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Synthesis and characterization of poly(dioxynaphthylene-1,4-dicarbonylnaphthylene)s with various isomeric naphthylene links

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Summary

Six all-naphthylene polyesters were prepared by the condensation of 1,4-naphthalenedicarboxylic acid (NA) chloride with 1,4-, 1,5-, 1,6-, 2,3-, 2,6- and 2,7-naphthalenediol (ND) isomers and effects of the isomerism of NDs on structure and properties of the polyesters were investigated.

The polymers-1,4, -1,5 and -2,6 with more or less linear ND link were insoluble and the others with bent ND link were soluble in the mixed solvent from phenol/p-chlorophenol/1,1,2,2-tetrachloroethane(TCE). The polymer-2,6 with the most linear ND link did not show a T_g and the highest decomposition initiation temperature(T_D) and T_g's and T_D's of the other polymers were only marginally dependent on their structures.

The polymer-2,3 is believed to have a macrocyclic structure consisting of four to six monomer units and the polymer-1,6 is amorphous in its stable chain conformation, while all the other polymers are semicrystalline. The polymers-1,4 and -1,5 exhibited an irreversible crystal-to-crystal transition at 380 and 320 °C, respectively, whereas the polymer-2,6 a reversible one at 240 °C. The polymer-2,7 exhibited an irreversible crystal-to-amorphous transition at 360 °C.

Introduction

In recent years aromatic polyesters containing naphthylene units have been accepted as high performance polymers due to their excellent thermal and mechanical properties(1-3). But the properties are known to be greatly dependent on the isomeric structure of the naphthylene units(4-10). From structural point of view, it is particularly interesting to study the effect of isomeric naphthylene links on chain structures and properties of the polyesters. It is reasonable to presume that 1,4-ND unit would provide a linear chain structure with an additional benzene ring protruded, whereas both 1,5- and 2,6-NDs would lead to more or less cranshaft-like structures and 1,6-, 2,3- and 2,7-NDs to bent structures.

In one of our recent articles(11) we have reported the synthesis, properties and chain structures of poly(dioxynaphthyleneisophthaloyl)s with the same six isomeric naphthylene links. Because of a combinatory effect of the presence of bent isophthaloyl and fairly bulky naphthylene units in the main chain, we had expected

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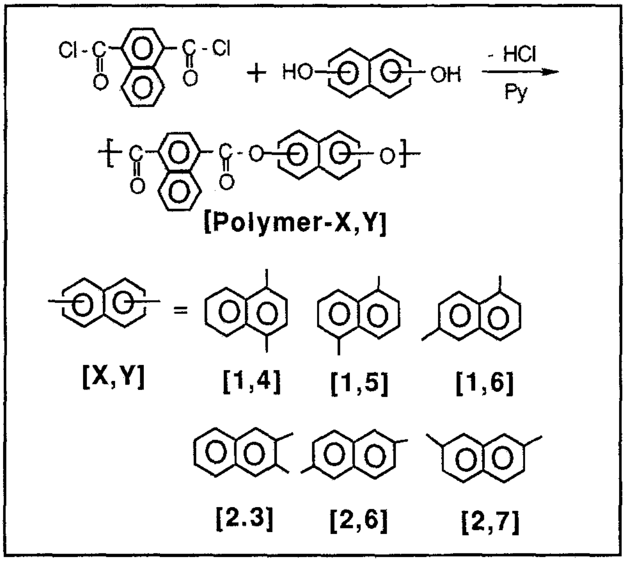
these aromatic polyesters to be amorphous. Contrary to our expectation, it has been found that most of the polyesters were prone to crystallize., and hence we have suggested that in the stable conformation of the polyesters the bent isophthaloyl groups does not align completely random, but instead somewhat regular, although the polyesters neither are stereospecific, nor have any preoriented configurations in their monomer units(12).



Scheme 1. Synthetic route to the polyesters.

