

Structure and Properties of Liquid Crystalline Naphthalenediol Copolyesters

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SYNOPSIS

Thermotropic liquid crystalline copolyesters with 1.4-, 1.5-, and 2.7-naphthalenediol (NDO) units were prepared by molten-state copolycondensation. It was found that the chain structure of the copolyesters is almost the same as the structure of recurring moieties of five units. The copolyesters have a glass transition temperature above 381 K, decomposition temperature above 703 K, and melting temperature between 513 and 559 K and their melts exhibit nematic texture and stir opalescence. The copolyester melts show a usual rheological behavior depending on the NDO unit content, but much lower extrudate swell. Light-scattering patterns of the copolyester films with low crystallinity are clearly asymmetric and therefore indicate the existence of preferred orientation of the copolyester chains. Scanning electron microscopy observation suggests that the as-spun fibers of 2.7-NDO-containing copolyesters were highly oriented and fibrillated. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

One of the most interesting recent developments in polymeric materials is the observation of liquid crystallinity in aromatic polyamides and polyesters. For the aromatic polyamides, liquid crystallinity is observed in solutions of the polymers in specific solvents and can be referred to as a lyotropic behavior. On the contrary, the aromatic polyesters exhibit thermotropic behavior because liquid crystallinity occurs in the melts within a specific temperature range.¹ Liquid crystalline polyesters have been processed into highly oriented fibers and plastics with high strength and modulus because of a high degree of chain orientation in the liquid crystalline melts. Many research activities on the synthesis and characterization of liquid crystalline polyesters have been carried out.¹ However, only a little information has been reported in the literature on thermotropic liquid crystalline copolyesters containing 1.4-, 1.5-, and 2.7-naphthalenediol (NDO) units.^{2,3}

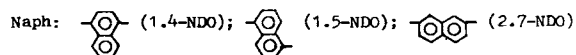
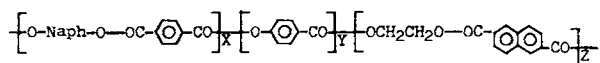
Toward this end, the liquid crystalline copolyes-

ters of 1.4-NDO, 1.5-NDO, or 2.7-NDO with terephthalic acid (TPA), *p*-hydroxybenzoic acid (PHB), and poly(ethylene 2.6-naphthalene dicarboxylate) (PEN), all of which are known to form nematic liquid crystalline melts,² are synthesized and their chain structure, thermal property, rheological behavior, crystallinity, light-scattering pattern, fiber structure, and mechanical properties are investigated.

EXPERIMENTAL

Preparation of Copolyesters

The copolyesters were prepared by acidolysis reactions from 1.4-, 1.5-, or 2.7-diacetoxynaphthalene (1.4-NDO, 1.5-NDO, or 2.7-NDO), with terephthalic acid (TPA), *p*-acetoxybenzoic acid (PHB), and poly(ethylene 2.6-naphthalene dicarboxylate) (PEN). The chemical structure of the copolyesters obtained here are shown below:



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The monomer ratios of the copolyesters are listed in Table I.

Characterization of Copolyesters

Infrared (IR) spectra were taken with Perkin-Elmer-983G IR spectrometer. Potassium bromide pellets containing 3 wt % copolyester powder were prepared for IR measurements.

Pyrolyses for direct-pyrolysis mass spectrometry were carried out in quartz probes with the direct insertion inlet of an electron impact mass spectrometer Finnegan 4021 with a data station and microprocessor.

For pyrolysis-gas chromatography, a vertical microfurnace-type pyrolyzer (CDS-190) was directly attached to a gas chromatography (Shimadzu-7AG) with a fused silica capillary column (0.32 mm o.d., 0.2 mm i.d., 30 m long) coated with 10% SE-30/Chromosorb W (AW DMCS) and FID 250°C. N₂, 35 mL/min, was used as the carrier gas. The column temperature was first held at 60°C for 2 min, then increased to 220°C at a rate of 6°C/min, and lastly held at 220°C for 10 min. Next, a pyroprobe coil was heated at a rate of 75°C/ms to 560°C or 635°C for 10 s. A sample size of about 0.5 mg was pyrolyzed under the flow of a carrier gas.

