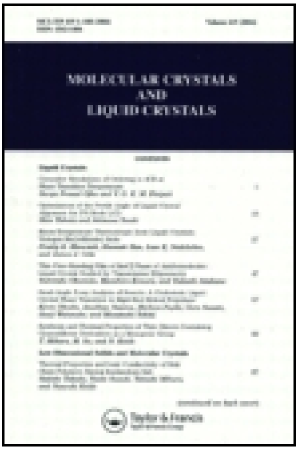

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Blends of Poly(Buty1ene Terephthalate) with Thermotropic Liquid Crystalline Polyesters. Morphology and Thermal Behavior

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BLENDS OF POLY(BUTYLENE TEREPHTHALATE) WITH THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS. MORPHOLOGY AND THERMAL BEHAVIOR †

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Abstract Blends of poly(butylene terephthalate) with liquid crystalline poly(decamethylene 4,4'-terephthaloyldioxydibenzoate) were studied in all the composition range by optical and electron microscopy and differential calorimetry. The morphology and phase transitions of the blends are markedly influenced by the composition and thermal history. The results suggest the occurrence of miscibility phenomena between the two components in the amorphous phase.

INTRODUCTION

The studies on the properties of liquid crystalline polymer (LCP) systems have received ever increasing attention on both scientific and technological grounds. Within this framework, polymer blends containing a LCP component can offer the opportunity of producing new molecular composites with improved mechanical and thermal resistance, and of modifying the processing conditions. The influence of LCP on the morphology, melt rheology and mechanical properties of blends with various commercial polymers has been stressed in some cases.[1-5]

Since a few years we have started the characterization of thermotropic LC poly(alkylene 4,4'-terephthaloyldioxydibenzoate)s (HTHm) and their blends with poly(butylene tere-

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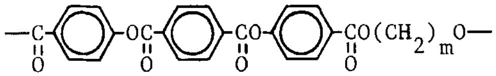
phthalate) (PBT) and poly(styrene)[6,7]



In this paper we report the results of further morphological and thermal investigations, including crystallization kinetics, on blends of PBT with the smectic polyester HTH10 (m = 10).

EXPERIMENTAL

Synthetic HTH10 ($|\eta| = 0.32$ dl/g in CF3COOH at 30°C)[8] and commercial PBT (Kodak Co.) ($\bar{M}_v = 37000$) were purified as previously described[7]. The blends PBT/HTH10 with HTH10 amounts in the range 0–100% w/w were obtained by coprecipitation from 2% wt. solutions of individual polymers in CF_3COOH at 50°C[7]. Optical microscopy studies of blend films were performed with a Reichert polarizing microscope equipped with a Mettler FP52 hot stage. The morphology of fractured or etched surfaces of samples was analyzed by a Jeol T300 scanning electron microscope.

The melting and crystallization behaviors were examined with a Perkin-Elmer DSC2 calorimeter. Samples (6–9mg) were heated at 20K/min to the isotropic liquid, then cooled and again heated at the same rate. The glass transition behavior was studied with a Perkin-Elmer DSC4 calorimeter on samples quenched in liquid nitrogen from 543K and then heated from 243K at 20K/min. Isothermal crystallizations of PBT and 90/10, 70/30, and 50/50 blends from the isotropic melt were performed in the DSC by rapid cooling (320K/min) of melt samples at 543K to a fixed crystallization temperature. The heat developed during the process was recorded as function of time and the fraction X_t of polymer crystallized was evaluated by the ratio of the exothermal area at time t over the overall crystallization area.

RESULTS AND DISCUSSION

MORPHOLOGY

The morphology of the blends was analyzed on melt-crystallized films and on fractured (or etched) surfaces of bulk samples quenched from the mesophase or the isotropic melt. In Figs.1 and 2 are shown electron micrographs of the blends with 30 and 50% of HTH10 content, respectively. The fractured surfaces of these samples reveal the presence of rod-like structures (diameter ≈2μ), perpendicular to the fracture plane, due to the LC component. Such structures appear quite well distributed in the polymer matrix with a good interphase adhesion (Fig.1) and their number increases with increasing amount of HTH10 (Fig.2).