As an extension of our efforts to delineate structure-property relations of the polyesters containing various ND isomers six all-naphthylene polyesters consisting of 1,4-dicarbonyl-naphthylene units and different ND isomeric links were prepared by the condensation of 1,4-naphthalenedicarboxylic acid dichloride with 1,4-, 1,5-, 1,6-, 2,3- 2,6- and 2,7-ND, as shown in Scheme 1, and their mesomorphic and crystalline structures and thermal properties were measured and discussed with respect to the effects of the isomeric structure of NDs. The polyesters are coded polymer-X,Y, where X and Y stand for the relative positions of the two hydroxy groups on the naphthalene ring.

Experiment

Chemicals. NA was used as received from Aldrich Chem. Co. NA dichloride was prepared by reacting NA with thionyl chloride. NDs(Aldrich) were purified by recrystallization from aqueous methanol. Pyriding and thionyl chloride were purified by the usual method. As dichloromethane(DCM)(Aldrich) was used an anhydrous grade obtained from Aldrich as packed under nitrogen. All the other reagents were commercially available and used without any purification.

Polymerization. A solution of NA dichloride(5 mmol) dissolved in 50 mL DCM was poured to a solution ND(5 mmol) dissolved in a mixture of DCM(50 mL) and pyridine(25 mL) at 0 °C with vigorous stirring under nitrogen. After stirring further for 1h at 0 °C and then overnight at ambient temperature, the reaction mixture was poured into excess n-hexane. The precipitates were filtered, washed in the order with boiling water, dilute HCl, water and methanol, and dried at 60°C in vacuum for 24 h. These samples were extracted with acetone in a Soxhlet for 24 h and the insoluble portions were collected, powdered and dried at 100 °C in vacuum.

Polymer characterization. Inherent viscosities were determined at 30 °C from a 0.1g/dL solution in a mixture of phenol, p-chlorophenol and TCE (25/40/35 w/w/w). Phase transition temperatures were measured on a du Pont 910 DSC at a heating rate of 20 °c/min under nitrogen. TGA measurements were made on a du Pont 951 TA at a heating rate of 20 °C/min under nitrogen.

X-ray diffraction measurement. These were performed with Ni-filtered CuKα radiation and a graphite monochromator. To investigate structural changes on heating, the samples were held in an Al holder which was sealed with 8 µm thick Kapton films on both sides. The samples were heated with two cartridge heaters and temperature of the samples was monitored by a thermocouple placed close to the sample. In determining scattering intensities from the samples, that from the Kapton was subtracted from total ones.

Results and discussions

Polymerization. Six new all-naphthylene polyesters consisting of 1,4-dicarbonylnaphthylene group and various isomeric ND units in their repeat units were prepared by the solution condensation of NA dichloride with various NDs in DCM containing pyridine.

In Table I are summarized the polymerization yields. It shows that the polymerization yields are fairly low and lie in the 60.5 - 88.1 % range. This arises from the removal of low molecular weight fractions by the acetone extraction. All the yields determined before the extraction recorded over 90%. Polymer-2,3 has especially low yield and accordingly high content in its low molecular weight fraction. This behavior might be ascribable to a much lower polymerizability of the second OH group than the first one of 2,3-ND. This lowered reactivity results from strong steric hindrance exerted by the bulky 1,4-dicarbonylnaphthylene unit already formed by reaction with the first OH group, because the two OH groups are located very close each other.

Inherent viscosity and solubility. Inherent viscosity values of both the as-polymerized and acetone-extracted samples are given also in Table 1. It shows that the polymers have inherent viscosities only in the 0.19 - 0.23 g/dL range and even the acetone-extraction did not greatly enhance the inherent viscosities. These low viscosities might be ascribable to the formation of low molecular weight polymers during polymerization, resulting from a steric hindrance exerted by NA, since the presence of the bulky, fused phenyl ring of NA must be an obstacle to a facile reaction with bulky ND molecules.

Solubility of the samples in the mixed solvent from phenol/p-chlorophenol/TCE seems to be governed by the structure of the ND units. As to see from Table 1, polymers-1,6, -2,3 and -2,7 having strongly bent ND structures are highly soluble, while the polymer-1,4 having a linear structure and polymers-1,5 and -2,6 having a crankshaft structure are completely insoluble and their inherent viscosities could not be measured from the solvent.

