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Segmented liquid crystalline copolyesters and blending with poly(ethylene terephthalate)

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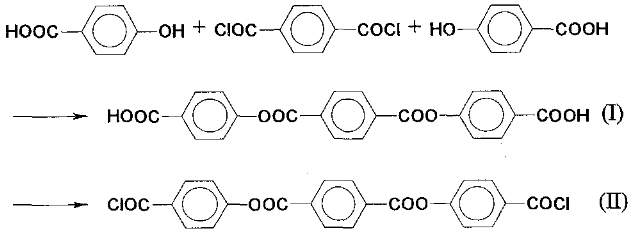
Summary

A series of segmented copolyesters with semi-regular structure was synthesized. In these copolymers, fully aromatic triad hard segments -HB-T-HB-, acting as mesogenic units, are linked each other by poly(ethylene terephthalate) (PET) segments with different average chain lengths as flexible spacers. The liquid crystallinity of the copolymers, i.e. the meso-phase forming ability, was studied against length of the spacer. In subsequent blending of these copolymers with PET matrix, results were compared with those from a commercial TLCP of PHB/PET random copolyester. Better mechanical properties were gained as expected since the compatibility of the segmented liquid crystalline copolyesters with the matrix is believed to be improved.

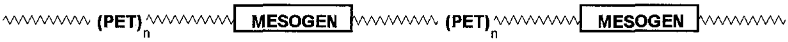
Introduction

In a previous paper(1), a method to prepare copolyesters of *p*-hydroxybenzoic acid and poly(ethylene terephthalate) (PHB/PET) with semi-regular structure was reported. The synthetic strategy in that described method was preparing an oligomeric PET with HB units blocked at both ends of the molecular chains, then coupling the oligomers with terephthaloyl chloride to form the -HB-T-HB- triad mesogen. In that case, it was rather difficult to guarantee the hard segment formation at the last coupling stage; and some side reactions in the first stage of oligomer preparation complicated the resulting chain sequence distribution(2).

In this work, a more direct strategy was adopted:



the mesogenic unit is pre-synthesized before incorporating with PET segments. In this way, a segmented PHB/PET copolyester with following schematic structure, HB(*n*), was obtained, in which the mesogenic units are exclusively -HB-T-HB- triad hard segments:



Experimental

Materials

PET resin ([η] 0.65) was supplied by YanShan Petrochemical Co.. A commercial TLCP Rhodester® C.L. (PHB/PET 60/40 random copolyester) was from Rhone-Poulenc Co.. Terephthaloyl chloride (TPC) was prepared from terephthalic acid by reaction with thionyl chloride in the presence of catalyst amount of *N,N*-dimethylformamide (DMF)(3). Bis-(hydroxyethyl) terephthalate (BHET), the "monomer" of PET, was prepared by controlled trans-esterification between ethylene glycol and dimethyl terephthalate (DMT) at temperature no more than 200°C(4). All other starting materials and solvents are obtained through commercial channel. They are used as received without further purification, except for those mentioned specifically in the synthesis sections for some strictly dehydrous processes.

Triad acid and acid chloride

Triad acid (I): 35 g *p*-hydroxybenzoic acid (HBA) (*c.a.* 0.25 mol) dissolved in 100 ml 1,1,2,2-tetrachloroethane (TCE) and 50 ml pyridine. A solution of 20.3 g TPC (0.1 mol) in 100 ml TCE was dropped in at room temperature. The mixture was then heated and precipitation occurred within a few minutes. Reflux continued for 1 hour before the reaction mixture was poured into 600 ml 95% ethanol + 100 ml concentrated HCl. Filtered after 1 hour and washed successively by water and acetone, the raw product of white powder after drying in vacuum oven at 120°C has a yield about 75-80% (exp. C: 64.66%, H: 3.725; theo. C: 65.02%, H: 3.473%).