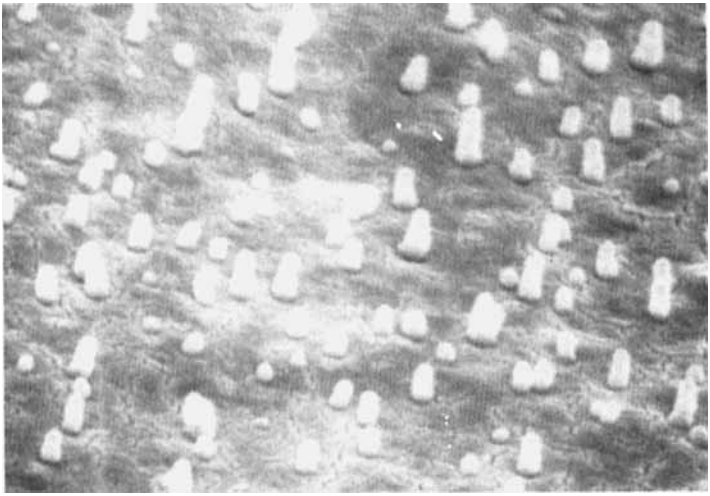


FIGURE 1. Scanning electron micrograph of fractured surface of PBT/HTH10 70/30 blend quenched from the mesophase (original magnification 20000 x).

At HTH10 contents >50% the morphology of the blends is essentially homogeneous without any distinct domain. Pure PBT samples do not present fracture surfaces with particular morphological features. Similar morphological observations have been reported for other polymer systems with LCP components[3,4]. The analysis of blend surfaces etched with sulphuric acid is more difficult due to the presence of holes and the

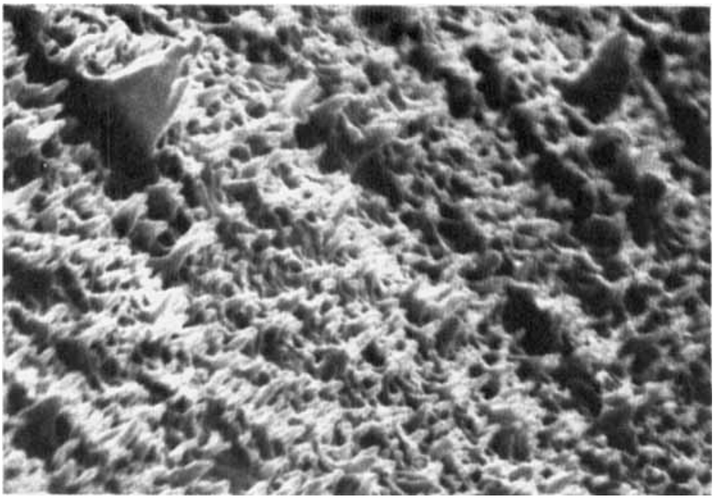


FIGURE 2. Scanning electron micrograph of fractured surface of PBT/HTH10 50/50 blend quenched from the isotropic melt (original magnification 10000 x).

formation of network-like structures.

In films of PBT/HTH10 blends isothermally crystallized from the isotropic melt, the optical microscope analyses do not reveal any phase separation between the components, at least for PBT contents >50%. The morphology and size distribution of PBT crystals are largely affected by the LCP component, and the spherulite growth rate in the temperature range 473-483K is found to decrease rapidly with increasing amount of HTH10.[9] The blends with lower PBT contents show in addition fan-shaped domains characteristic of the LC polyester.