Glass transition temperature, T_g , was examined using a Perkin-Elmer differential scanning calorimeter DSC-2 at heating rate of 20°C/min, and the sample weight was about 8 mg. The temperature was calibrated with indium and tin. All T_g 's were obtained on unannealed samples of as-prepared polymers. Thermostability was investigated with a Perkin-Elmer TGS-2 at a heating rate of 10°C/min in air.

Thermotropic liquid crystalline behavior was observed at elevated temperature after shear deformation with a polarizing microscope equipped with an electrically heated stage. The copolyesters were set up between two parallel glass slides separated by about 50 μ m.

Melt viscosities were determined with an Instron Model 3211 capillary rheometer. Apparent shear rate

at the wall $\dot{\gamma}_{app}$ (s⁻¹) were calculated from conventional expressions. Corrections to the shear rate for a nonparabolic velocity profile were applied to a Robinowitsch.

For wide-angle X-ray diffraction analysis, the original copolyester powders were pressed into thin plates that were affixed to the sample holder in an X-ray machine (Rigaku 3015) using Ni-filtered CuK α radiation (40 kV, 15 mA).

Light-scattering characteristics of the copolyester films were examined by a He-Ne ($\lambda = 6328 \text{ \AA}$) laser fitted with a red filter on an optical bench with a pair of crossed polarizers. A 1 mm pinhole was placed behind the films. The distance between the copolyester film and a negative film was about 11 cm.

Fibers were extruded and melt-spun from an Instron 3211 capillary rheometer with a die of a diameter of 0.0501 in. and an L/D ratio of 40. The as-spun fibers were taken up on a rotating roll driven by a motor. SEM photomicrographs of as-spun fibers were made using a Cam-Scan high-resolution scanning electron microscope Model 4. The fiber samples observed were prepared by breaking at room temperature. Tensile stress-strain curves on the as-spun fibers were obtained using a tensile tester Model YG-001. The crosshead speed was 8 mm/min. The fibers tested were equilibrated at 65% RH at 25°C.

RESULTS AND DISCUSSION

Infrared Spectra of the Copolyesters

Figure 1 shows representative IR spectra of three series of liquid crystalline copolyesters with 1.4-, 1.5-, and 2.7-NDO units. Compared with the IR spectrum of the original monomer mixture,³ three types of IR spectra also display the characteristic C=O stretching vibration in the ester linkage at 1750 cm⁻¹ and the C—O—C unsymmetrical stretching vibration connected with the parabenzene ring in 1280 cm⁻¹ region,^{3,4} but they hardly display the very characteristic C=O stretching vibration

Table I Monomer Ratios of the Copolyesters (mol %)

Sample	1.4-NDO					1.5-NDO							2.7-NDO						
	No.	1	2	3	4	5	1	2	3	4	5	6	7	1	2	3	4	5	6
NDO or TPA, X	10	22	26	43	62	10	22	26	33	43	52	62	11	18	25	29	38	46	62
PHB, Y	82	70	67	49	30	82	70	67	60	49	40	30	83	76	69	64	55	47	29
PEN, Z	8	8	7	8	8	8	8	7	7	8	8	8	6	6	6	7	7	7	9

