

## A New Class of Poly(ester hydrazide) Copolymers with Liquid Crystalline Properties. Synthesis and Characterization

Donatella CAPITANI,\* Nicola DE PRISCO, Paola LAURIENZO,<sup>†,††</sup> Mario MALINCONICO, Noemi PROIETTI,\* and Antonio ROVIELLO\*\*

*Istituto di Chimica e Tecnologia dei Polimeri, C. N. R., Via Campi Flegrei, 34–80078 Pozzuoli (Naples), Italy*

*\*Istituto di Chimica Nucleare, C. N. R., Via Salaria km 29.300–00016 Monterotondo Stazione (Rome), Italy*

*\*\*Dipartimento di Chimica, Università degli Studi “Federico II”, Via Cinthia, 6–80126 Naples, Italy*

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**ABSTRACT:** A series of copolyesters (PE) of low molecular weight containing propoxy-substituted aromatic ring and/or ethylenic sequences between aromatic units were prepared by melt polycondensation between corresponding diacids and diacetates, and used as precursor of poly(ester-*co*-polyhydrazide) (PEH) new copolymers. The PEs showed to have thermotropic properties, with transition temperatures which depend on the chemical composition and with a good interval of stability of the mesophase. The corresponding PEHs were obtained by high-temperature polycondensation of carboxyl-terminated PEs with terephthalic dihydrazide. The PEHs showed as well a stable mesophase in the melt, and improved thermal stability respect to polyesters. All the polymers were characterized by elemental analysis, inherent viscosity, infrared and <sup>13</sup>C solid state NMR spectroscopy, thermal and thermogravimetric analysis and optical microscopy. Fibers of PEHs were obtained by melt-spinning and characterized by WAXS analysis.

**KEY WORDS** Liquid Crystallinity / Copolymers / Polyester / Polyhydrazide / Fiber /

In the last decades, many efforts have been pointed on the synthesis of rigid-chains polymers with high heat resistance and good mechanical properties for extreme environment applications.<sup>1–6</sup> Heat resistant polymers are defined as organic materials which maintain their mechanical characteristics at  $T > 300^\circ\text{C}$  for several days or hours. Such temperatures can be reached during manufacturing or utilization of products.<sup>7</sup> Polyhydrazides and their polyoxadiazole derivatives, polyimides, polybenzoxazoles, and polybenzothiazoles are classified as heat-resistant polymers. At early, scarce attention was paid to their processability, and so to real possibilities of application. More recently, then, research on heat-resistant polymers is directed to improve processing window. In fact, the characteristics which render these polymers attractive for utilization in severe conditions are the same which make them hard to process: high melting temperatures (sometimes above decomposition temperature), high melt viscosity and low solubility.

Aromatic polyhydrazides<sup>8,9</sup> have recently attracted our attention. They are obtained from the reaction between aromatic diacids and dihydrazides, and are viewed as precursor of much more stable aromatic polyoxadiazoles, in the same way as polyamic acids are precursor of polyimides. We found that the insertion of mesogenic units containing short methylenic sequences lowers  $T_m$  giving rise to a window of processability

compatible with that of more common polyesters and polyamides, while keeping a still high  $T_g$ .<sup>10</sup> Unfortunately, the resulting polymers did not show any stable mesophase in the melt, which would further improve their processability, as occurs in the case of liquid crystalline thermotropic polyesters.

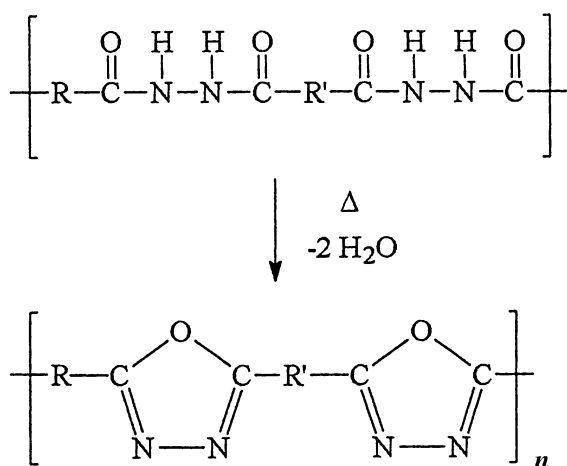
Liquid crystalline polymers are characterized by low melt viscosity and their fibers show excellent mechanical properties with stiffness close to theoretical values. A very well known class of thermotropic polyesters are commercially available under the name of Vectra. Vectra is commercialized in two classes: Vectra A and Vectra B. Vectra B are thermotropic polyesteramides.<sup>11,12</sup> The introduction of amidic groups which form hydrogen bondings between the chains leads to an increase in isotropization temperature ( $T_i$ ), to a better stability of nematic phase and, sometimes, to the formation of a smectic phase. The disadvantages are an increase of crystallization temperature ( $T_c$ ) and of  $T_m$ , which sometimes are so high to infer the processability of the polymer.<sup>13–17</sup> The  $T_m$ 's can be lowered by introducing “Defects”, as flexible spacers between aromatic units or bulky side groups on the main chain. Unfortunately, the decrease in  $T_m$  leads to a decrease in mechanical properties and thermal stability.<sup>18–26</sup>

In the present paper, synthesis and structural and thermal characterization of new copolyesterhydrazides

<sup>†</sup>To whom correspondence should be addressed.

