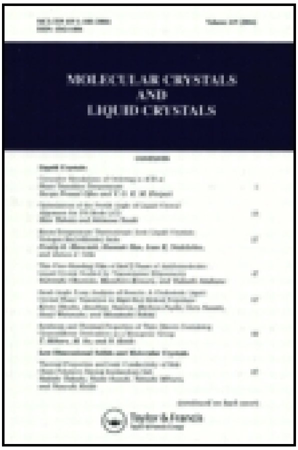

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Synthesis and Characterisation of New Copolyesterhydrazides with Thermotropic Properties

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Synthesis, chemical and chemical-physical characterisation of new thermotropic copolymers containing ester and hydrazidic units are reported. The polymers consist of polyester blocks linked together through p-phenylenhydrazidic units. By varying the nature and the relative percentage of the comonomers in the polyester block, it is possible to obtain thermotropic copolymers with melting temperatures well below the degradation, with a good range of stability of the mesophase, and with heat resistance properties similar to those of homopolymeric polyhydrazides.

Keywords: polyesters; polyhydrazides; thermotropicity

INTRODUCTION

Heat resistant polymers are defined as organic materials which maintain their mechanical characteristics at T>300°C for several days or hours. Such temperatures can be reached during manufacture or use of products[1]. Recently, research on heat-resistant polymers is directed to improve their processing. In fact, the characteristics which render these polymers attractive for utilisation in severe conditions are the same which make their processability very difficult: high melting temperatures (sometimes above decomposition temperature), high melt viscosity and low solubility. Polyhydrazides[2] and thermotropic polyesters and polyesteramides, as Vectra[3], belong to this class of polymers. Vectras are characterized by low melt viscosity and excellent mechanical properties as fibers with rigidity values close to the theoretical ones. The introduction of amidic groups which form hydrogen bonding between the chains leads to an increase in isotropization temperature (Ti), to a better stability of nematic phase and, sometimes, to the formation of a smectic phase. The disadvantages are an increase of crystallization temperature (Tc) and of Tm, which sometimes are so high to render their processing impractical. The introduction of flexible spacers or of side groups to lower the Tm leads to a drop of mechanical and heat resistance properties[4,5].

In the present paper, we report on synthesis, structural and thermal characterisation of new copolyesterhydrazides (PEHs), in which the thermotropic polyester fraction is modified to lower the Tm, so improving the processability, while the introduction of hydrazidic groups should maintain good thermal stability, particularly after cyclization to the more stable polyoxadiazole, and high mechanical properties.

EXPERIMENTAL

Typical procedure for the synthesis of a copolyester (PE4)

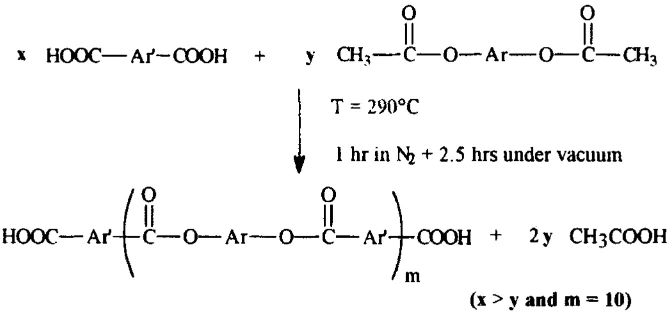
A three-necked flask equipped with a nitrogen inlet, a mechanical stirrer and a distillation column is charged with 2.24g (0.010 mol) of 2-propyloxy terephthalic acid, 1.66g (0.010 mol) of terephthalic acid, 1.71g (0.0082 mol) of methylhydroquinone diacetate and 1.59g (0.0082 mol) of hydroquinone diacetate. The reaction flask was evacuated and purged with nitrogen three times, then it was heated under reduced pressure at 110°C for 2 minutes to dry the reagents. 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 conversion. After about 1 hr the mixture was viscous and the reaction was let to go on under reduced pressure (about 5mm Hg) for 4 hours at the same temperature. The final recovered polymer was characterised without any purification.

Typical procedure for the synthesis of a copolyesterhydrazide (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 above described for the synthesis of PE4. The reagents were dried following the same procedure. The polycondensation reaction was conducted at 290°C under N_2 stream for 45 min. and for further 2 hours at a reduced pressure of 5 mm Hg, while distilling water. Finally, the polymer was recovered by cooling, and finely ground to powder.

RESULTS AND DISCUSSION

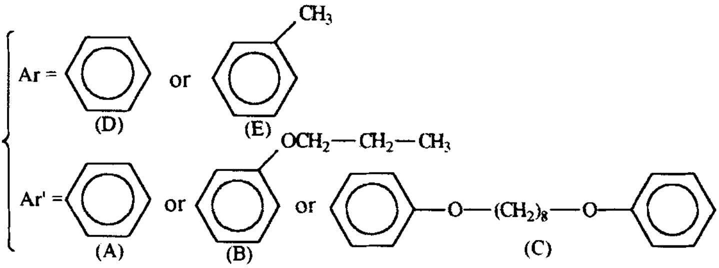
The PEHs are obtained in two steps. In the first one, the precursor polyester blocks have been prepared by polycondensation in the melt at high temperatures between diacids and diacetates in the chosen composition, according to the following scheme of reaction:



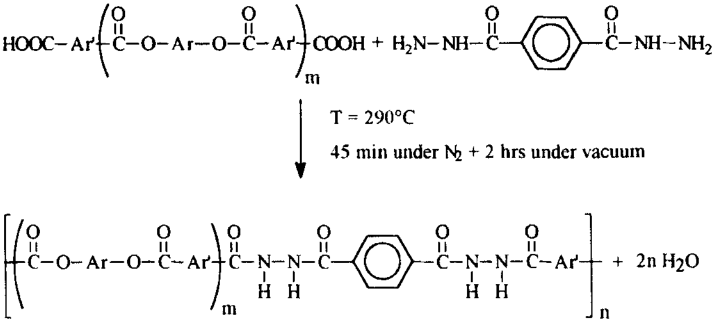
$$x\ HOOC{-}Ar'{-}COOH + y\ CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}Ar{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow[\text{1 hr in } N_2 + 2.5 \text{ hrs under vacuum}]{T = 290°C} HOOC{-}Ar'\left(\overset{\overset{O}{\|}}{C}{-}O{-}Ar{-}O{-}\overset{\overset{O}{\|}}{C}{-}Ar'\right)_m{-}COOH + 2y\ CH_3COOH$$

(x > y and m = 10)

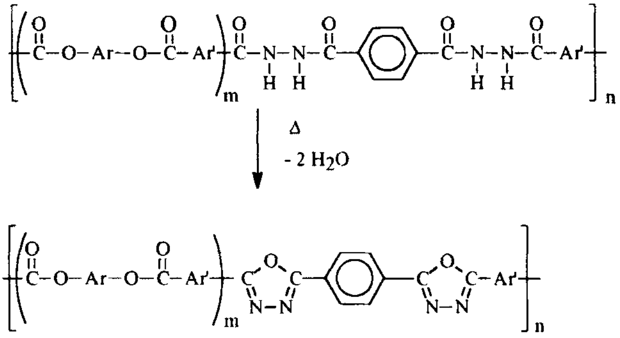
where:



Successively, the copolyesters are condensed with terephthalic dihydrazide:



A partial conversion of hydrazidic units to oxadiazoles during the polycondensation is evidenced by IR spectroscopy (band at 1560 cm^{-1}):



Codes, inherent viscosities and molar compositions of PEHs are summarised in Table I.

TABLE I Codes, inherent viscosities (η_{inh}) and molar compositions of PEHs

Code	η_{inh}[a] (dl/g)	D	E	A	B	C
PEH 1	0.32	50%	50%	50%	---	50%
PEH 2	0.32	50%	50%	---	50%	50%
PEH 3	0.27	50%	50%	30%	20%	50%
PEH 4	0.49	50%	50%	50%	50%	---

[a] c=0.5g/dl in NMP/LiCl 5%, T=25°C

The copolyesters and copolyesterhydrazides have been carefully characterised by thermal and thermogravimetric analyses, wide-angle X-ray spectroscopy and optical microscopy. A comprehensive report on all collected data, both of precursors and final polymers, will be published in a forthcoming paper. Some relevant physical data of PEHs, such as melting (Tm), isotropisation (Ti), glass transition (Tg) and degradation (T_{degr}) temperatures and the weight loss (%) detected at 500°C in a dynamic experiment are summarised in Table II.

TABLE II Thermal data of PEH copolymers (heating rate: 20°C/min)

Sample	T_g (°C)	T_m (°C)	T_i (°C)	T_{degr} (°C)	weight loss (%) at 500°C
PEH 1	66	185	380	420	18
PEH 2	60	160	300	320	54
PEH 3	66	170	340	380	36
PEH 4	118	---	360	420	21

As expected, the presence of polymethylenic sequences in the polyester block gives rise to polymers with relatively low Tm and good stability window of the mesophase, but also depresses the Tg. The use of high percentages of propyloxy-substituted aromatic units instead of the "Griffin monomer" [6] destroys the crystallinity while keeping the thermotropicity. From the above results we can also see that the introduction of aromatic hydrazidic repeating units does not destroy the liquid crystallinity of the starting polyesters, while assuring a quite good thermal stability. Better results are obtained with PEH4 sample, which presents high Tg and low weight loss at 500°C.

An optical micrograph of PEH1 sample showing Schlieren textures typical of a nematic mesophase is reported in Fig. 1 as an example.

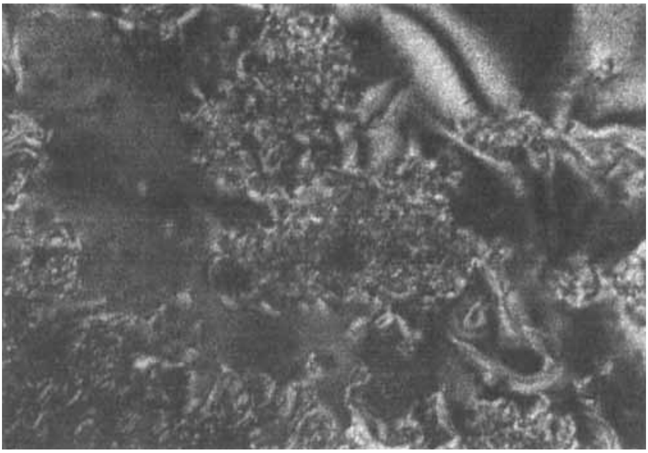


FIGURE 1 Nematic schlieren textures of PEH1 sample. Crossed Polars, T=160°C (⟼ = 50 μm)
See Color Plate I at the back of this issue.

The existence of a nematic mesophase is confirmed by WAXS analysis of fibers obtained through melt spinning, which moreover shows that the fibers are almost non-crystalline and partially oriented along chain axis.

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