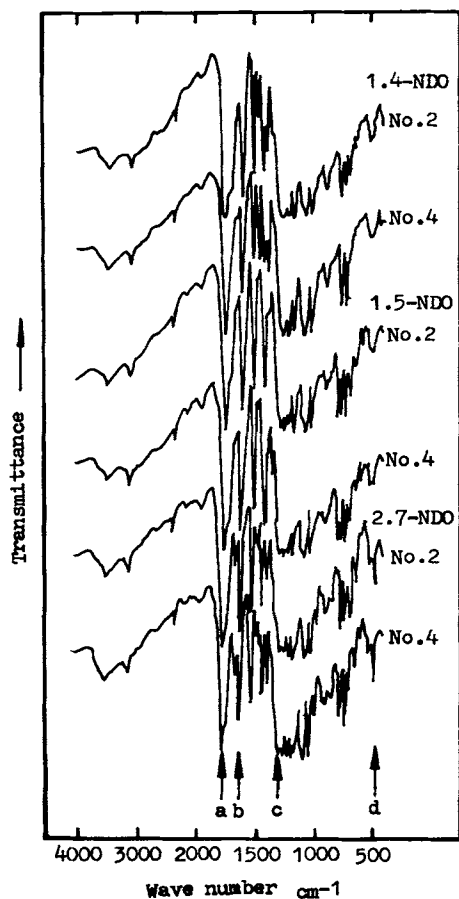


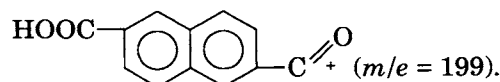
Figure 1 IR spectra of the liquid crystalline copolyesters with different naphthalenediol (NDO) units. Wavenumbers: (a) 1750; (b) 1605; (c) 1280; (d) 478 cm^{-1} , as indicated by the arrows.

in aromatic carboxylic acid at 1690 cm^{-1} , the characteristic O—H stretching vibration in carboxylic acid in 2550–3000 cm^{-1} range, or the strong C—O stretching vibration in the acetoxy group at 1040 and 1230 cm^{-1} at the same time. There is very few carboxyl and acetoxy groups in the copolyester chains because the monomer copolycondensation makes acetic acid (byproducts of copolycondensation) evaporate. The absorbency vibration at 1605, 1340, and 478 cm^{-1} indicate the naphthalene unit.

Direct Pyrolysis Mass Spectra and Gas Chromatography of the Copolyesters

The electron impact mass spectra of the copolyesters with 1.4-, 1.5-, and 2.7-NDO units exhibit intense peaks that correspond to the molecular ions $\text{HO}-\text{Naph}-\text{C}^+=\text{O}$ ($m/e = 121$), HOOC

$-\text{C}^+=\text{O}$ ($m/e = 149$), and $\text{HOCH}_2\text{CH}_2\text{OOC}$ $-\text{COO}-$ ($m/e = 269$) and also show the peaks of $\text{HO}-\text{Naph}-\text{OOC}-\text{COOH}$ ($m/e = 308$) and of



The results obtained indicate that the copolyesters consist of original monomer units.

Pyrolysis-gas chromatography diagrams of the NDO-containing copolyesters at the pyrolytic temperatures of 560 and 635°C are shown in Figure 2. The characteristic peaks become sharper with increasing pyrolytic temperature from 560 to 635°C. Table II illustrates the peak assignments of the pyrograms.⁵ It is apparent that the thermal fragments reflect the chain structure of the copolyesters. Ac-

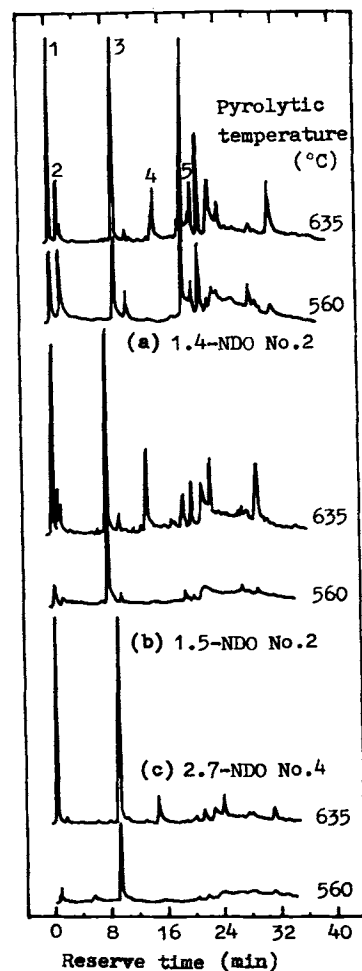



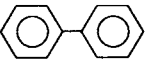


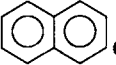



Figure 2 Pyrolysis-gas chromatography diagrams of the liquid crystalline copolyesters with different NDO units at different pyrolytic temperatures.

Table II Thermal Fragments from Pyrolysis of the Copolyesters and Their Reciprocal Chain Structure

	Peak No.				
	1	2	3	4	5
Reserve time (min)	1	2	10(9) ^a	15(14) ^a	21
Thermal fragment	CO CO ₂		HO- 		
Chain structure	-COO-	-OC-  -CO-	-O-  -CO-	-OC-  -CO-	-OC-  -CO-

^a Data in brackets are from the copolyesters with the 1.5-NDO unit.