<sup>††</sup>Present address: Istituto di Chimica e Tecnologia dei Polimeri, c/o comprensorio Olivetti, Fabbricato 70, Via Campi Flegrei, 34, 80078 Pozzuoli (Naples), Italy.

are reported. The introduction of hydrazidic groups between polyester blocks is aimed to impart to the copolymers good thermal stability, particularly after cyclization to the more stable polyoxadiazole:



while the polyester moiety guarantees processability and thermotropicity of the polymers. The copolymers have been characterized by viscosimetry, elemental analysis, infrared spectroscopy, solid state NMR, thermal and thermogravimetric analyses, optical microscopy and wide angle X-Ray analysis.

## EXPERIMENTAL

### Materials

Terephthalic acid (A) (Fluka), hydroquinone, methylhydroquinone (Aldrich) and acetic anhydride (Baker) are reagent grade and used without further purification.  $\alpha$ ,  $\omega$ -bis-4-(carboxyphenoxy)octane (C), 2-propyloxyterephthalic acid (B) and terephthalic dihydrazide have been prepared according to previously reported procedures.<sup>27–30</sup>

Methylhydroquinone (E) and hydroquinone diacetates (D) have been prepared according to well known standard procedures.

All the solvents were of analytic grade and purified according to standard procedures.

### Viscosity Measurements

Viscosity measurements of PEHs were performed in a thermostated bath at 25°C with a Cannon-Ubbelohde viscometer, at  $c = 0.5 \text{ g dL}^{-1}$  in *N*-methyl-pyrrolidone/lithium chloride (10 wt%).

### Determination of End-Groups

Determination of acid end-groups was accomplished by titration of a solution of 100 mg of PEs in 50 mL of phenol/tetrachloroethane 60/40 w/w mixture with a solution of KOH in ethanol, using a Metrohm Titroprocessor 636 equipped with an Ag/AgCl electrode.

### Infrared Spectroscopic Analysis

Fourier transform infrared (FT-IR) spectra were performed by a Perkin-Elmer spectrometer model Paragon 500, with a resolution of  $4 \text{ cm}^{-1}$  (10 scans collected). Samples were prepared by compressing the powders into KBr disks.

### Solution NMR Analysis

Samples of terephthalic polyhydrazide (PHZ), polyester PE4 and copolymer PEH4 have been dissolved in Dimethyl- $d_6$ -Sulfoxide containing LiCl (5% by weight) dissolved in.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were performed at 600.13 MHz and 150.9 MHz with a Bruker AMX600 spectrometer.  $^{13}\text{C}$  NMR spectra were obtained using the following acquisition parameter: the  $90^\circ$  degree pulse was  $8 \mu\text{s}$ , time domain 128 K, spectral width 220 ppm, relaxation delay 4 s.  $^{13}\text{C}$  spectra were broad band power gated decoupled from protons with a WALTZ 16 sequence.

### Solid State NMR

Solid state  $^{13}\text{C}$  CP MAS NMR spectra at 50.28 MHz were performed on a Bruker AMX-200 spectrometer equipped with an amplifier 1H 200.13 MHz, 120 W CW and with a variable temperature unit. The spin rate was always kept at 8 kHz. The  $90^\circ$  degree pulse width was  $3.5 \mu\text{s}$ , the contact time for the cross-polarization experiment was  $\tau = 1 \text{ ms}$ . The proper contact time was carefully chosen according to a previously published procedure.<sup>31</sup> The recycle time was 4 s. All spectra were obtained with 512 data points in the time domain, zero filled and Fourier transformed using 1024 data points.

### Differential Scanning Calorimetry

Analysis by DSC was performed on a Mettler T. A. -3000 apparatus, equipped with a control and programming unit for the elaboration of data, and with a calorimetric cell (DSC-30), which allows scans from  $-170$  to  $600^\circ\text{C}$ . All the experiments were run in  $\text{N}_2$  atmosphere at an heating rate of  $20^\circ\text{C min}^{-1}$ .

### Thermogravimetric Analysis

Thermal degradation under  $\text{N}_2$  was performed on a Mettler Thermogravimetric Analyzer (TGA) TG50 model, at an heating rate of  $20^\circ\text{C min}^{-1}$ .

### Optical Microscopy

Optical microscopy analysis has been performed on thin films with an optical microscope Zeiss Mc 100 equipped with a Linkman Tms 901 apparatus for the control of temperature and an hot stage Linkman Thms 600.

### WAXS Analysis

Fibres patterns (Cu- $K_{\alpha}$  Ni-filtered radiation) were collected by a flat film camera, using a SEIFERT diffractometer.

### Typical Procedure for the Preparation of a Copolyester (PE4)

The experimental apparatus used for the polycondensation reactions consists of a three-necked flask equipped with a stainless steel stirrer, a nitrogen inlet and a distillation column, which leads to a receiver with provision for applying vacuum. The flask is charged with 2.24 g (0.010 mol) of 2-propyloxy terephthalic acid, 1.66 g (0.010 mol) of terephthalic acid, 1.71 g (0.0082 mol) of methylhydroquinone diacetate and 1.59 g (0.0082 mol) of hydroquinone diacetate. The flask was evacuated and purged with nitrogen three times to remove air, then it was heated under reduced pressure in an oil bath at 110°C for 5 min to dry the reactants. The temperature was then raised to 290°C while stirring in a nitrogen atmosphere, and the acetic acid which slowly distilled out was collected in a cylindrical vial immersed in liquid nitrogen to favour the distillation. After about 1 h the mixture was viscous and the reaction was let to go on under reduced pressure (about 5 mmHg) for further 4 h at the same temperature. The final product was purified from unreacted monomers by extraction with hot dimethylsulfoxide (DMSO). The recovered polymer was repeatedly washed with water then dried at 100°C under vacuum before characterization.