Triad acid chloride (II): 29 g raw product I was mixed with 250 ml thionyl chloride $SOCl_2$ and 3.5 ml *N,N*-dimethylformamide (DMF) and refluxed at 80-90°C for 8 hours. After remove of the excessive $SOCl_2$ by distillation under reduced pressure, the product was broken up and washed in 150 ml ligroin. Filtered and washed, the product of yellowish white powder after drying at 100°C for 2 hours has a yield of 85%. Due to the handling difficulties, it was used in polymerization without further purification.

Polymerization

HB(1) ($n = 1$): 13.29 g raw product of II (*c.a.* 0.03 mol) and 7.62 g BHET (0.03 mol) were put together in 250 ml TCE. 15 ml pyridine and 10 ml triethylamine (TEA) were then added. Increase the temperature to 100°C for 2 hours, then reflux at 140°C for 48 hours. The reaction mixture of homogeneous dark brown solution was poured into 600 ml 95% ethanol and soaked for 1 hour. Filtered and washed successively by 200 ml 5% HCl, water, and acetone, the product of pale gray powder after drying at 100°C for 24 hours has a yield of 65%.

HB(3) ($n = 3$): 8.86 g raw product of II (*c.a.* 0.02 mol) and 4.96 g ethylene glycol (EG) (0.08 mol) were put together in 100 ml TCE. 40 ml pyridine and 25 ml triethylamine (TEA) were added. Increase the temperature to 100°C and heat for 24 hours. A solution of 12.18 g TPC (0.06 mol) in 100 ml TEC was dropped in after cooling. Reflux at 140°C for additional 24 hours. The reaction mixture was poured into 600 ml 95% ethanol and soaked for 1 hour. Filtered and washed successively by 200 ml 5% HCl, water, and acetone, the product of pale gray powder after drying at 100°C for 24 hours has a yield of 75%.

HB(7) ($n = 7$): 4.43 g raw product of II (*c.a.* 0.01 mol) and 4.96 g ethylene glycol (EG) (0.08 mol) were put together in 100 ml TCE. 40 ml pyridine and 25 ml triethylamine (TEA) were added. Increase the temperature to 100°C and heat for 24 hours. A solution of 14.21 g TPC (0.07 mol) in 100 ml TEC was dropped in after cooling. Reflux at 140°C for additional 24 hours. The reaction mixture was poured into 600 ml 95% ethanol and soaked for 1 hour. Filtered and washed successively by 200 ml 5% HCl, water, and acetone, the product of pale gray powder after drying at 100°C for 24 hours has a yield of 60%.

All the copolymers are post-polymerized in solid state at 180°C in vacuum for 24 hours to increase the molecular weight. The color of the products darkened after this treatment.

Measurements

Inherent viscosities η_{inh} were measured in *p*-chlorophenol at 45°C. Only one point at a concentration of about 0.5 g/dl was measured.

The chemical composition and chain sequence distribution of the copolymers were determined by ^{1}H-NMR spectra obtained from Varian UNITY200 spectrometer, using deuterized trifluoroacetic acid as solvent at ambient temperature.

The optical texture and melting behavior were observed on a hot-stage with a Carl-Zeiss PHMK 80/2603 cross-polarized microscope up to the temperature of 350°C. The thermal properties of the copolymers and the polyblends were studied on a Perkin-Elmer DSC7 differential scanning calorimeter.

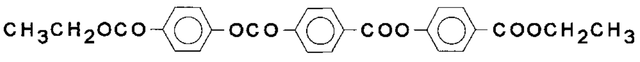
Blending

All the compounding materials were dehumidified in vacuum at 120°C before blending and molding. Samples were blended in a CS-194 Mini-Max extruder from the Custom Scientific Instrument Inc. at 250°C (280°C for the commercial TLCP compositions). Blending parameters were set to keep residential time of the materials in the extruder no more than 1 minute. Cylindrical dumb-bell shaped testing species (with a testing length 8.99 mm and diameter 1.59 mm) were prepared in a CS-183 Mini Max molder at 280°C (300°C for the TLCP containing samples) for 2 minutes, with a mold temperature of 180°C. The inter-chain trans-esterification reaction between the LC segments, as well as between the LCPs and PET, were minimized under such conditions. The molded species were subsequently tested in the CS-183 evaluating system for mechanical properties.

