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Block copolymers with poly(ethylene terephthalate) and liquid crystalline polyester segments: effect of reaction time

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Summary

Block copolymers of poly(ethylene terephthalate) (PET) and a thermotropic liquid crystalline polyester have been synthesized by high temperature solution polycondensation. The influence of the reaction time on thermal behavior of the block copolymers has been determined by Differential Scanning Calorimetry (DSC). Block copolymers were also characterized by Carbon 13 Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA).

Introduction

Interest in thermotropic liquid crystalline polymers (LCPs) has increased due to their great potential in the combination of ease of processability and superior mechanical properties (1-4). Blending conventional thermoplastic polymers with LCPs can lead to easier processing and matrix reinforcement (5-7).

A block copolymer can be used as compatibilizer to improve the compatibility of polymer blends based on the miscibility and/or reactivity of block segments with at least one of the blend components (8). There are not many examples of block copolymers with liquid crystalline polyester chemically fixed to a non-thermotropic polymer. Block copolymers containing liquid crystalline segments should reveal better mechanical properties as compared with blends of homopolymers and their study is of increasing importance (9,10). Liquid crystalline polymers can act as reinforcing agents in a blend, however, one of the main drawbacks is poor adhesion to the matrix. Lack of adhesion appears in almost all blends containing LCPs. Our approach to overcome this problem is to use a block copolymer containing a liquid crystalline segment and another segment identical to the matrix.

The purpose of this work is to report the influence of the reaction time in the synthesis of the thermotropic block copolymers of poly(ethylene terephtalate) (PET) with 4,4′-dihydroxy-α,ω-diphenoxy decamethylene and terephthaloyl chloride comonomers.

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Experimental

Materials.

Poly(ethylene terephthalate) (PET), commercial resins received as pellets [η]=0.635dL/g measured in 0.5% (w/v) solutions in trifluoroacetic acid at 30°C, Mv=45300, from Rhodia S. A. were ground to help dissolution. 4,4′-dihydroxy-α,ω-diphenoxy decamethylene, was prepared by reation of hydroquinone and 1,10-dibromodecane, as described (11). Diphenyl ether (Aldrich Chemical Company Inc.), terephthaloyl chloride (Trade TCI Mark, Japan) and acetone (Reagen Quimibrás Indústrias Químicas S.A.) were used without purification.

Synthesis of the copolyesters.

In a 50mL reaction flask 1.2g (0.0674mmol) of poly(ethylene terephthalate) (PET) with 10mL of diphenyl ether were added. The flask was placed in a oil bath and heated to 180°C for 24h to dissolve PET before the addition of the comonomers. After cooling, 0.59g (1.65mmol) of 4,4′-dihydroxy-α,ω-diphenoxy decamethylene and 0.33g (1.63mmol) of terephthaloyl chloride were added to the flask. The mixture was heated to different temperatures for different times with a constant slow stream of dry N_2 to remove HCl completely (Table 1). The reaction mixture was precipitated while hot into acetone to prevent solidification, extracted in a Soxhlet with acetone and dried (10,12).

Table 1. Block copolymers synthesized (PET/LCP-60/40).

Block copolymer	Reaction time (h)	Reaction temperature (°C)	Yield wt %
COP(1)	20	160	76
COP(2)	40	200	89
COP(3)	60[a]	240	82

(a) this reaction was made in three stages: the mixture was heated to 180°C for 20h, to 240°C for 20h and to 200°C for 20h, as described in the literature (10)

Characterization of the copolymers.

The copolyesters were analyzed by FTIR (Perkin-Elmer 1720X infrared spectrophotomer): drift, number of scanning lines 50, and resolution 200cm^{-1}. IR spectra of copolyesters exhibited the characteristic bands of the aromatic rings, ether, hydroxilic, methylene, and ester groups.

Solid state ^{13}C NMR spectra were recorded on a 300MHz Bruker spectrometer. The ^{13}C NMR spectra show the characteristic chemical shifts of phenyl ether, phenyl ester, carbonyl and methylene groups. ^{13}C NMR and assignments of PET, LCP and COP(1) are given in Figure 1.

Polyesters often show a tendency for transesterification during processing. By comparing the ^{13}C NMR spectra of the homopolymers (PET and LCP) and the copolymer COP(1), Figure 1, it can be seen that there is no significant change in the chemical shifts. This behavior may be related to a low degree of transesterification, which are insufficient to be determined by this technic (5).

Thermogravimetric analysis was obtained by a Perkin-Elmer TGA-7 instrument at a heating rate of 10°C/min using nitrogen purge.