Elemental analysis: C = 68.13, H = 6.33, O = 25.54% (theoretical values: C = 70.94, H = 5.98, O = 23.05%). Infrared Spectroscopy: C = O stretching 1730  $\text{cm}^{-1}$ .

### Typical Procedure for the Synthesis of a Copolyester-hydrazide (PEH4)

5.09 g (0.0020 mol) of PE4 and 0.39 g (0.0020 mol) of terephthalic dihydrazide were placed in the same experimental apparatus described above for the synthesis of PE4. The reagents were dried following the same procedure. The polycondensation reaction was conducted at 290°C under  $\text{N}_2$  stream for 45 min and further 2 h at a reduced pressure of 5 mmHg, while distilling water. Finally, after cooling and finely ground to powder, the polymer was recovered.

Elemental analysis: C = 69.04, H = 5.99, O = 23.70, N = 1.27% (theoretical values: C = 70.59, H = 5.90; O = 22.19; N = 1.3%). Infrared Spectroscopy: N-H stretching 3200  $\text{cm}^{-1}$ ; C = O ester stretching 1730  $\text{cm}^{-1}$ ; C = O hydrazidic stretching 1630  $\text{cm}^{-1}$ ; C-N stretching 1270  $\text{cm}^{-1}$ .

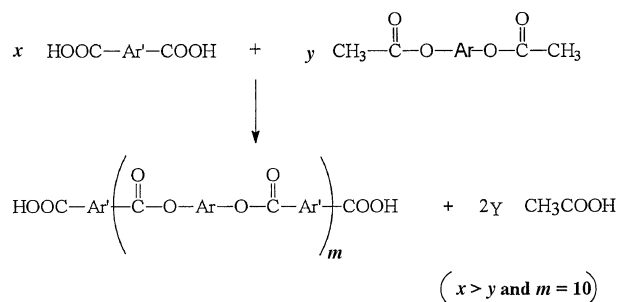
### Synthesis of Poly(terephthalic hydrazide) (PHZ) for NMR Studies

The polymerization of terephthalic hydrazide with terephthaloyl dichloride has been carried out in Di Methyl Acetamide (DMAc)/LiCl solution, according to well known standard procedures.<sup>8</sup>

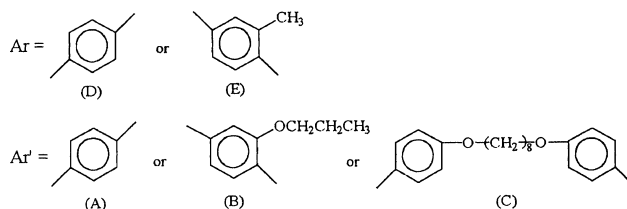
## RESULTS AND DISCUSSION

### Synthesis and Molecular Characterization of Copolyesters and Copolyesterhydrazides

Four different types of precursor polyester (PE) blocks have been prepared by polycondensation in the melt at high temperatures between diacids and diacetates in the chosen composition, according to the following scheme of reaction:



where:



Diacetates are used instead of diols as they are stable at high temperatures.<sup>26</sup> The temperature has been fixed at 290°C as all the monomers are in the molten state (excepted terephthalic acid, which melts with decomposition at  $T = 300^\circ$ ) and the system is well stirrable; the polycondensation is conducted under vacuum to remove all the acetic acid which forms, favouring high conversions.<sup>15, 22, 26, 32-37</sup> The reaction is stopped when the acetic acid evolved and collected corresponds to the theoretical value (after almost 3 h). In this experimental conditions, we can hypothesize a value of conversion,  $p$ , close to 1. From the Carothers equation valid for an equilibrium polycondensation, we know that the degree of polymerization is linked to the molar composition of the reagents through the relation:

$$X_n \cong \frac{1+q}{1+q-2pq}$$

**Table I.** Codes,  $X_n$  and molar compositions of PEs

Code	$X_n$	D	E	A	B	C
PE 1	10	50%	50%	50%	–	50%
PE 2	10	50%	50%	–	50%	50%
PE 3	11	50%	50%	30%	20%	50%
PE 4	10	50%	50%	50%	50%	–

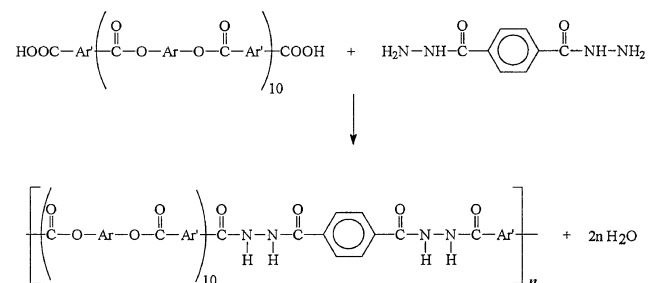
where, in our case,  $q$  is the ratio between moles of diacids ( $x$ ) and moles of diacetates ( $y$ ).

