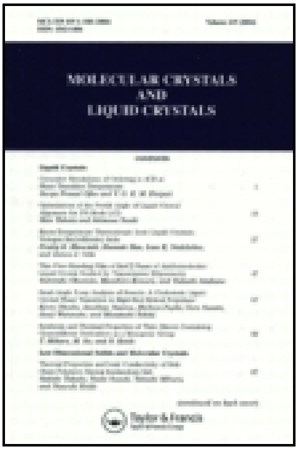

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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From Conventional to Liquid Crystalline Polyesters

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FROM CONVENTIONAL TO LIQUID CRYSTALLINE POLYESTERS

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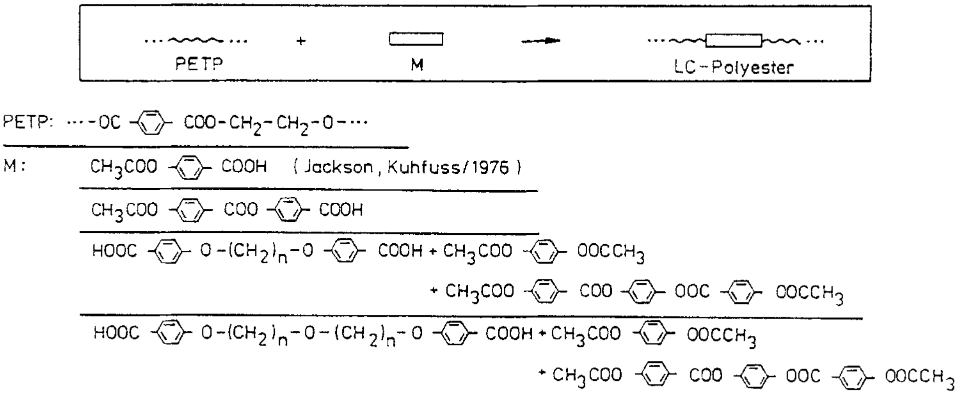
Abstract To obtain liquid crystalline copolyesters with improved thermal behavior, p-acetoxybenzoyloxy-benzoic acid and a variety of dicarboxylic acids derived from p-hydroxybenzoic acid in combination with acetylated hydroquinone derivatives have been used as poly(ethylene terephthalate) (PETP) modifiers. The influence of the modifier structure on thermotropic properties of the copolyesters and results of dynamic mechanical measurements are discussed.

INTRODUCTION

Liquid crystalline (LC) main-chain copolyesters are of considerable interest because of their applications in high-strength materials. LC-polyesters composed of rigid, rod-like mesogenic units have typically melting points in the temperature range where chemical decomposition is beginning to be a problem for any melt processability. To depress the melting points and to interrupt the crystalline order, several copolymerization methods using monomers with flexible spacers, bulky side groups or bent comonomers are available. Further, it has been demonstrated [1] that LC-behavior exists in copolymers produced by the acidolysis reaction of PETP and p-acetoxybenzoic acid (PAB). This reaction yields LC-copolyesters with an enhanced content of p-oxybenzoate (POB) units and improved mechanical properties with respect to processing and use conditions. To stabilize the LC-behavior of the acidolysis products, we used p-acetoxybenzoyloxy-benzoic acid (PABB) instead of PAB. But the specimens prepared with more than 60 mole-% PABB showed like PETP/PAB copolyesters [2] a heterogeneous morphology due to the existence of a dispersed POB-rich phase. In order to suppress the formation of POB blocks, a variety of dicarboxylic acids containing flexible aliphatic spacers in combination with acetylated hydroquinone derivatives has been used as PETP modifiers. Routes for PETP modification with mesogenic building units M are shown in the following scheme.



In this way, the solid-nematic transition as well as the mesophase properties of the copolyesters can be systematically altered by different spacer lengths.

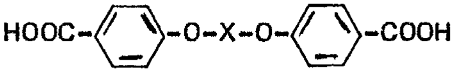
EXPERIMENTAL

PETP, containing conventional antimony catalyst, was a commercial product. PABB was prepared from p-acetoxybenzoylchloride and p-hydroxybenzaldehyde followed by oxidation with Cr_2O_3 in acetic acid solution (cr 227 °C n 250 °C(dec.) is). BABB was synthesized by reaction of hydroquinone with p-acetoxybenzoylchloride (cr 189 °C n 320 °C(dec.) is). Hydroquinone diacetate (HDA) or 1,4-bis(4-acetoxybenzoyloxy)-benzene (BABB) were used as difunctional phenols.

Dicarboxylic acids summarized in Table I were prepared by etherification of p-hydroxybenzoic acid with 1,ω-dichloroalkanes or 1,1-dichlorodiethyl ether [3].

Details on the preparation of the copolyesters are given in the literature [1]. Dicarboxylic acids and disubstituted hydroquinones were used in the 1:1 mole ratio.

TABLE I Dicarboxylic acids used as modifiers.



X	Symbol	Melting point (°C)
$(CH_2)_2$	ETOBA	350
$(CH_2)_3$	PROBA	324
$(CH_2)_4$	BUOBA	341
$(CH_2)_5$	PEOBA	286
$(CH_2)_6$	HEOBA	298
$(CH_2)_2$-O-$(CH_2)_2$	DEOBA	310

The textures and transition temperatures of polymeric materials were observed with a polarizing microscope. Thermal analyses were performed with a Perkin-Elmer DSC-1B apparatus at a heating rate of 8 K/min.

A dynamic mechanical analyzer (Perkin-Elmer) was used to measure the loss angle, tanδ , at 0.02 Hz between 20 °C and 150 °C. Each sample was heated with 5 K/min to 150 °C, and then cooled with the same rate to room temperature. The DMA scans were begun at the latter temperature.