Phase transition temperatures were measured on a Perkin-Elmer DSC-7 instrument under a nitrogen flow with both heating and cooling rate at 20°C/min. The peak maxima were taken as the transition temperatures.

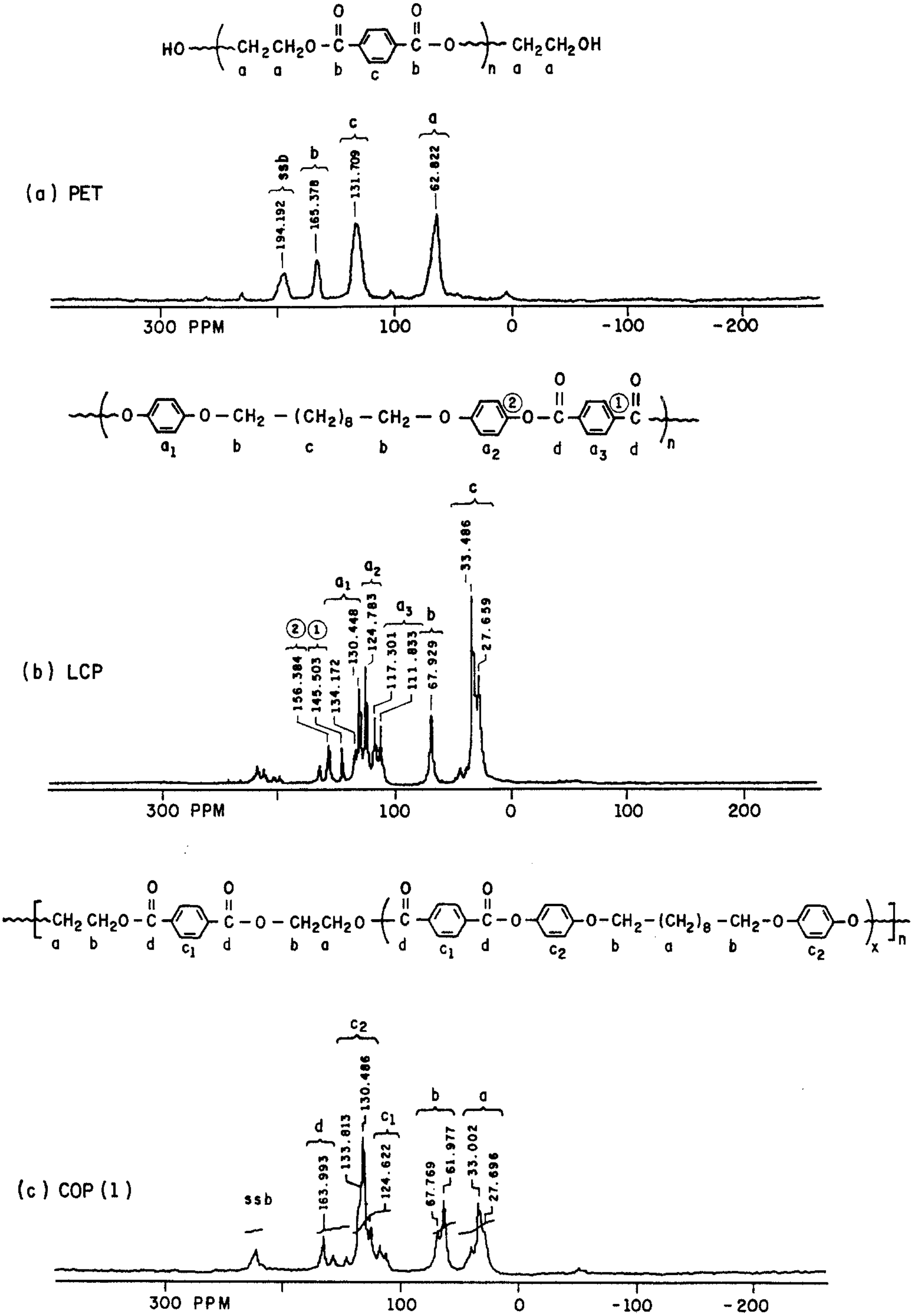

Figure 1. NMR spectra of ^{13}C CP/MAS of (a) PET, (b) LCP and (c) COP(1) at 75,5MHz.

None of the copolymers were soluble in common organic solvents, however they were soluble in strong acids, such as trifluoroacetic acid and p-chlorophenol, at elevated temperatures.