So applying the above equation with  $x > y$  we can obtain copolyesters of controlled molecular weight and with  $-\text{COOH}$  end groups. For  $X_n = 10$ , the ratio between moles of diacetates and moles of diacids must be of 0.82/1. We fixed a value of  $X_n$  of 10, to have copolyester segments long enough to display important characteristics, such as formation of a stable mesophase in the melt and high melting temperature. At same time, when these oligomers are incorporated in the final copolyesterhydrazides, a significant concentration of hydrazidic linkages, according to conversion, will be present in the polymers and be able to influence their properties.

The molecular weight,  $M_n$ , of copolyesters has been determined by titration of acid-end groups with KOH. The experimental degree of polymerization,  $X_n$ , defined as the ratio between  $M_n$  and the molecular weight of the repeating unit,  $M_u$  (in our case,  $M_u$  is calculated considering the percentage in which each comonomer is present) can be evaluated.

Codes, molar composition and  $X_n$  of the prepared copolyesters are reported in Table I. The experimental values of  $X_n$  are in good agreement with the predicted theoretical ones.

The subsequent condensation of the PE precursors with terephthalic dihydrazide to synthesize copolyesterhydrazides (PEH) is conducted in bulk at high temperature:



The results of elemental analysis performed on both PEs and PEHs are reported in Table II. There is good agreement between theoretical and experimental values.

Inherent viscosities of PEHs (Table III) are in the range 0.3–0.5 dL g<sup>-1</sup>. These values, although not so high, can be considered as reasonable for rigid-rod

**Table II.** Elemental analysis of PEs and PEHs samples

Sample	%C	%H	%O	%N
PE1	70.70 (71.41)	5.72 (5.94)	23.58 (22.65)	–
PEH1	70.5 (70.94)	5.71 (5.84)	22.76 (21.65)	1.48 (1.57)
PE2	68.13 (70.97)	6.33 (5.98)	25.54 (23.05)	–
PEH2	69.04 (70.58)	5.99 (5.90)	23.70 (22.19)	1.27 (1.33)
PE3	71.08 (71.40)	5.85 (5.77)	23.07 (22.83)	–
PEH3	70.85 (71.00)	5.80 (5.68)	22.02 (21.93)	1.33 (1.39)
PE4	69.05 (69.85)	4.58 (4.36)	26.37 (25.79)	–
PEH4	67.68 (68.45)	4.56 (4.35)	25.78 (25.15)	1.98 (2.05)

Figures in parentheses refer to theoretical values.

**Table III.** Inherent viscosities ( $\eta_{\text{inh}}$  dL g<sup>-1</sup>) of PEHs samples ( $c = 0.5$  g dL<sup>-1</sup> in NMP/LiCl 10%,  $T = 25^\circ\text{C}$ )

Sample	$\eta_{\text{inh}}$
PEH1	0.32
PEH2	0.32
PEH3	0.27
PEH4	0.49

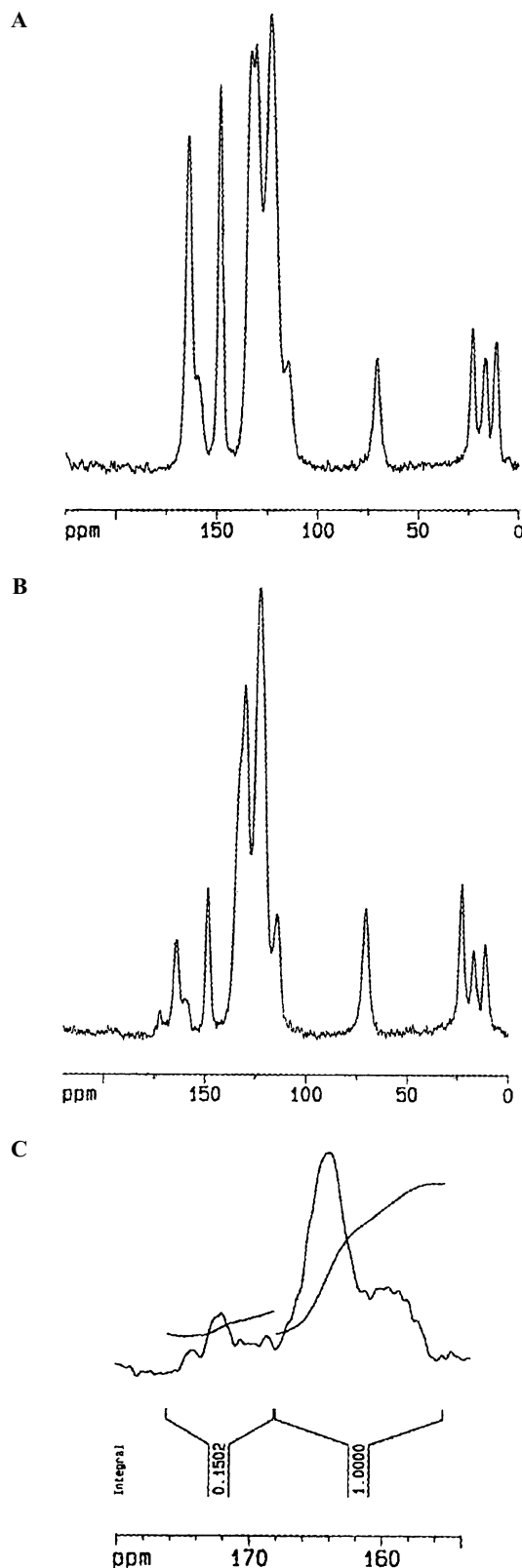
**Table IV.** Chemical shifts (in ppm) of PHZ

