7 reveal a melting transition, while the polymers-2,3 and -1,6 exhibit no one. This means that the former four samples are crystalline and the latter two are amorphous. In Table II, melting points ($T_m$) of the crystalline polymers were in a range of 341-417°C. The polymer-2,6 whose naphthylene unit is nearly linear and symmetric shows the highest $T_m$ of 417°C, whereas the polymers-1,4 and -1,5 have much lower $T_m$ of 344°C and 341°C, respectively. The relatively low $T_m$ values for the latter are

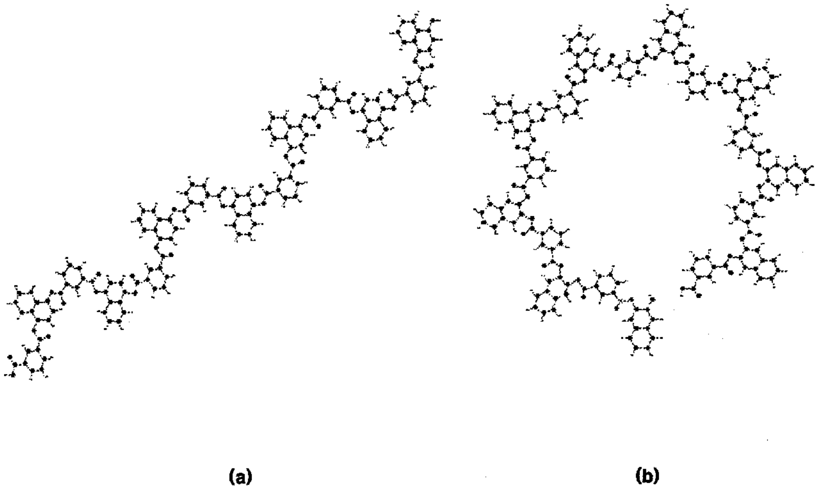
(a) (b)

Figure 3. Typical examples of molecular geometry in the (a) polymer-1,4 and (b) polymer-2,3.

perhaps because they form loose chain packing due to the presence of the bulky, fused pendant phenyl rings as to the polymer-1,4 and the step-like bent structure as to the polymer-1,5. However, the fact that the polymer-2,7 having bent naphthylene structure shows crystallinity with $T_m$ of 408°C can hardly be explained, though its degree of bending is smaller than that of the polymers-2,3 and -1,6.

The values for heat of melting ($\Delta H_m$) also are shown in Table II. The $\Delta H_m$ values of the crystalline polymers are in the vicinity of 15 kJ/mol except for the polymer-1,4 with 7.3 kJ/mole. As the polymer-1,4 exhibited relatively week melting endotherm, in order to see the possibility of further crystallization in this polymer, we annealed it at 310°C for 60 min. When the polymer-1,4 was annealed, its $\Delta H_m$ value dramatically increased from 7.3 to 15 kJ/mol (see Figure 1(a) and (b)), suggesting that it can intrinsically as much crystallize as the other crystalline polymers but can less do during its polymerization.

**Crystalline Structure.** We made a confirmation of the crystalline structures by wide-angle X-ray diffractometry. In Figure 2, the X-ray diffractograms of the polymers are reproduced. The X-ray diffraction patterns consist of a series of fairly sharp peaks, superimposed by a diffuse halo which may arise from the amorphous fractions. The diffractograms of the polymers-1,4, -1,5, -2,6, and -2,7 clearly show a crystallinity, while the two polymers-2,3 and -1,6 do not. Although their chain structures must be quit different, the polymers-2,6 and -2,7 have a common aspect in their X-ray diffraction patterns. All these observations by X-ray are in good agreement with the DSC result.

