

Copolyesters. IV. Copolyesters of Polycaprolactone and Poly(butylene Terephthalate)

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Synopsis

The copolyesters of poly(butylene terephthalate) and polycaprolactone were prepared by melt polycondensation. The charged form of the caprolactone unit was either caprolactone or polycaprolactonediol. The chemical structure of the copolyesters was investigated by proton NMR. It was found that the content of the caprolactone unit in copolyesters was lower than the charged value. The copolyesters prepared from both caprolactone and polycaprolactonediol were found to be random copolymers. T_m , T_g , and crystallinity of the copolyesters decreased as the content of caprolactone unit increased due to the copolymerization effect. The tensile strength, modulus, and hardness decreased as the content of caprolactone unit increased, which was consistent with the trend of crystallinity.

INTRODUCTION

Copolymerization is one of the common methods to modify polyesters. Caprolactone was used to modify poly(butylene terephthalate) (PBT) by reacting PBT chips with caprolactone, and thermoplastic elastomers were obtained.^{1,2}

In this paper, we prepared copolyesters of PBT and polycaprolactone (CPO) by direct melt polycondensation of 1,4-butanediol, terephthalic acid, and caprolactone or polycaprolactonediol. The chemical structure, thermal properties, and tensile properties were determined to investigate the composition–property relationship.

EXPERIMENTAL

Terephthalic acid was supplied by China American Petrochemical Co., Ltd. (Taiwan). 1,4-Butanediol, caprolactone, and tetrabutyl orthotitanate were all Merck reagent grade. Polycaprolactonediol with molecular weight of 2000, 1250, and 530 were Aldrich reagent grade.

The PBT/CPO copolyesters were prepared by two methods. First (method 1), $(1 - x)$ mole of terephthalic acid, $2(1 - x)$ mole of 1,4-butanediol, x mole of caprolactone, and 0.2 wt % of tetrabutyl orthotitanate (used as catalyst)

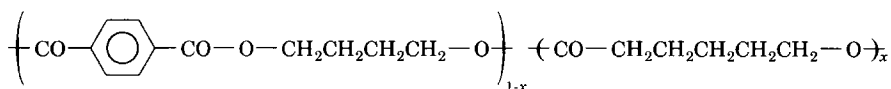
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were reacted at 200–210°C. During 2 h of reaction, water was distilled out. Then, the reaction temperature was raised to 240–250°C and vacuum was applied slowly. After most 1,4-butanediol was distilled out, high vacuum (0.5 torr) was applied for 2 h. In the second method (method 2), copolyesters were prepared by the same procedures except polycaprolactonediacids with molecular weight of 2000, 1250, and 530 were used instead of caprolactone.

The intrinsic viscosity (IV) of the copolyesters was determined in phenol/TCE(syn-tetrachloroethane) (60/40 wt/wt) at 30°C. The thermal properties were determined by Du Pont 910 DSC at a heating rate of 20°C/min. The proton NMR (nuclear magnetic resonance) spectra in CF₃COOD were determined by a 400 MHz NMR (Bruker AM 400 NMR) (d-lock) at 30°C. The sheet samples were prepared by compression molding. The tensile properties at 25°C were measured by a universal test machine (China Materials Technology and Science, Ltd., Model AC-2T) at crosshead speed of 5 mm/min according to ASTM D638 and the hardness at 25°C was measured by a Shore D Durometer (Ueshima Seisakusho Ltd.) according to ASTM D2240.

RESULTS AND DISCUSSION

The mol % of caprolactone unit is used here to characterize the charged composition and the composition of the copolyesters based on x :



The charged mol % of caprolactone of the copolyesters in the preparation step and corresponding synthesis method are shown in Table I. The intrinsic viscosities (IV) of all copolyesters were greater than 0.7 dL/g as shown in Table I.

TABLE I
Charged Composition, Determined Composition, and IV of the Copolyesters

Notation	Preparation method ^a	Charged mol % of caprolactone	mol % of caprolactone ^b	IV ^c (dL/g)
PBT/CPO1	1	21	18	0.79
PBT/CPO2	1	35	28	1.00
PBT/CPO3	1	45	34	1.00
PBT/CPO4	1	58	46	0.96
PBT/CPO5	1	66	53	1.04
PBT/CPO6	2*	21	17	0.90
PBT/CPO7	2*	35	27	0.97
PBT/CPO8	2*	45	32	0.96
PBT/CPO9	2*	58	44	1.10
PBT/CPO10	2 [†]	35	26	0.93
PBT/CPO11	2 [‡]	35	26	0.89