Nucleus	<sup>1</sup> H	<sup>13</sup> C
Aromatic CH	8.00	129
Aromatic C (quaternary)		135
C=O		166
NH	11	

polymers, which have an high aspect ratio in solution (aspect ratio = Length / Diameter of the macromolecular chain). The polymers tend to assume a non-random conformation in solution, and this, in turns, lowers their solution viscosities. The significant increase of solution viscosity for PEH4 must be related to the absence of the “Griffin monomer”. PE4 is the only fully aromatic main chain polyester in the investigated series. The rigidity of this chain might help the achievement of higher conversion to the final copolyesterhydrazide, by favouring the reaction of end groups.

#### NMR Analysis

<sup>1</sup>H and <sup>13</sup>C chemical shifts from spectra in solution of DMSO-*d*<sub>6</sub> of PHZ and PE4 are shown in Tables IV and V. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of PEH4 copolymer the resonances of both PHZ and PE4 are observed.



**Figure 1.**  $^{13}\text{C}$  CP MAS NMR spectra of PE4 (A), PEH4 (B), and a particular of the 180–155 ppm range of the PEH4 spectrum (C) with integrals to measure the ratio between two comonomers.

Unfortunately, the scarce solubility of the copolymer unpairs the quantitative interpretation of above results. To bypass this problem we used  $^{13}\text{C}$  CP MAS technique.

**Table V.** Chemical shifts (in ppm) for NMR spectra of PE4 in DMSO- $d_6$

Nucleus	$^1\text{H}$	$^{13}\text{C}$
CH <sub>3</sub>	0.9 and 1.1	11
C-CH <sub>2</sub>	1.7	23
-O-CH <sub>2</sub>	2.15	71
Aromatic	≈ 8	130–140
C = O		166

**Table VI.**  $T_g$ ,  $T_m$ , and  $T_i$  (°C) of PEs taken from I run in dynamic DSC experiments (heating rate: 20° min<sup>-1</sup>)

Sample	$T_g$	$T_m^1$	$T_m^2$	$T_i$
PE1	54	150	225	390
PE2	52	130	150	300
PE3	60	140	200	340
PE4	105	–	–	340

**Table VII.**  $T_g$ ,  $T_m$ , and  $T_i$  (°C) of PEHs taken from I run in dynamic DSC experiments (heating rate: 20° min<sup>-1</sup>)

Sample	$T_g$	$T_m^1$	$T_m^2$	$T_i$
PEH1	66	145	220	380
PEH2	60	135	160	300
PEH3	66	140	190	340
PEH4	118	–	–	360

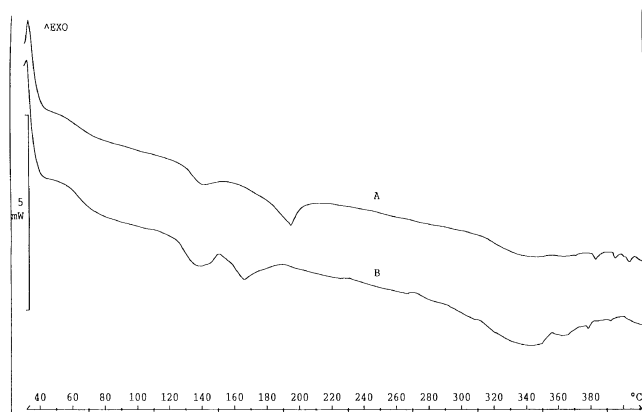
In the Figure 1A and 1B, the  $^{13}\text{C}$  CP MAS spectra of, respectively, PE4 polyester and PEH4 copolymer are reported.

From the spectrum of Figure 1C, which shows detailed zones between 180–155 ppm of the spectrum of copolymer PEH4, we can attribute the resonances in the range 168–175 ppm to carbonyls of the hydrazide comonomer, and those between 155 and 168 ppm to carbonyls of the ester comonomer. From the integral of these resonances we can measure the relative amount of comonomers which results of the order of 15%. However, since CP MAS is not a linear technique, we must admit large errors so that our estimate should be evaluated  $\sim 15\% \pm 7\%$ .

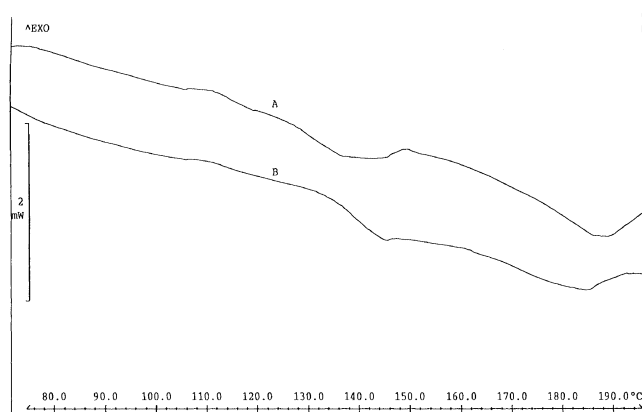
#### Thermal Analysis

Thermal analysis was performed in the range 30–400°C. Tables VI and VII report  $T_m$ ,  $T_i$  and  $T_g$  of polyesters and polyesterhydrazides in first heating run. It is worth to notice that experiments in second run after cooling are not reported as, due to the high  $T_i$ 's, some degradation of the sample is unavoidable and hampers the reorganization of the structure. Obviously, the transition temperatures vary with the composition of comonomers. In Figure 2 the thermograms of PE3 and PEH3 referred to the first runs are reported as example.