The fact that the four polymers including the polymer-2,7 are crystalline is contradictory to our expectation, because they all contain a highly bent isophthaloyl moiety in their chain structures and also because the polymers-1,5 and -2,7 have either the step-like or highly bent structure in naphthylene moiety, although the polymers-1,4 and -2,6 have linear ones. At present we assume that in the stable

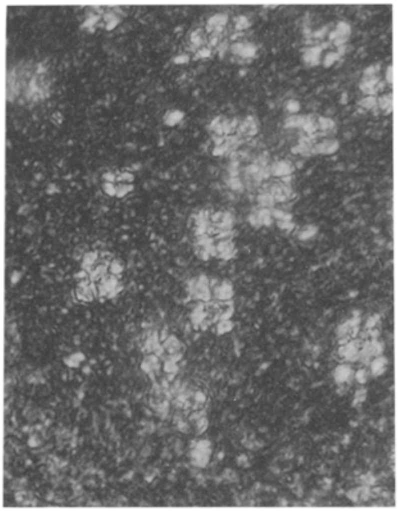

Figure 4. A photomicrograph of the polymer-2,3 melt (255 °C).

Table III. Thermal Pyrolysis Behavior[a]

| Polymer Code | $T_D^i$ (°C) | $T_D^{max}$ (°C) | $wt^R$ (%) |
|---|---|---|---|
| 1,4 | 431 | 470 | 52 |
| 1,5 | 444 | 480 | 63 |
| 1,6 | 462 | 491 | 59 |
| 2,3 | 408 | 494 | 52 |
| 2,6 | 490 | 527 | 54 |
| 2,7 | 477 | 505 | 68 |

[a] $T_D^i$ is the temperature where initial weight losses began. $T_D^{max}$ is the temperature where 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.

conformations of the polymers-1,4, -1,5 and -2,6, all the ester linking groups and aromatic rings including naphthalene lie almost on the same plane and in addition, the bent isophthaloyl groups are aligned not completely random, but instead somewhat regular, as schematically depicted in Figure 3(a) for the example of polymer-1,4, where they are directed up and down in alternate fashion. It is not clear yet that by which factors this assumed conformation could be determined, but the interchain attraction presumably plays a role in molecular packing of the crystalline polymers. When the naphthylene structure is too bent such as the polymers-2,3 and -1,6, the interchain attraction seems to be overruled by protrusion of naphthylene groups (e.g., Figure 3(b)), and the polymers could not crystallize. Moreover, the crystallization ability of the polymer-1,6 can be further destroyed by the random liking mode of unsymmetrical ND toward isophthaloyl moiety.

In the melt state, only the polymer-2,3 seemed to be able to form a mesophase (see Figure 4). At first sight, it may appear hard to believe that this polymer can be liquid crystalline because it has sharply bent 2,3-naphthylene unit in the repeating unit. In figure 3, comparison of molecular shape of one conformer of two the polymers demonstrates that such a naphthylene group in the polymer-2,3 chain is much more extruded than that of any polymer-1,4 conformer. Perhaps, it could be supposed that interlocking effect by extruding the 2,3-naphthylene unit might strongly favor mesophase formation. The same interlocking effect has been reported by Jin et al.[8] with the copolyester prepared from terephthalic acid, *p*-hydroxybenzoic acid and 2,3-ND at the equivalent molar ratio of feed, but further study is needed to confirm our observation.

**Thermal stability.** Thermal stability of the polymers was investigated by TGA. In Table III this result is summarized. The initial decomposition temperatures ($T_D^i$) are higher than 400°C and the temperatures at the maximum rates of weight loss

($T_D^{max}$) ranged from 470 to 527°C. Polymer-2,6 showed the highest $T_D^i$ of 490°C and $T_D^{max}$ of 527°C. All of the polymers showed more than 50 wt% residue at 600°C. This TGA result demonstrates that the polymers are of excellent thermal stability although the 2,6-polymer is the most thermally stable. With five polymers except the polymer-2,6, no correlation between chain structure and thermostability could be drawn, perhaps because a difference of bond's strength originated from the isomerism in their chain structures is too small to have a potent effect on the thermostability and to observe such a correlation.

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