According to the height of characteristic fragmental peaks, relative contents of several kinds of monomer units in the copolyester chains are qualitatively known. These results suggest that the pyrolysis-gas chromatography method is useful in analyzing the chain structure of insoluble aromatic copolyesters.

Thermal Properties of the Copolyesters

The differential scanning thermograms of the copolyesters with 1.4-, 1.5-, and 2.7-NDO units indicate that the T_g is in the range of 108–137°C (Table III), which is higher than that of PHB/PET copolyesters.⁶ There is no cold crystallization exotherm or melting endotherm in the thermograms, which is understandable because these copolyesters would be expected to be completely amorphous. The examination with polarizing microscopy, however, indicates that most of the copolyesters melt in the temperature range of 240–286°C (Table III), which suggests that the copolycondensations of the rigid PHB with 1.4-, 1.5-, or 2.7-NDO/TPA and the flexible PEN markedly depress the melting temperature, T_m , as expected. It is apparent that the T_m of the

copolyesters containing 1.4-, 1.5-, and 2.7-NDO units is suitable for conventional melt-spinning processes.

Typical rising temperature weight loss curves are plotted in Figure 3, and each curve shows the weight loss for sample in air, together with the first derivative plot. The results summarized in Table III show that the thermostability depends slightly on the copolyester composition.² All the copolyesters have a decomposition temperature T_{d10} in the range of 430–510°C. The decomposition temperature T_{dmax} at the maximum rate of weight loss is between 490 and 535°C. It can be found that the copolyesters with NDO units are as stable as poly(4-hydroxybenzoate)s,⁷ PHB/PET copolyesters,⁶ and PHB/PET/vanillic acid terpolyester.⁸

Rheological Behavior of the Copolyester Melts

In Figure 4, shear viscosities at fixed temperatures are plotted as a function of shear rate $\dot{\gamma}$ for 1.4- and 2.7-NDO-containing copolyesters. It can be seen that for such copolyesters the temperature dependence is the same as that observed for ordinary (isotropic) polymer melts, i.e., viscosity decreases with

Table III Thermal Properties of the Copolyesters with NDO Units (°C)

Sample	1.4-NDO					1.5-NDO					2.7-NDO				
	No.	1	2	3	4	5	2	3	4	5	6	2	3	4	6
T_g^a		115	118	108	137		122	117	122	127		117	129	137	132
T_m^b		360	255	250	261	325	240	245	247		269	286	256	256	266
T_{d10}^c		495	500	480	505	505	500	500	485	490	510	510	430	500	500
T_{dmax}^d		525	535	510	525	525	520	520	520	520	530	520	490	500	510

^a From DSC scanning.

^b From thermal polarizing microscope.

^c The temperature at the weight loss of 10%.

^d The temperature at the maximum rate of weight loss.

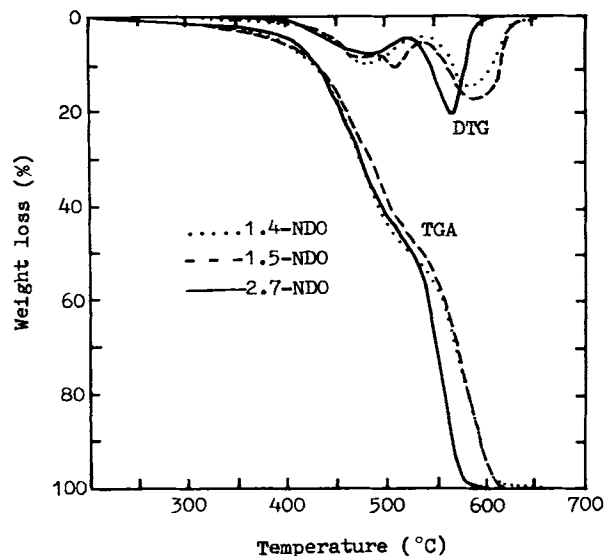


Figure 3 Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of the NDO-containing copolyesters under air at the heating rate of 10°C/min.