Results and Discussion

The block copolymers have been obtained and characterized as linear polymers. The IR and ^{13}C NMR data show that the structure of the polymers should correspond to the predicted structure (10,13):

$$\text{HO-PET-OH} + \text{ClOC-}\phi\text{-COCl} + \text{HO-}\phi\text{-O-(CH}_2\text{)}_{10}\text{-O-}\phi\text{-OH}$$

$$\downarrow$$

$$[\sim\text{PET-O-(OC-}\phi\text{-COO-}\phi\text{-O-(CH}_2\text{)}_{10}\text{-O-}\phi\text{-O-)}_x\sim]_n$$

The copolymers and the LCP listed in Table 2 showed liquid-crystalline behavior above their melting temperatures as observed on the hot stage of a polarizing microscope; this indicates that the extent of the degree of transesterification is very low (14,15).

The thermal behavior of block copolymers was studied by DSC. The transition temperatures are listed in Table 2. Previously, in order to determine the thermal stability of these polymers, thermogravimetric analysis was carried out under dynamic conditions under a nitrogen atmosphere.

Table 2. Properties of polymers from DSC[(a)] and TGA measurements.

Polymers	Tm (°C)	Ti (°C)	ΔT (°C)[(b)]	TGA[(c)]
LCP[(d)]	259	312	53	406
COP(1)	236	>312	-	391
COP(2)	237	>312	-	428
COP(3)	223	>312	-	403
PET	251	-	-	397

(a) values from DSC thermograms of the second heating cycle. (b) ΔT=Ti-Tm (Ti: isotropization temperature, Tm: melting temperature). (c) thermal stability, the temperature (°C) at which a 5% weight loss occurred. (d) this LCP was prepared in slurry using diphenyl ether as solvent by a method described in the literature (12).

The thermal stabilities of all thermotropic polyesters were determined in nitrogen by TGA, and the results obtained are summarized in Table 2. The thermal stability limit, which is taken as the temperature at which a 5% weight loss occurred, indicates that COP(2) has the best thermal stability for melt processing at elevated temperatures.

Table 2 shows that all copolymers have lower melting transitions than those of the homopolymers. Both segments in the block copolymers have a strong influence on their mutual crystallization behavior (16). This result confirms the observation that a reaction between a liquid crystalline polymer and a thermoplastic polymer leads to melting transitions below the transitions of both homopolymers. All copolymers underwent thermal decomposition before reaching isotropization temperature (17).

Different reaction times were evaluated for the synthesis of the copolymers. Copolymer made in 60 hours, COP(3), has the lowest Tm when compared to copolymers made in 20 or 40 hours. For COP(1) and COP(2) no significant variation was observed. The isotropization temperatures of the copolymers cannot be seen in the selected temperature range. It is possible that the Ti may be near or together with the degradation temperature. The copolymer made in 40 hours at 200°C, COP(2) in Table 1, had the best yield and is more stable at hight temperatures than COP(1) and COP(3). Figure 2 shows the DSC thermograms of the polymers.

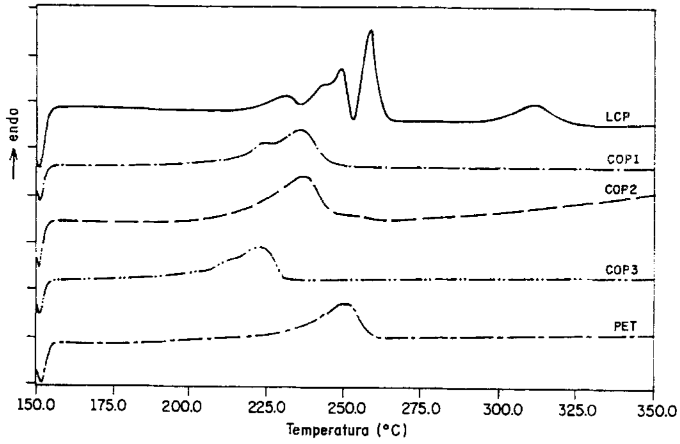

Figure 2. DSC thermograms of the polymers at a heating rate of 20°C/min.

Conclusion

In this paper block copolymers of poly(ethylene terephthalate) and a thermotropic liquid crystalline polyester have been studied with respect to the influence of the reaction time on thermal behavior of the block copolymers. Liquid crystalline behavior was observed in all the copolymers. The Tm of block copolymers is lower than that of the corresponding homopolymers. A reaction time of 40 hours leads to the best yield and a block copolymer with the best thermal stability. These block copolymers are being used in polymer blends with PET, PC and PBT and the results will be published separately.

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