THERMAL PROPERTIES

In Fig.3 is represented the phase behavior of PBT/HTH10 blends on heating the original samples to isotropization (Ti), on cooling from the melt (Tc) and on subsequent heating (Tm). Surprisingly, Ti increases with decreasing HTH10 content from 90 to 30%, as also found by optical microscopy, while the relevant heat of transition decreases from 11.8 to 3.0 $J \cdot g^{-1}$ of HTH10. Such behavior can be related mainly to enthalpic

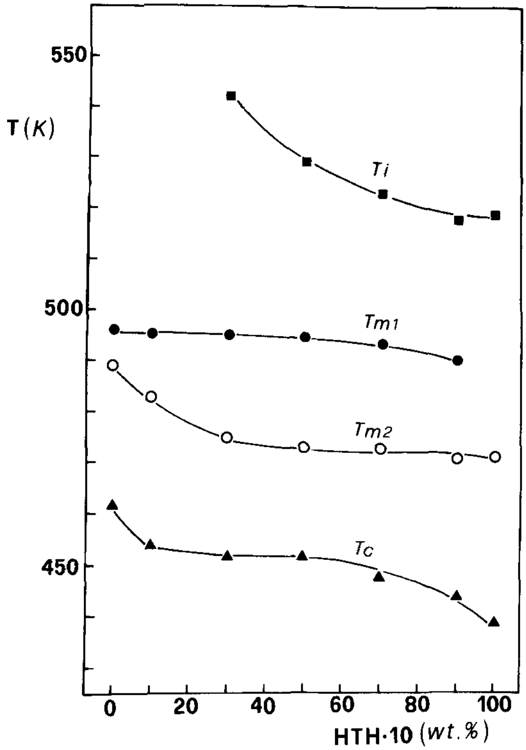


FIGURE 3. Phase diagram of PBT/HTH10 blends: Ti isotropization temperature, Tc crystallization temperature, Tm melting temperatures (see text) (20K/min).

effects arising from interaction phenomena of the two polymers in the melt, the entropy change decreasing more rapidly from $22.7 \cdot 10^{-3}$ to $5.5 \cdot 10^{-3}$ $J \cdot K^{-1} \cdot g^{-1}$ of HTH10. The blends cooled from the isotropic melt at 20K/min show a continuous decrease of the crystallization temperature and melting temperature (Tm_2), while the temperature of the higher melting peak (Tm_1), ascribed to reorganization phenomena of PBT crystals during the heating, is practically unaffected by the composition. Samples with HTH10 contents $\geq 50\%$, when cooled from the isotropic liquid at rates $\leq 10K/min$, exhibit an additional melting peakat 470K, indicating the presence of a separated crystal phase of the HTH10 polymer in these blends. These results are in agreement with the X-ray analysis of melt-crystallized samples, which shows for HTH10 contents higher than 30% reflections characteristic of the crystal phases of individual polymers without supporting the existence of cocrystallization phenomena[7] Samples isothermally crystallized from the melt in the range 469-478K, where only PBT crystallizes, display a melting behavior dependent on Tc and composition. Their melting temperature (Tm_2) varies in a linear fashion with Tc, according to the Hoffmann-Week equation[10] and the extrapolated equilibrium melting temperature decreases from 515K for PBT to 508K for the 50/50 blend.

The DSC thermograms of PBT/HTH10 blends quenched from the isotropic phase display on heating one glass transition intermediate between those of PBT (318K) and HTH10 (297K). A marked depression of Tg is observed in the composition range 0-50% of HTH10, while slight variations occur at higher concentrations of the LCP (Fig.4). Annealing at room temperature or at higher temperatures of quenched samples induces an increase of Tg in PBT rich samples (Fig.4), probably due to crystallization phenomena of PBT[11] The presence of a single Tg in the blends suggests that the components are miscible in the amorphous phase, the larger effects being observed for blends with high PBT contents.

ISOTHERMAL CRYSTALLIZATION KINETICS

The effect of the HTH10 content on the overall crystallization rate of PBT from the isotropic melt is summarized in Fig.5, where the reciprocal of half-time of crystallization is plotted against the crystallization temperature for various blends. A marked decrease of the crystallization rate of PBT in the blends is observed at each Tc, the lowest values corresponding to the 90/10 blend, while minor differences are found in the values of the 70/30 and 50/50 blends.