temperature. We should note that there is less of a dependence of viscosity on temperature for the copolyesters containing fewer 1.4- and 2.7-NDO units. The effect of shear rate on the melt viscosities of 1.5-NDO-containing copolyester melts at 265°C is shown in Figure 5. As 1.5-NDO content increases from 22 to 43 mol %, the melts become shear-sensitive at a lower shear rate. Similar behavior is observed for PHB/PET copolyester melts with increasing PHB content from 60 to 80 mol %.^{9,10} This shear-sensitivity may be attributed to the increase of the liquid crystallinity of the melts. Figure 6 gives plots of the melt viscosities vs. 1.5- and 2.7-NDO contents for the copolyesters with shear rate as a parameter. It is seen that, at low shear rates, the viscosities increased as the 1.5-NDO content was increased to 36 mol % and then decreased as the 1.5-NDO content was increased further to 43 mol %, whereas at high shear rates, the melt viscosities increased with increasing 1.5-NDO content to about 43 mol %, probably due to partial replacement of the PHB unit by the huge 1.5-NDO unit. The melt viscosities of the 2.7-NDO-containing copolyesters, however, decreased down to the lowest value with increasing 2.7-NDO content from 18 to 29 mol %. Similar results have also been observed in liquid crystalline PHB/PET copolyester melts.¹⁰

Extrudate dimensions were determined for the copolyester strands that had been collected during the capillary flow studies. The ratios of extrudate

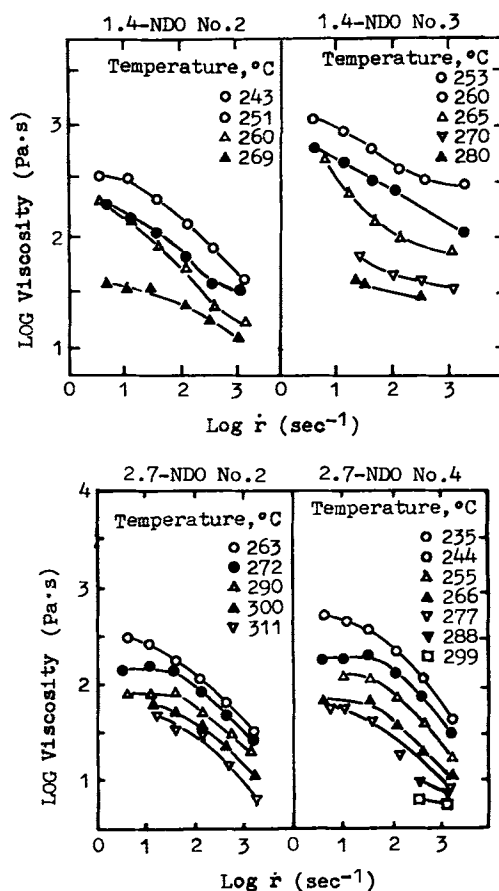


Figure 4 Melt-viscosity dependence on the shear rate for the copolyesters with the (a) 1.4-NDO unit and (b) 2.7-NDO unit.

diameter to capillary diameter (De/D) as functions of shear rates and capillary length to diameter ratio (L/D) for the NDO-containing copolyesters at several temperatures are shown in Figures 7 and 8. At

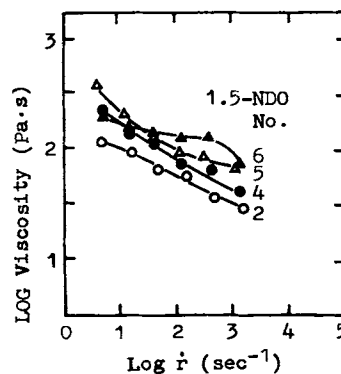


Figure 5 Melt-viscosity dependence on the shear rate for the copolyesters with different 1.5-NDO unit contents at 265°C.

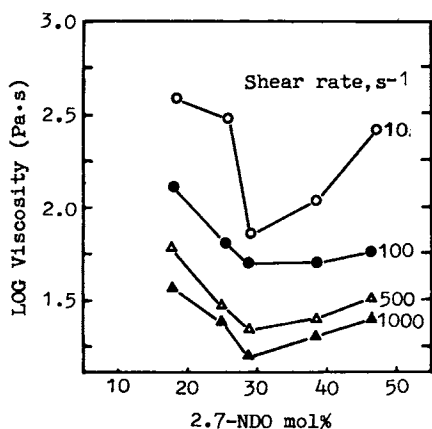
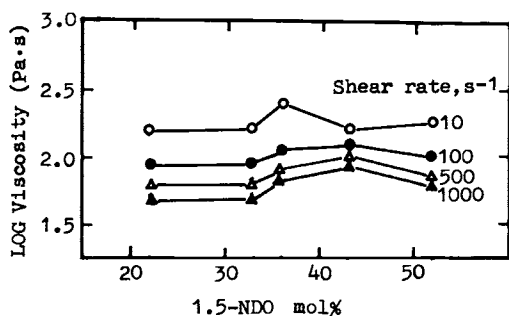