Glass transition. T_g's of the polymer samples were determined from their second DSC heating scans. The samples had been heated to 250 - 350 °C at a rate of

20 ℃/min and then cooled to ambient temperature at the same rate. The T_g values obtained are summarized in Table II. It shows that all the T_g values of the polymers fall in a fairly narrow range of 137 - 168 °C. This indicates that the T_g of the polymers are mainly governed by the presence of two heavy and rigid naphthylene groups existing in their repeat units. The naphthylene units having disc-like structure should reveal a strong interchain attraction, as confirmed in our earlier study(11) and by others(13), and T_g values should be governed more by this disc-disc attraction than by the isomeric structure of the repeat units, meaning that the effect of isomeric structure on T_g must be relatively small.

Table I. Yields and inherent viscosities

Code	Yield[a] (wt %)	Inh. Vis.[b](dL/g) Extracted	Unextracted
polymer-1,4	88.1	insoluble	insoluble
polymer-1,5	70.4	insoluble	insoluble
polymer-1,6	63.1	0.23	0.19
polymer-2,3	60.5	0.22	0.21
polymer-2,6	76.2	insoluble	insoluble
polymer-2,7	77.4	0.24	0.23

a) Measured after extracted with acetone.
b) Measured from 0.1 g/dL solution of phenol/ p-chlorophenol/TCE (25/40/35 w/w/w).

Table II. Thermal properties

Code	T_g (°C)	T_t (°C)	T_D (℃)	T_D^{max} (°C)	wt^R (%)
Polymer-1,4	163	379	379	459	48
polymer-1,5	137	319	368	473	52
polymer-1,6	168	-	378	480	54
polymer-2,3	142	348	397	464	53
polymer-2,6	-	368	407	522	41
polymer-2,7	149	369	389	488	47

T_t : Temperature of the peaks indicated with arrows in Figure 1.
T_D : Temperature at initiation of decomposition.
T_D^{max} : Temperature at maxmimum rate of decomposition.
wt^R : Weight % remained at 600 °C.

Polymer-1,6 has the highest T_g (168 °C), presumable due to a high rotational barrier of 1,6- ND units against NA units. Polymer-1,4 having two linear 1,4-

naphthylene moities in its repeat units exhibits as high a T_g (163 °C) as polymer-1,6. This might be attributed to the presence of a protruded benzene ring attached to the 1,4-phenylene group of the 1,4-ND unit. In spite of repeated scan the polymer-2,6 did not give a distinctive peak assignable to a T_g. This polymer having a nearly linear chain structure must exert such a strong attractive interchain interaction that its chain rigidity must be extraordinarily high and hinder a T_g from appearing. Polymers-1,5, -2,3 and -2,7 have T_g values falling in such a narrow range that no distinctive relation with their structures can be drawn.

Melting transition. Before making investigations on crystalline structure of the acetone-extracted polymers the existence of melting transition was examined by DSC at a heating rate of 20 °C/min. The DSC thermograms obtained are reproduced in Figure 1. It shows that all the samples except polymer-1,6 give identifiable peaks in the 300 - 400 °C range, as indicated with arrows in Figure 1 and T_t in Table II, although their peak intensities are not so distinctive as satisfactorily assignable for melting transitions. When the samples were annealed at temperatures above T_g, the intensities of the peaks increased sharply. However, it could also be found, as shown in Table II, that in some samples, especially in polymer-1,4, these peaks are positioned too close to the decomposition temperatures of the samples to assign them as melting transitions, and detailed investigations on the character of these transitions were made by wide-angle X-ray diffractometry with heating stage. These results are discussed in the structural transition part.

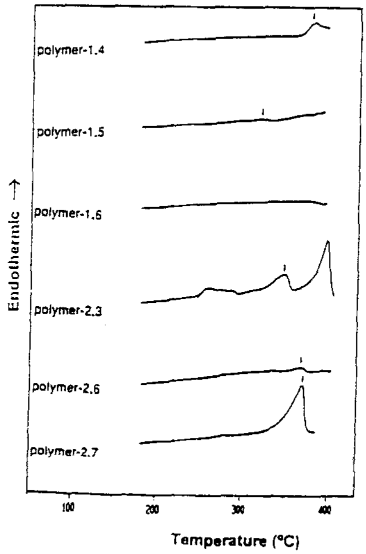


Figure 1. DSC thermograms of polymers-X,Y.