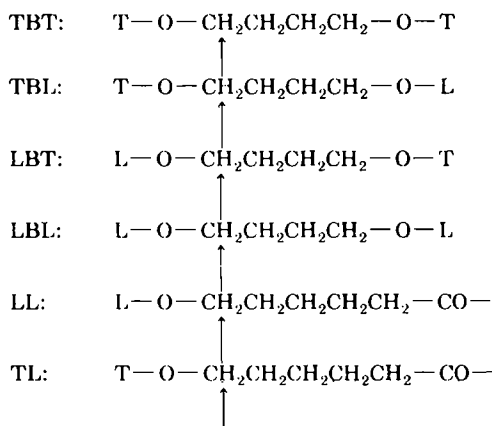
^aThe molecular weight of polycaprolactonediacids is: *1250, [†]2000, and [‡]530.

^bThe mol % of caprolactone unit in copolyesters determined by proton NMR analysis.

^cIntrinsic viscosity determined in phenol/TCE at 30°C.

The proton NMR spectra of PBT, CPO, and blend of PBT and CPO are shown in Figure 1. The assignment of the peaks for PBT and CPO is also shown in Figure 1. The proton NMR spectrum of blend of PBT and CPO is just the superposition of those of PBT and CPO.

The proton NMR spectra of PBT/CPO4 and PBT/CPO9 are shown in Figure 2. The proton NMR spectra of PBT/CPO4 and PBT/CPO9 were different from those of the blend of PBT and CPO. The peaks in the range from 3.8 to 4.6 ppm are worth noting. The peaks in this region were due to the resonance of methylene protons attached to carboxylate group. There were six resonance peaks corresponding to different sequences of different carboxylated methylene protons. By comparing with the resonance peaks of PBT and CPO, each peak is assigned in Table II. The methylene protons of interest are indicated by the arrow as follows:



where T is the terephthalate unit and L is the caprolactone unit.

The presence of TL sequence peak indicated that the terephthalate unit was esterified with the caprolactone unit in both PBT/CPO4 and PBT/CPO9. The chemical structure of the two copolyesters can be analyzed from the four resonance peaks of the four sequences of butylene unit, TBT, TBL, LBT, and LBL. The degree of randomness (B) can be calculated by^{3,4}

$$B = I_{\text{TBL}} / (I_{\text{TBL}} + I_{\text{TBT}}) + I_{\text{LBT}} / (I_{\text{LBT}} + I_{\text{LBL}})$$

where I denotes the peak area of each sequence peak. For random copolymers, $B = 1$, for blends, $B = 0$, for block copolymers, B is close to 0, and for alternative copolymers, $B = 2$.

B was found to be 1.00 for PBT/CPO4 and 0.99 for PBT/CPO9. Thus the two copolyesters were random copolymers. The models for the formation of PBT in the presence of tetrabutyl orthotitanate have been described by Pilati and co-workers.⁵⁻⁷ Both the direct esterification and transesterification reactions were catalyzed tetrabutyl orthotitanate. Although the forms of initial caprolactone units of the two synthesis methods were different, the transesterification reaction rendered random distribution; thus copolyesters prepared from the two methods exhibited almost the same structure (random type).