Figure 6 Melt viscosity vs. (a) 1.5-NDO and (b) 2.7-NDO unit content of the copolyesters at different shear rates (265°C).

low shear rate, De/D values were even less than 1.0. With increasing shear rates, the De/D values increased and became greater than 1.0, but at the shear

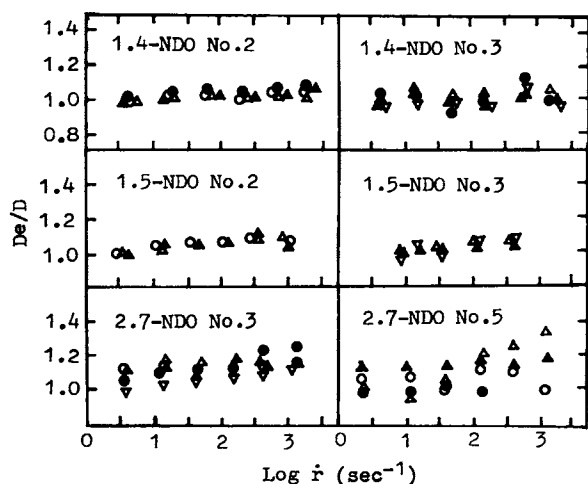


Figure 7 Ratio of extrudate diameter to capillary diameter (De/D) vs. shear rate for the copolyesters with different NDO unit contents at different temperatures: (O) 240°C; (●) 250°C; (Δ) 260°C; (▲) 270°C; (∇) 280°C.

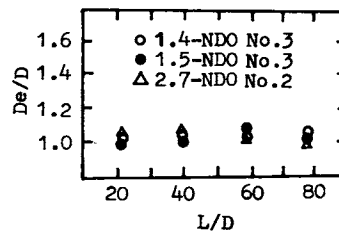


Figure 8 Ratio of extrudate diameter to capillary diameter (De/D) vs. L/D for the shear rate of 100 s⁻¹ and the temperature of 265°C for the NDO-containing copolyesters.

rate of 100 s⁻¹, De/D remained a constant value of about 1.05 within the L/D range of 20–80. The NDO-containing copolyesters display such a low extrudate swell because the elastic recoil of the copolyester chain did not have time to occur before the extrudates solidified.¹¹ Another possible explanation may rest in the structure of the liquid crystalline melts. It is believed that these melts consist

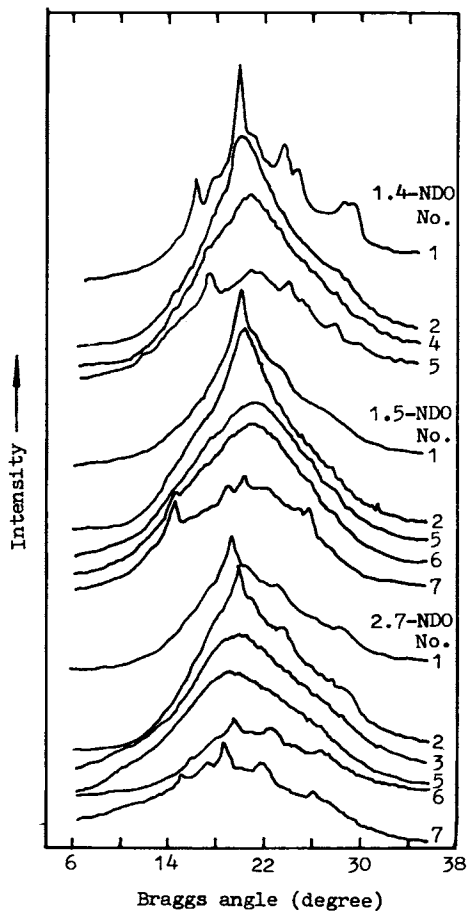


Figure 9 X-ray diffractograms of the copolyesters with different NDO unit contents.