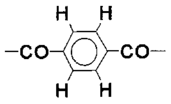
Results and Discussion

Characterization

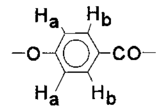
From the NMR spectrum of a model compound:



the proton chemical shifts of the triad hard segment in the copolyesters can be assigned accurately:



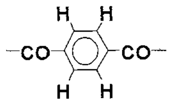
$\delta = 8.48$



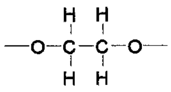
$\delta = 7.45, 7.41\ (H_a); 8.29, 8.25\ (H_b)$

or $\delta \approx 7.0\ (H_a); 8.1\ (H_b)$ at chain ends

and the chemical shifts in PET segment are known:



$\delta = 8.25$



$\delta = 4.90$

or $\delta = 4.70$ and 3.70 at chain ends

Then the molecular weights and the actual compositions can be calculated accordingly (**Table 1**).

Table 1. Characterization of the copolymers

	HB(1)	HB(3)	HB(7)
$\overline{n}$	0.5	2.0	4.6
$\overline{M}_n$	5,350	3,770	3,660
$\eta_{inh.}$	0.219	0.241	0.147

Liquid Crystallinity

Some properties of the HB(*n*) series segmented copolymers were already discussed in previous paper(1). From the results in **Table 2**, however, the copolymers synthesized in this work have quite different behaviors to the phase diagram previously reported. For example, all the three samples are thermotropic and the isotropic transition temperatures are all above 350°C. This is supposed to be due to the different chain sequence distribution from the different synthetic strategies, especially in the mesogen structure, which ought to be 100% -HB-T-HB- triad in the present work, but probably not so perfect in the previous. The texture of the mesophase observed in the polarized microscope is also a sort of two-phase system as previously reported. With increase of the spacer length, the birefrigence of the mesophase domain is getting weaker and weaker, and the portion of the mesophase smaller and smaller. No isotropic transitions were observed up to 350°C. DSC results are in agreement with the optical observation. The heat of fusion increases steadily with increasing spacer length, as noticed in many other cases(2).

Table 2. Thermal behaviors of the copolymers

	HB(1)	HB(3)	HB(7)
T_m°C (visual)	225-250	235-245	230-235
T_m°C (DSC)	221, 237	237	207, 203
ΔH_f (J/g)	16	46	59

Blending with PET

Because the copolymers obtained are of rather low molecular weight according to the inherent viscosity (**Table 1**), their own mechanical properties are very weak. But as shown in the following figures (**Figure 1-3**), the blends with PET have a better result than one might expect, especially compared with those from the stronger, but less compatible, commercial TLCP (**Figure 4** and **5**). The effects as a compatibilizer in tertiary blending system, however, are not significant (**Figure 6**).

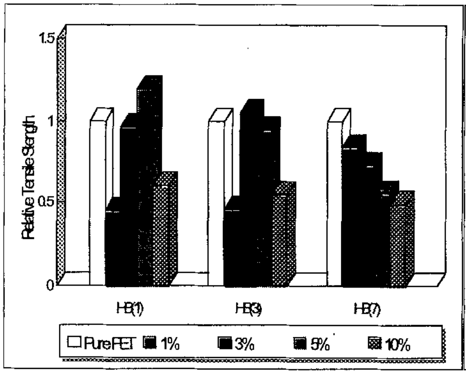


Figure 1. Tensile strength of PET blends with different amounts of HB(*n*)