All the polymers present more than one peak of melt-



**Figure 2.** DSC traces (1st run) of PE3 (A) and PEH3 (B) samples.



**Figure 3.** DSC traces of PEH3 sample: A = first run; B = second run after isothermal crystallization.

ing, exception made for the PE4 and PEH4 copolymers which do not show any clear melting endotherm. The almost total absence of crystallinity of these two polymers is due to the high concentration of propoxy-substituted aromatic rings. The presence of multiple endotherms in all the other polymers, rather common in liquid crystalline polyesters,<sup>38</sup> is related to the complex molecular structure and can be ascribed to different crystalline arrangements. To verify such hypothesis, experiments of melting and successive isothermal crystallization from the melt have been made. As example, we report in Figure 3, for PEH3, the first run of a sample heated from 30 to 200°C and the second run of a sample heated until 220°C, quenched until 125°C and crystallized at this  $T$  for 30 min. In this way, we aimed to influence the position and intensity of the first melting peak. In Figure 3B, two melting peaks are still present, and  $T_m^1$  increases from 140 to 145°C. The total  $\Delta H_m$  increases from 3 to 4.5 J g<sup>-1</sup>, as expected after an isothermal crystallization. We can attribute the two different peaks to two different crystalline forms, as they persist also when the material is allowed to crystallize slowly. Different sequences of the comonomers into the polymer chain could be responsible of this poly-

**Table VIII.** Starting degradation temperatures ( $T_{\text{degr}}$ , °C) and weight loss at 500°C of PEs

Sample	$T_{\text{degr}}$	Weight loss at 500°C
		%
PE1	420	40
PE2	310	57
PE3	380	34
PE4	400	35

**Table IX.** Starting degradation temperatures (°C) and weight loss at 500°C of PEHs

Sample	$T_{\text{degr}}$	Weight loss at 500°C
		%
PEH1	440	18
PEH2	330	54
PEH3	400	36
PEH4	420	21

morphism.

Moreover, both the starting copolyesters and the final polyhydrazides show a broad endotherm above 300°C (except PE2 and PEH2,  $T < 300^\circ\text{C}$ ) attributed to the isotropization from a liquid crystalline to an amorphous phase (as will be confirmed by optical microscopy). A good interval of stability of the mesophase is obtained in every case.

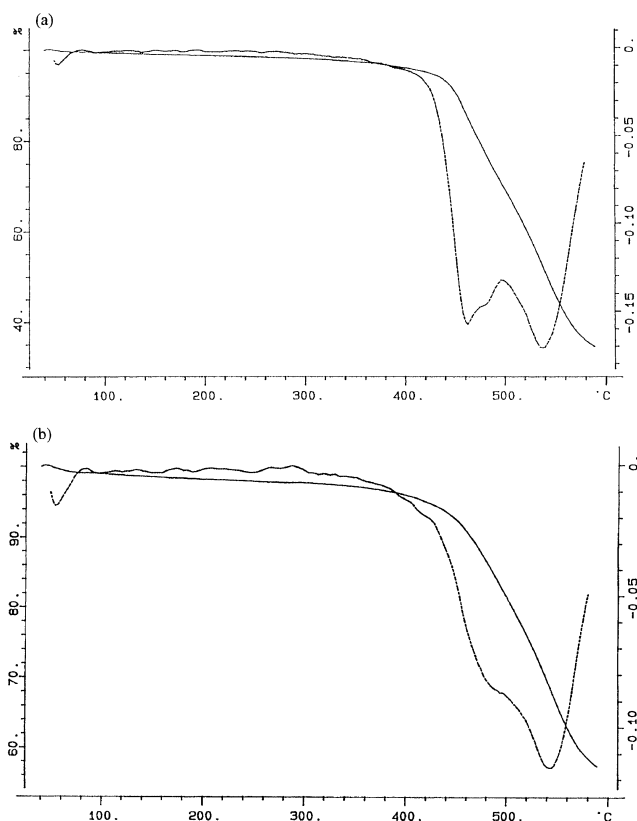
The  $T_m^1$  and  $T_m^2$  of PEs and of corresponding PEHs are quite similar. In our opinion, the loss of carboxyl end groups of PEs, which tend to increase the melting temperature of prepolymers, is compensated by the introduction of hydrazidic units, able as well to give hydrogen bondings.

The  $T_g$ 's are higher in the PEHs, as expected because of the combined effect of the insertion of hydrazidic groups and of the increased molecular weight. As it can be noted, the PE4 and PEH4 samples have the highest  $T_g$ . It is in fact the presence of the C comonomer, absent in PEH4, that renders the chains of the other PEH's more flexible, due to the presence of a polyethylenic sequence (Griffin's monomer).

The  $T_i$  are, instead, scarcely influenced by the insertion of hydrazidic units; this should be due to the fact that, at the temperature at which the isotropization occurs, the hydrogen bonds introduced by the presence of hydrazidic segments are no more effective, and only the polyester moiety of the copolymer influences the chain mobility.