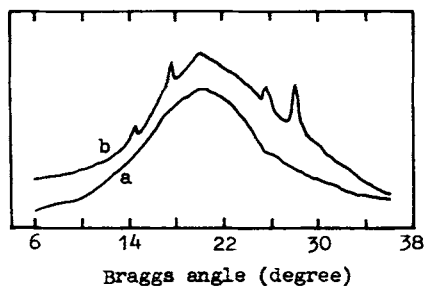


Figure 10 X-ray diffractograms of the copolyesters from NDO-TPA/PHB/PEN (33/60/7) (No. 4) (curve a) and NDO-TPA/PHB (35/65) without the PEN unit (curve b).

of domains whose sizes and shapes may not change much during flow.⁹

Crystallinity of the Copolyesters

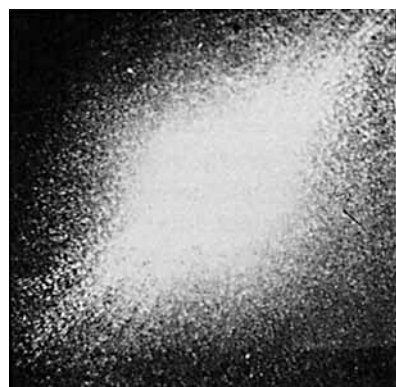
Figure 9 illustrates the wide-angle X-ray diffractograms of the copolyesters with 1.4-, 1.5-, and 2.7-NDO units. As can be seen from Figure 9, all copolyesters containing 70 mol % or more PHB units have a stronger diffraction peak at $2\theta = 18\text{--}20^\circ$, which results from the order of PHB segments.³ All copolyesters containing 52 mol % or more NDO/TPA units have diffraction peaks at $2\theta = 17.5^\circ, 24^\circ, \text{ and } 28^\circ$; $2\theta = 14.5^\circ, 19^\circ, \text{ and } 26^\circ$; and $2\theta = 15^\circ, 17^\circ, 22^\circ, \text{ and } 26^\circ$, which result from the order of the 1.4-NDO/TPA segment, 1.5-NDO/TPA segment, and 2.7-NDO/TPA segment, respectively. The copolyesters containing 30–70 mol % of the PHB unit and 22–52 mol % of NDO/TPA units have no diffraction

peak, which suggests that these copolyesters are amorphous. This amorphous structure results from random distribution of five monomer units on the copolyester chain. The 1.5-NDO/TPA/PHB copolyester without the PEN unit exhibits four characteristic peaks at $2\theta = 14.5^\circ, 18^\circ, 26^\circ, \text{ and } 28^\circ$ in wide-angle X-ray diffraction (Fig. 10). Clearly, introducing the PEN unit will result in the disappearance of the peak at $2\theta = 28^\circ$.

Structure of Melts, Films, and Fibers of the Copolyesters

All the molten copolyesters appear a bright color under crossed polars and are easily oriented along the flow direction when pressure is applied to the copolyester melts. On the other hand, the copolyesters are examined visually for the occurrence of stir opalescence in the melts. Obviously, the copolyesters with 1.4-, 1.5-, and 2.7-NDO units exhibit typical thermotropic liquid crystalline behavior.

It is sunlight scattering of liquid crystalline melts that makes the melts exhibit a turbid and stir opalescence characteristic. The H_v scattering patterns of the copolyester films are shown in Figure 11. These patterns are clearly asymmetric and therefore indicate the existence of the preferential orientation of the copolyester chains within the films. The scattering patterns of elliptical shapes are observed for all films. The direction of the long axis of the elliptical shapes is perpendicular to the oriented direction. The length of short axis of the ellipsoid decreases with increasing chain orientation, which suggests that the films have a superstructure con-



(a) Low oriented
(1.5-NDO No.3)



(b) Moderately oriented
(1.5-NDO No.3)



(c) Highly oriented
(2.7-NDO No.1)

Figure 11 Light-scattering H_v patterns of oriented copolyester films with different orientations.