The crystallization kinetics have been analyzed by means of the Avrami equation:[12]

$$1 - X_t = \exp(-Kt^n) \qquad (1)$$

where K is the rate constant and n the Avrami exponent dependent on the growth geometry and nucleation type of the

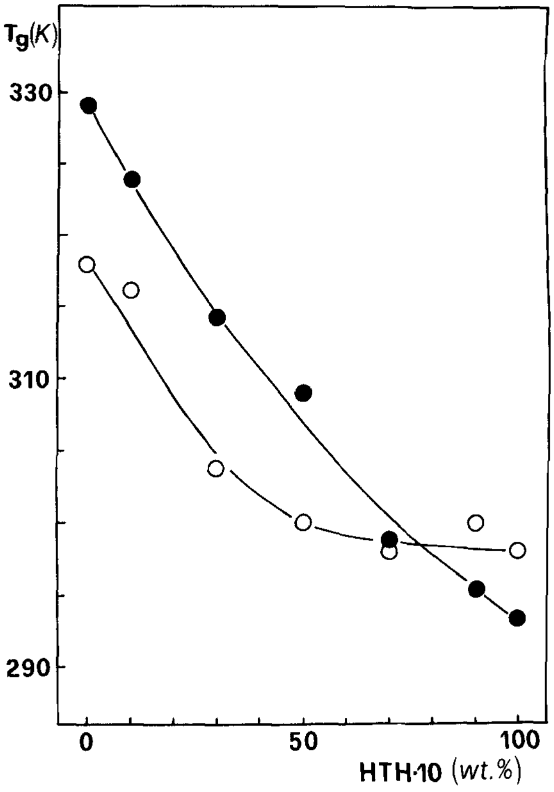


FIGURE 4. DSC glass transition temperatures (Tg) of PBT/HTH10 blends quenched from the melt (○) and annealed for one hour at 373K (●).

crystals. Plots of Log$|-\ln(1-X_t)|$ vs. Log$|t|$ result to be linear at each Tc for all the PBT/HTH10 samples, with slope $\bar{n}$ varying from 2.75 for PBT to 3.25 for the 50/50 blend. These values are consistent with a spherulitic growth of the crystals initiated by heterogeneous nucleation and are in agreement with those reported for PBT.[13,14] Accordingly, the variation of K with composition, at a fixed Tc, can be related to the growth rate G and the nucleation density $\bar{N}$ of PBT crystals in the blends by the relation:[12]

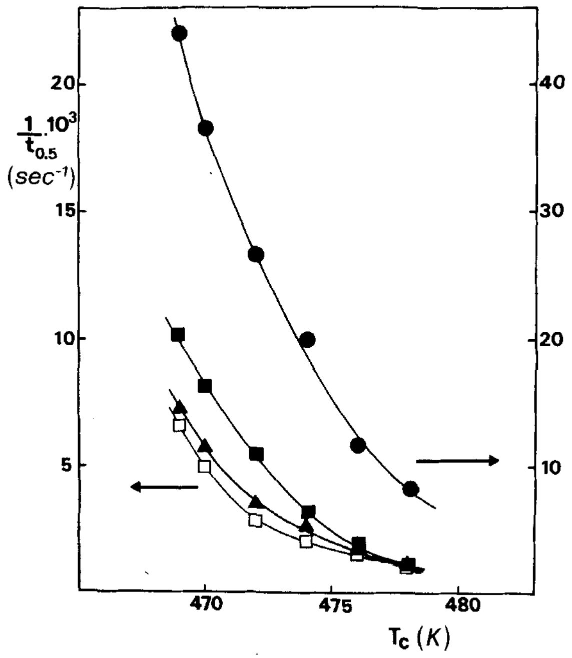


FIGURE 5. Reciprocal of half-crystallization time ($1/t_{0.5}$) of the isotropic melt of PBT/HTH10 blends as function of crystallization temperature (Tc): -●- PBT, -□- 90/10, -■- 70/30, and -▲- 50/50 blends.

$$K = \frac{4}{3}\pi\frac{\rho_c}{\rho_a}G^3\bar{N} \qquad (2)$$

where ρ_c and ρ_a are the densities of the crystalline and amorphous phase, respectively. It is found that at Tc = 478K the values of $\bar{N}$ are lowered from $7.5\cdot10^8 cm^{-3}$ for pure PBT to $3.5\cdot10^6 cm^{-3}$ for the 90/10 blend and to $3.4\cdot10^7 cm^{-3}$ for the 70/30 blend. Thus, the decrease of the crystallization rate of PBT in the blends may be accounted for mainly by a depression of the activity of primary heterogeneous nuclei in the melt caused by the LCP component.