Thermal stability. Thermal degradation behaviors of the polymers were investigated by TGA in nitrogen and these results are summarized also in Table II. Table II shows that polymer-2,6 has the highest degradation initiation temperature T_D of the polymers. This may be ascribed to its linear structure leading to the greatest rigidity of its main chain, which again results to the strongest disc-disc attraction.

In spite its low molecularity polymer-2,3 has the second highest T_D. This might indicate that the already mentioned macrocyclic ring must be fairly stable against thermal decomposition.

Due to the quite strong attraction between aromatic naphthylene discs, all the polymers record wt^R higher than 40 %. If the polymers are heated, the naphthylene discs formed by scission of labile bonds linking them would readily crosslink and carbonize.

Crystalline structure. Investigations on crystalline structures of the polymers were made by wide-angle X-ray diffractometry. The X-ray diffractograms taken at room temperature are reproduced in Figure 2. It shows that the diffraction patterns consist of a series of fairly sharp peaks resulting from ordered molecular packing and superimposed diffuse haloes arising from amorphous fractions.

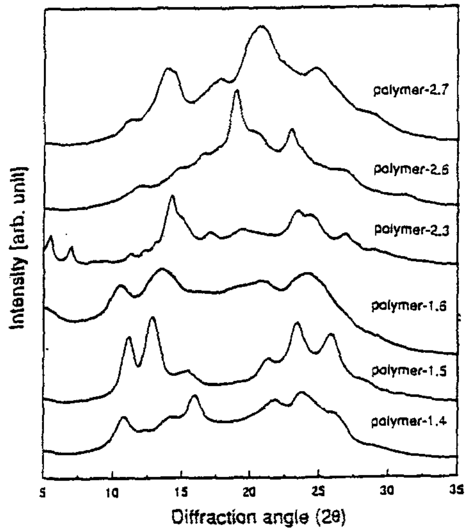


Figure 2. Wide-angle X-ray diffractograms of polymers-X,Y at room temperature.

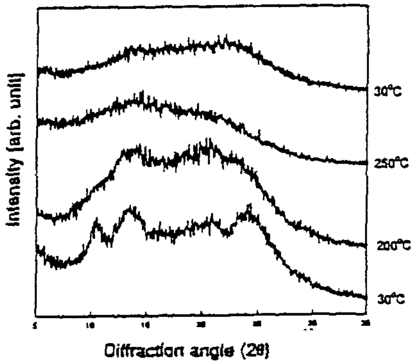


Figure 3. X-ray diffractograms of polymer-1,6 at various temperatures.

According to our interpretation of these diffractograms, polymers-1,4, -1,5, -2,6 and -2,7 must be semicrystalline, since their diffractograms show patterns typical for semicrystalline polymers.

The diffraction pattern of polymer-2,3 is quite different from that of the other samples. This pattern leads to assuming that the polymer has either a linear chain structure or a macrocyclic structure, in both cases with very low molecular weight. Taking into consideration the strongly bent link of 2,3-ND which must exert a very strong steric hindrance toward 1,4-NA, a macrocyclic structure consisting of four to six monomer units seems more favorable than a short chain structure. To get a more detailed understanding of the structure of this macrocyclic ring, the synthesis and purification of a well-defined macrocycle from 1,4-NA and 2,3-ND is in progress now.

Polymer-1,6 shows fairly broad peaks, indicating a very weak order in its molecular packing. Even this weak order disappears, as shown in Figure 3, when the sample experiences a heat treatment above its T_g, and hence the stable structure of this sample must be of amorphous nature.