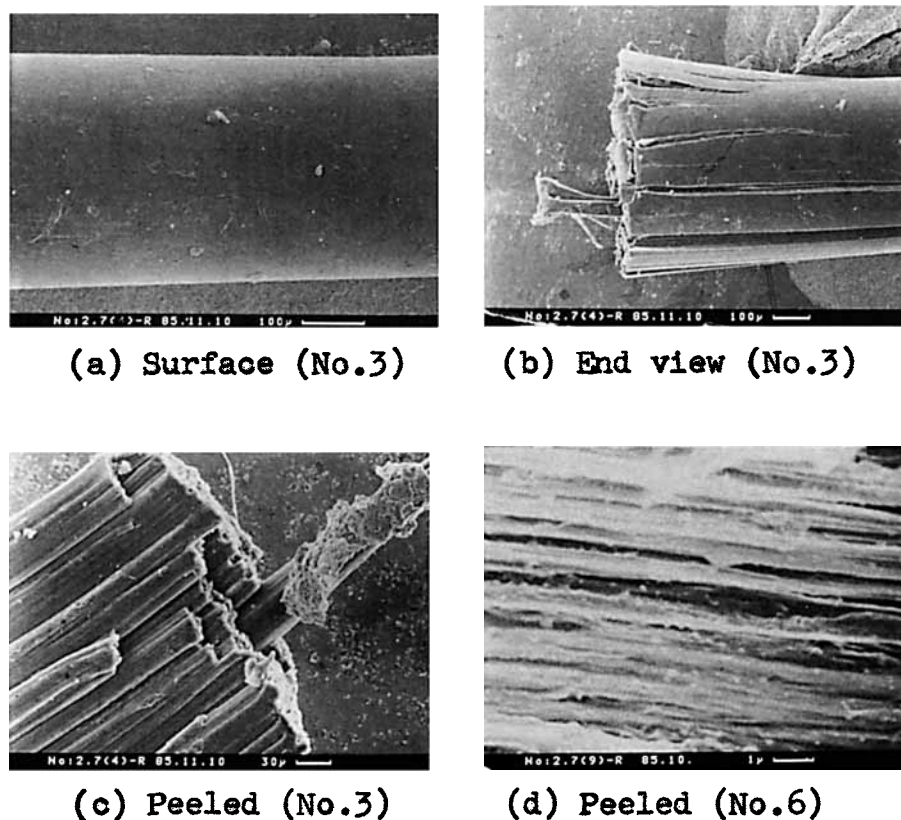


Figure 12 Scanning electron micrographs for the as-spun fibers of 2.7-NDO-containing copolyesters.

sisting of oriented rigid-rod assemblies. This superstructure results from the flow-orientation property of liquid crystalline melts, from which can be inferred that the copolyesters with NDO units are easily processed into high tensile and modulus materials with high orientation.²

The scanning electron micrographs were taken to study some morphological features of the as-spun fibers of 2.7-NDO-containing copolyesters. The fibers were forceably split (peeled) after nicking or bending in order to observe their internal structure. Representative SEM photomicrographs of surfaces, cross sections, and a peeled view of the fibers are shown in Figure 12. The surface is very smooth and less defective. The extensive fibrillar structure of the peeled fibers are more pronounced and are oriented in an elongational direction.¹³ The fibers exhibit fibrils or fibrous bundles on the order of 1–30 μm . These structure characteristics are quite similar to those obtained for cellulose triacetate film from a liquid crystalline solution¹³ and for PHB/PET as-spun fibers from a liquid crystalline melt at high draw-down ratios.¹⁴

Mechanical Property of the Copolyester Fibers

2.7-NDO-containing copolyester fibers are found to have moderately high tensile strengths, and moduli are in the range of 5.4–10 and 100–188 g/d. The elongations to break are 12–14%.

CONCLUSIONS

Liquid crystalline NDO-containing copolyesters with low crystallinity and high thermostability possess moderate melting temperatures between 240 and 269°C and are suitable for conventional melt-processing processes. The viscosities of the copolyester melts are significantly affected by shear rate, temperature, and NDO unit content. The extrudate die swell of the melts is very low and nearly independent of capillary length-to-diameter ratio. A well-developed, highly oriented fibrillar structure is observed for 2.7-NDO-containing copolyester fibers that have a moderate tensile modulus and strength.

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