#### Thermogravimetric Analysis

The more significant data obtained from dynamic experiments of TGA on PEs and PEHs samples are collected in Tables VIII and IX, while in Figure 4a and 4b the TGA thermograms with 1st derivative curve of PE1 and PEH1 are reported as example. Degradation



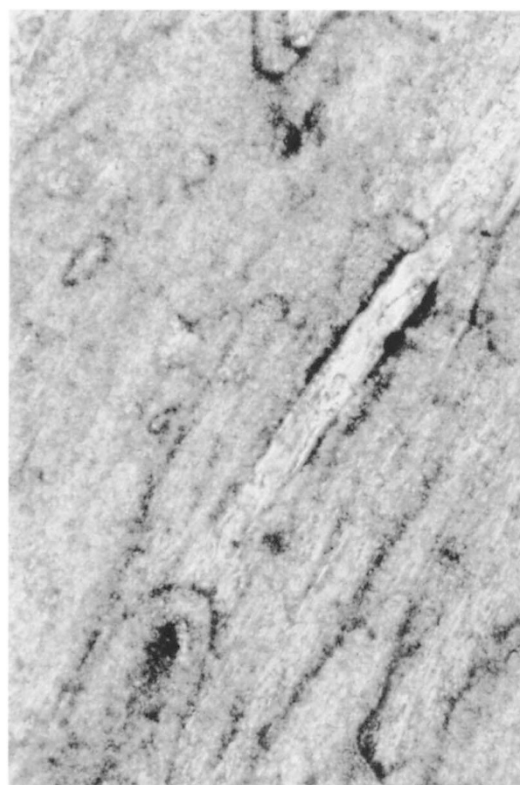
**Figure 4.** TGA traces of PE1 (a) and PEH1 (b) samples.

tion temperatures refer to the temperatures at which the weight loss starts and are heavily influenced by chemical composition, as expected. The absence of terephthalic comonomer (PEH2) leads to an abrupt decrease in  $T_{\text{degr}}$  and increase in weight loss at 500°C. As matter of fact, better results are obtained with PEH1 and PEH4 samples, which have the highest terephthalic units content (50%). Although there are no significant differences on the temperatures of starting degradation between the polyhydrazides and the precursor polyesters, we must notice the better thermal stability of the PEHs in terms of weight loss at a given temperature. It is conceivable to assume that the influence on the weight loss is limited because of the very low content of hydrazide chosen in the present work.

The cyclization temperatures are really hardly detected as a small inflection at the beginning of degradation step. The partial superimposition of cyclization reaction and degradation makes impossible to isolate the polyoxadiazole derivatives, almost through thermal cyclization.

#### Optical Microscopy

Thin films of samples have been put in the hot stage and observed under crossed polars during thermal cycles. The polyesters and polyesterhydrazides have been heated from  $T_{\text{amb}}$  to their isotropization temperature



( ————— = 50 μm)

**Figure 5.** PE1: typical schlieren textures. Crossed polarizes,  $T = 300^\circ\text{C}$ .

and successively cooled until  $T_{\text{amb}}$  again. Photos have been taken during these scans.

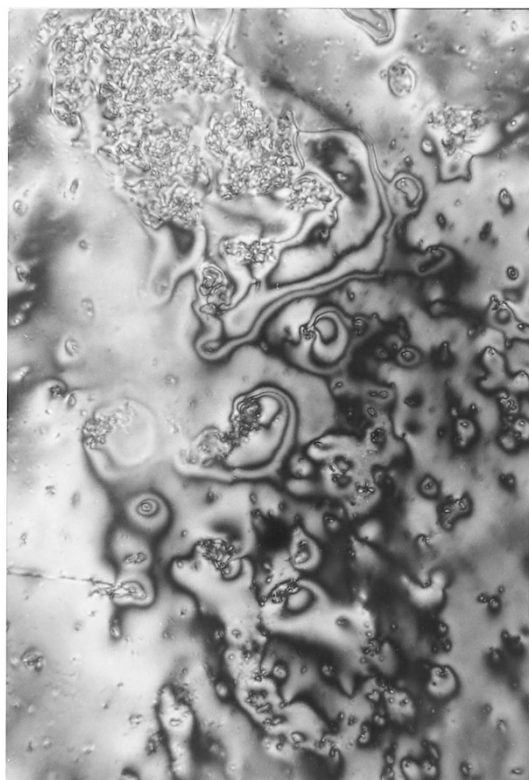
A microcrystallinity is initially present in all samples; moreover, a diffuse birefringence persists after melting and this has already been found in liquid-crystalline polymers.<sup>39</sup>

In the interval between melting and isotropization, classical textures of nematic phases are observed.<sup>40</sup> Typical schlieren textures, nematic drops and interference effects, very similar to examples reported in literature, are present (see plates n<sup>o</sup>. 5, 10, and 15 of the above mentioned book). As example, we report in Figures 5–8 some pictures of PE1 and PEHs samples.