THERMODYNAMIC INTERACTION PARAMETERS

The compatibility of a polymer pair A and B in the mixtures may be roughly estimated at each composition on the basis of the values of the thermodynamic interaction parameters χ_{AB} and $(\chi_{AB})_{sp}$ of the two components:[15] The value of $\chi_{AB} = 0.194$ at 298K for the polymer pair PBT/HTH10 was evaluated by using the solubility parameters of the polymers.[15] This value results to be higher than that corresponding to the critical value $(\chi_{AB})_{cr} = 0.07 \div 0.04$, suggesting that the two polymers are incompatible at some compositions. The values of the spinodal $(\chi_{AB})_{sp}$ were calculated at each blend composition by the relation:

$$(\chi_{AB})_{sp} = \frac{1}{2}\left(\frac{1}{x_A v_A} + \frac{1}{x_B v_B}\right) \qquad (3)$$

where v_A and v_B are the weight fractions of PBT and HTH10 in the blend, respectively, and x_A and x_B are the degrees of polymerization expressed in terms of a reference volume,[15] taken as the molar volume of PBT at 298K. In Fig.6 the values of $(\chi_{AB})_{sp}$ are plotted as function of the composition of the blends for two different values of the degree of polymerization x of HTH10 and compared with the value of χ_{AB}. It is noted that $\chi_{AB} \lesssim (\chi_{AB})_{sp}$ for HTH10 contents lower than about

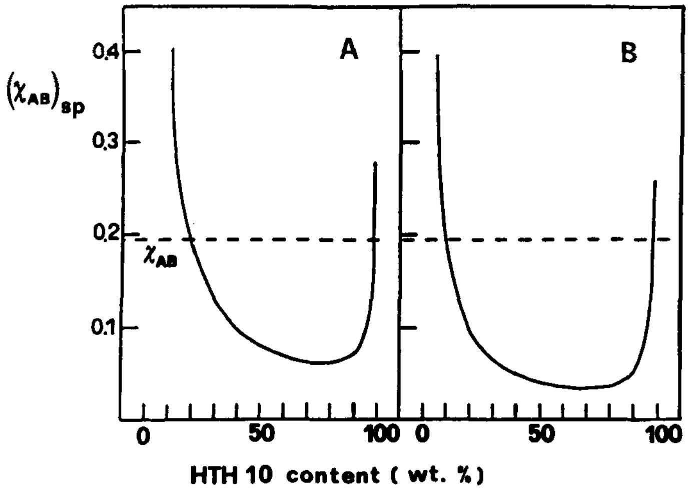


FIGURE 6. Spinodal thermodynamic interaction parameter $(\chi_{AB})_{sp}$ for PBT/HTH10 blends at 298K as evaluated for two different values of the degree of polymerization x for HTH10: A, x = 5; B, x = 10.

20%, thus indicating that a partial miscibility of the two polymers may occur at room temperature.

CONCLUDING REMARKS

The morphological examination of PBT/HTH10 samples, as obtained from solution or cooled from the isotropic melt, does not reveal macrophase separation of the polymer components, at least for HTH10 contents <50%. The analysis of the isothermal crystallization process of PBT from melt blends indicates that primary nucleation and growth rate of PBT spherulites are depressed by the HTH10 polyester. In blends cooled from the isotropic melt separation of the crystal phases of the two polymers occurs with contents of HTH10 ≥ 50%. The melting temperatures decrease with increasing HTH10 content, probably due to a diluent effect of the LCP, rather than to a morphological effect. Moreover, the glass transition behavior supports the occurrence of miscibility phenomena of the polymers in the amorphous phase, particularly in those blends in which HTH10 is the dispersed phase.

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