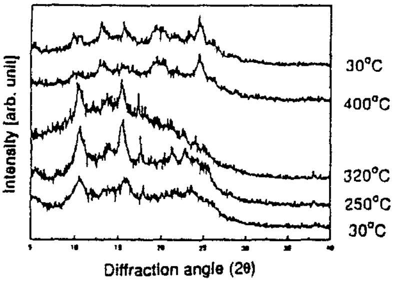


Figure 4. X-ray diffractograms of polymer-1,4 at various temperatures.

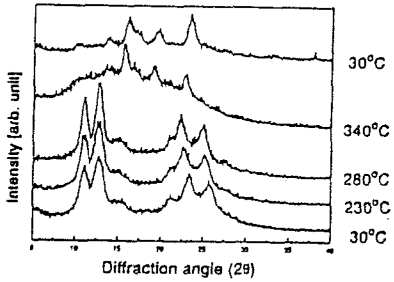


Figure 5. X-ray diffractograms of polymer-1,5 at various temperatures.

Structural transition. To get an understanding of the nature of the DSC peaks indicated with arrows in Figure 1, the wide-angle X-ray diffractogrms were taken at lower and higher temperatures than the T_t's, whereby special attention was paid such that the samples are not damaged by thermal decomposition.

The X-ray diffractogram of the polymer-1,4 taken at various temperatures is reproduced in Figure 4. It shows that up to 350 °C the sample keeps its crystalline structure which is believed to be orthorhombic, according to our tentative interpretation. When it is quickly heated to 380 °C, the crystalline structure changes into the other one and this new structure does not return to the original one, even though the sample is annealed for prolonged time at temperatures above its T_g. This irreversibility means that the initial acetone-extracted polymer-1,4 does not have a stable molecular packing, which is just then formed, when heated to 380 °C.

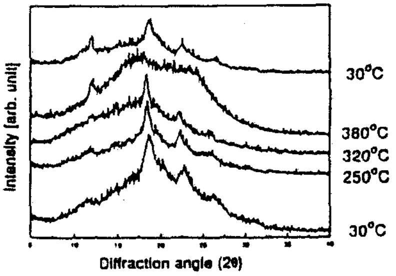


Figure 6. X-ray diffractogrms of polymer-2,6 at various temperatures.

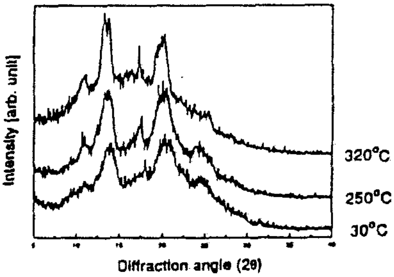


Figure 7. X-ray diffractograms of polymer-2,7 at various temperature

In Figure 5, 6 and 7 are reproduced the X-ray diffractograms of polymer-1,5, -2,6 and -2,7, respectively, measured at various temperatures. Figure 5 shows that also here an irreversible crystal-to-crystal change takes place at 320 °C. Even on prolonged annealing the initial structure was never recovered, either. However, sample-2,6 exhibits, as shown in Figure 6, a reversible structural transformation at 240 °C, which is believed to be a crystal-to-liquid crystal transition. When the molten sample is recrystallized at 240 °C and cooled below this temperature, the original structure is reformed. This reversibility might be ascribable to the lowest rotational barrier resulting from the polymer's linear chain structure consisting of linear and symmetrical linking mode of 2,6-ND toward linear 1,4-NA. Interpretation of the X-ray diffraction patterns of Figure 7 leads to a belief that polymer-2,7 has an orthorhombic packing structure. The existence of a crystalline structure in this sample is rather surprising, because the monomer unit 2,7-ND has a nonlinear bent link. When this sample is heated to 360 °C very rapidly and then cooled down, it losts its crystalline packing and becomes amorphous. But in this sample, the melting temperature lies so close to its degradation temperature, a reliable structural transition could not safely be deduced.

In summary, the DSC peaks indicated by arrows in Figure 1 are related with structural transitions, reversible or irreversible or crystal-to-crystal or crystal-to-amorphous.Very detailed studies on the initial crystalline structures of the acetone-extracted polymers are under way now and these results will be reported in a forthcoming publication.

Acknowledgment

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