#### WAXS Analysis

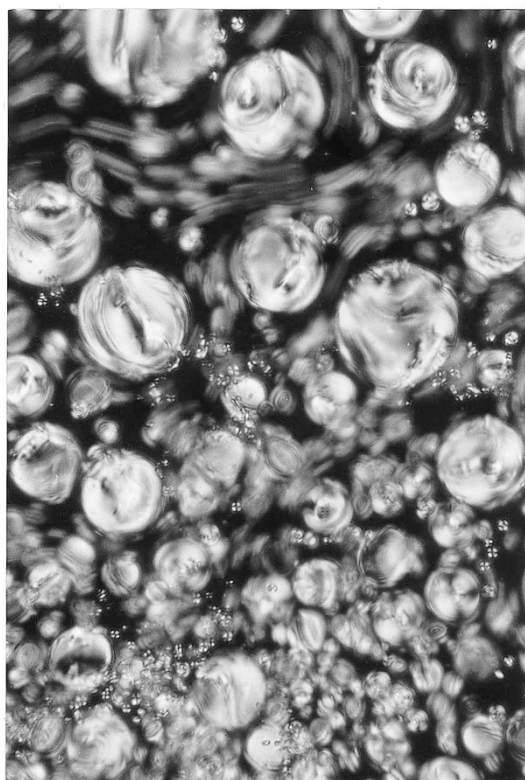
WAXS analysis was performed on fibers of PEHs samples. Fibers have been obtained by laboratory melt-spinning, using a glass syringe heated on a flame. The fibers are rigid and brittle, probably as consequence of non controlled crystallization conditions.

Figure 9 shows the WAXS pattern of a PEH4 fiber as an example. The pattern shows crystalline reflections ( $d = 2.85\text{\AA}$ ;  $3.26\text{\AA}$ ;  $4.33\text{\AA}$ ) with a certain degree of orientation, as indicated by the polarization equatorial of the reflections. Because of the existence of crystalline reflections, the formation of a ne-



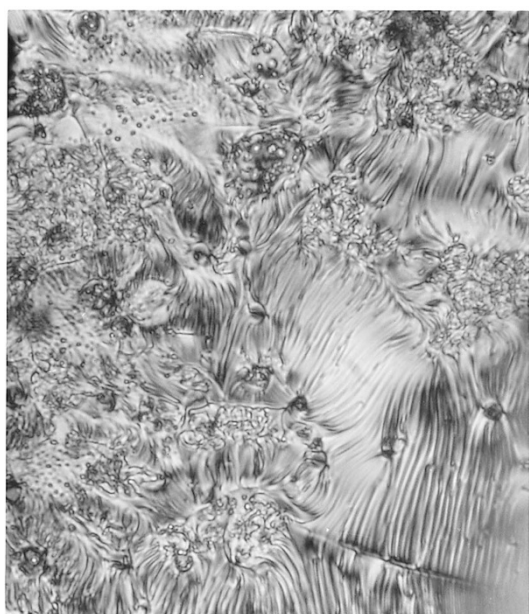
( ——— = 50  $\mu\text{m}$ )

**Figure 6.** PEH3: typical schlieren textures. Crossed polarizers,  $T = 260^\circ\text{C}$ .



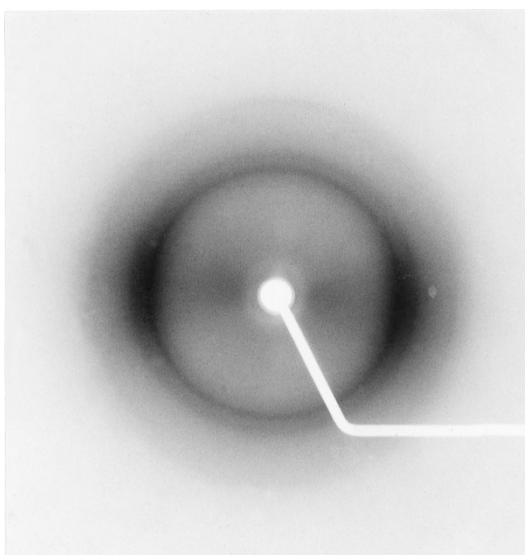
( ——— = 70  $\mu\text{m}$ )

**Figure 8.** PEH1: nematic drops at the isotropization point. Crossed polarizers,  $T = 380^\circ\text{C}$ .



( ——— = 50  $\mu\text{m}$ )

**Figure 7.** PEH4: nematic textures with typical alignment. Crossed polarizers,  $T = 290^\circ\text{C}$ .



**Figure 9.** WAXS pattern (flat film camera,  $\text{Cu-K}\alpha$ , Ni-filtered radiation) of a fiber of PEH4.

nematic mesophase cannot be evidenced at room temperature. Work is in progress to collect the patterns at high temperatures, where the crystalline organization of the macromolecules is destroyed.

## CONCLUSIONS

Copolyesters oligomers containing “Griffin’s monomers”, terephthalic units and propoxy-side groups at different composition have shown to exhibit thermotropic properties, with formation of nematic



phases with a good range of stability in the melt. By varying the relative percentages of the comonomers it is possible to lower the melting temperatures well below the degradation, with values near to the processing temperatures of common polyesters. The presence of polyethylenic sequences (Griffin's monomer) or alkoxy-substituted aromatic rings causes some loss in thermal stability if compared to fully aromatic polyesters.

Copolyesterhydrazides obtained by bridging copolyester blocks through hydrazidic units retain the thermotropic behavior and maintain the heat resistance properties with some improvement of the weight loss at a given temperature. Cyclization temperatures are high, hardly detected and partially superimposed to degradation, so the polyoxadiazole derivatives have not been isolated.

More work is in progress on the possibility to isolate the more stable polyoxadiazoles by varying the nature of the dihydrazide comonomer, in order to lower the cyclization temperature.

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