RESULTS AND DISCUSSION

From all prepared composition series, the properties of samples containing 40 mole-% PETP are summarized in Table II. The glass transition temperatures T_G have been obtained from storage modulus versus temperature spectra (0.02 Hz).

TABLE II Thermal properties of copolyesters containing 40 mole-% PETP

Composition (mole-%)	T_G (°C)	m.p. (°C)
PABB 60	91	277
ETOBA 30/BABB 30	79	225
PROBA 30/BABB 30	66	212
BUOBA 30/BABB 30	69	217
PEOBA 30/BABB 30	68	167
HEOBA 30/BABB 30	64	172
HEOBA 30/HDA 30	-	177
DEOBA 30/BABB 30	74	163

Generally, with increasing chain flexibility caused by alkylene spacers, T_G's and melting temperatures decrease. Reduction of the melting point by use of modifiers inducing less rigid chains is illustrated in Figure 1. The homogeneous melts are liquid crystalline. With the exception of PETP/PABB and PETP/HEOBA/HDA, after an annealing time of about 30 min. nematic schlieren textures appeared at 240 °C. In the first two cases, the melts exhibited untypical textures. At temperatures above 300 °C, the nematic - isotropic transition was accompanied by gradual decomposition. The upper limits for proportions of PETP in products exhibiting LC-behavior are about 80 % with PABB and 50 % with HDA. Obviously, flexible spacers as well as the nonreactive ether bonds instead of COO-groups in the modifiers give rise to a substantial depressing of the polymers' melting points and favor the formation of glassy solids on cooling the nematic melts.

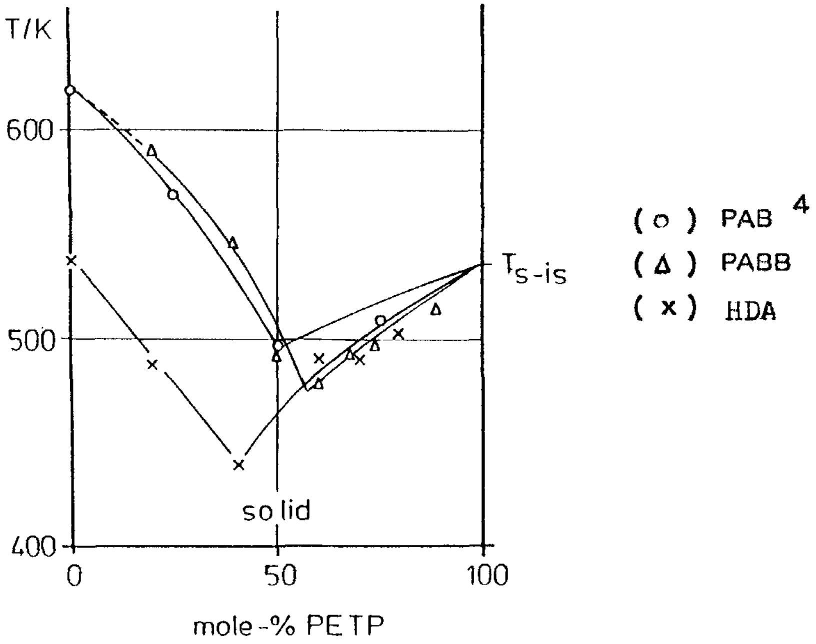


FIGURE 1 Plot of melting temperature versus mole percent of PETP containing different comonomers.

Comparing with unmodified PETP characterized by at least two low temperature phases having different crystallinity, the increased tendency of the LC-copolyesters to form the glassy state is recognizable from tanδ -temperature spectra (Figure 2). The α -peaks of LC-copolyesters associated with the glass transition are of higher intensity and sharpness. Further, storage modulus-temperature spectra do not give hints to a two phase morphology as has been found for PETP/PAB.[5].

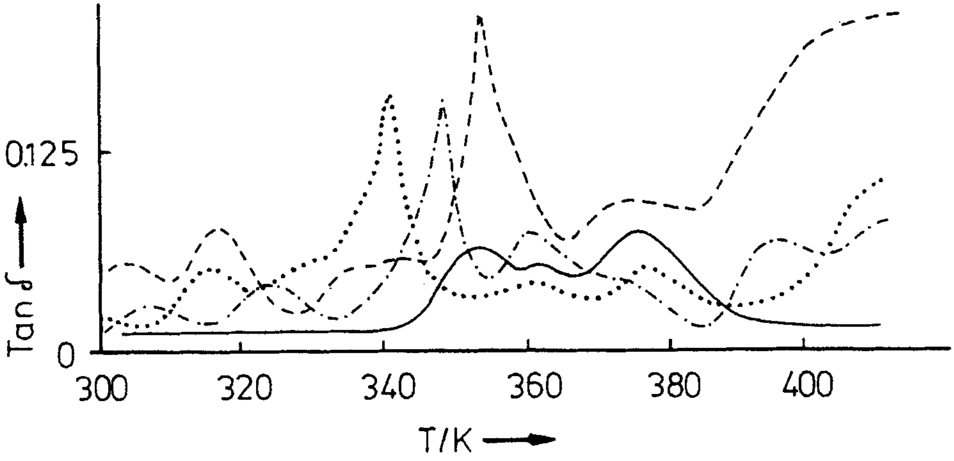


FIGURE 2 Tanδ spectra for PETP (–) and the 40/30/30/ mole ratio copolyesters: PETP/ETOBA/BABB (– – –), PETP/PEOBA/BABB (• • •), PETP/DEOBA/BABB (– • •–).

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