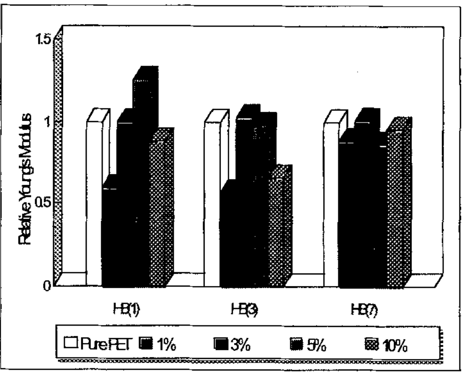


Figure 2. Modulus of PET blends with different amounts of HB(*n*)

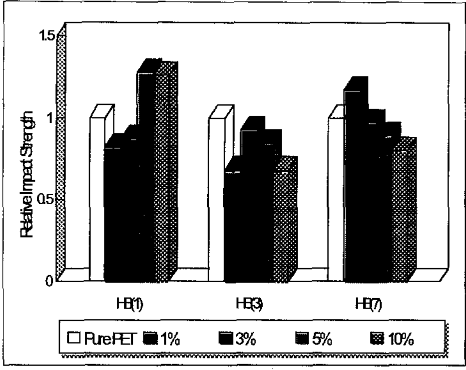


Figure 3. Impact strength of PET blends with different amounts of HB(*n*)

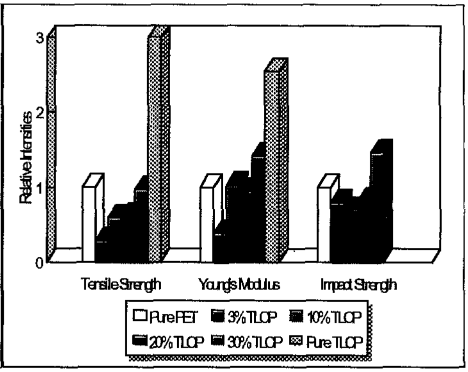


Figure 4. Mechanical properties of PET blends with different amounts of the commercial TLCP

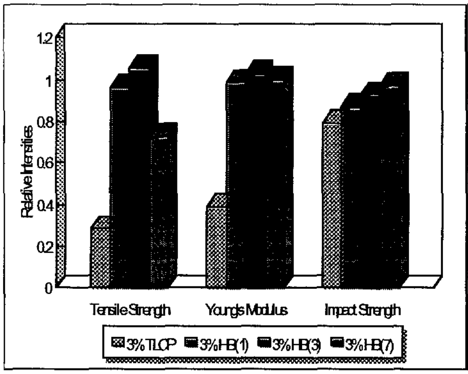


Figure 5. Comparison of mechanical properties of PET blends with different HB(*n*) and with the commercial TLCP

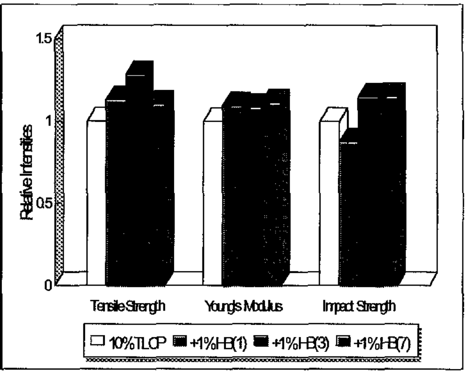


Figure 6. Effect of HB(*n*) as a compatibilizer in PET and the commercial TLCP blending system

Conclusion

With a new synthetic strategy, a series segmented PHB/PET copolyesters containing perfect -HB-T-HB- triad mesogenic hard segment and different lengths PET spacers can be obtained. Thermal properties and liquid crystalline inclination of these materials with semi-regular chain structure are of interest for further investigations. Their expected compatibility with PET matrix in polyblends shows better mechanical properties in the resulting *in-situ* composite than that from a stronger but less compatible commercial TLCP of PHB/PET random copolymer.

References:

1. Yan Qing, He Jiasong (1992) Polym Bull 29: 633

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3. Tomita K (1976) Polymer 17: 221