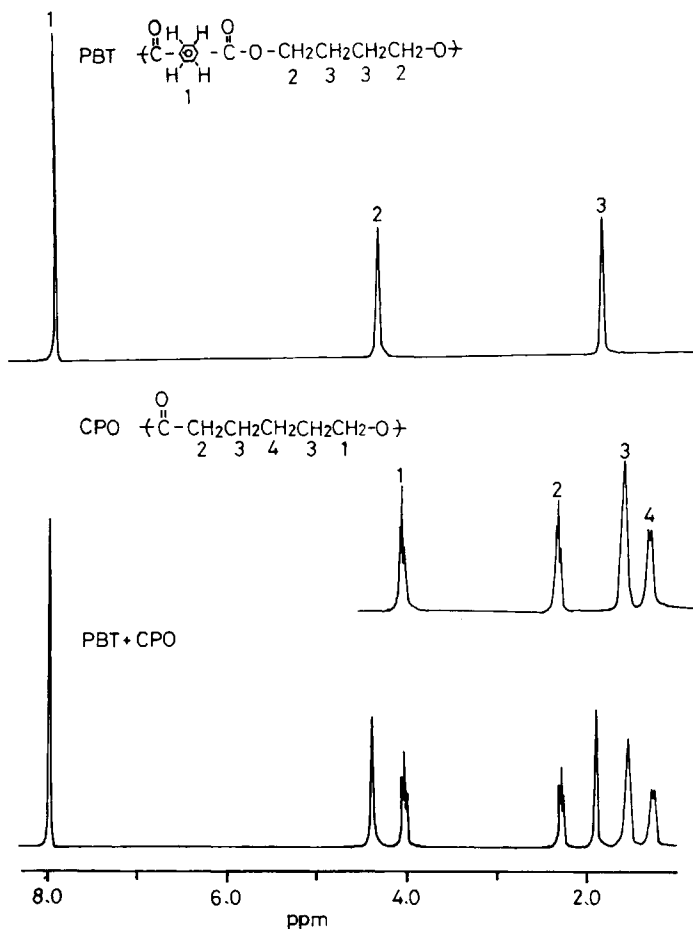


Fig. 1. Proton NMR spectra of PBT, CPO, and blend of PBT and CPO.

The peak area ratio of peak a and peak b (shown in Fig. 2) can be used to determine the real composition of the copolyesters. Peak a was due to the resonance of aromatic protons of the terephthalate unit, and peak b was due to the resonance of the methylene protons attached to carboxylate group (peak 2 of CPO in Fig. 1) of the caprolactone unit. Thus, the mol % of the caprolactone unit of the copolyesters can be calculated by

$$x = (I_b/2) / [(I_b/2) + (I_a/4)] * 100\%$$

The determined mol % of caprolactone unit of the copolyesters is shown in Table I. The mol % of the caprolactone unit of the copolyesters was found to be lower than the charged value. At the first reaction stage (at 200–210°C), direct esterification of 1,4-butanediol and terephthalic acid led to bis(hydroxybutyl) terephthalate and oligomers. In addition, reaction between 1,4-butanediol and caprolactone or polycaprolactonediol occurred and resulted in some intermediates such as $\text{HO}-(\text{CH}_2)_4-\text{O}-\text{CO}-(\text{CH}_2)_5-\text{OH}$ (compound I). In order to prepare high molecular weight copolyesters, high

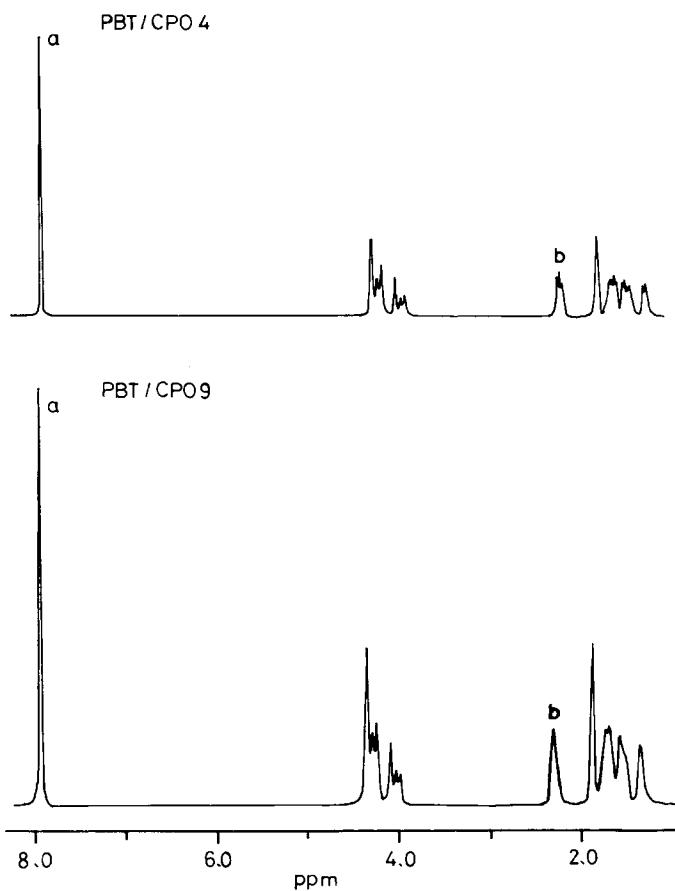


Fig. 2. Proton NMR spectra of PBT/CPO₄, and PBT/CPO₉.

TABLE II
Assignments of Different Carboxylated Methylene Protons with Different Sequences

Sequence	Chemical shift (ppm)
TBT	4.33
TBL	4.27
TL	4.22
LBT	4.08
LBL	4.02
LL	3.97

vacuum was applied to evacuate the excess 1,4-butanediol to force the equilibrium favor polymerization at the final stage, some intermediates derived from the caprolactone unit such as compound I were distilled out due to the more volatile nature as compared to those derived from the terephthalate unit. Thus, the content of caprolactone unit in the copolyesters was lower than the charged value.

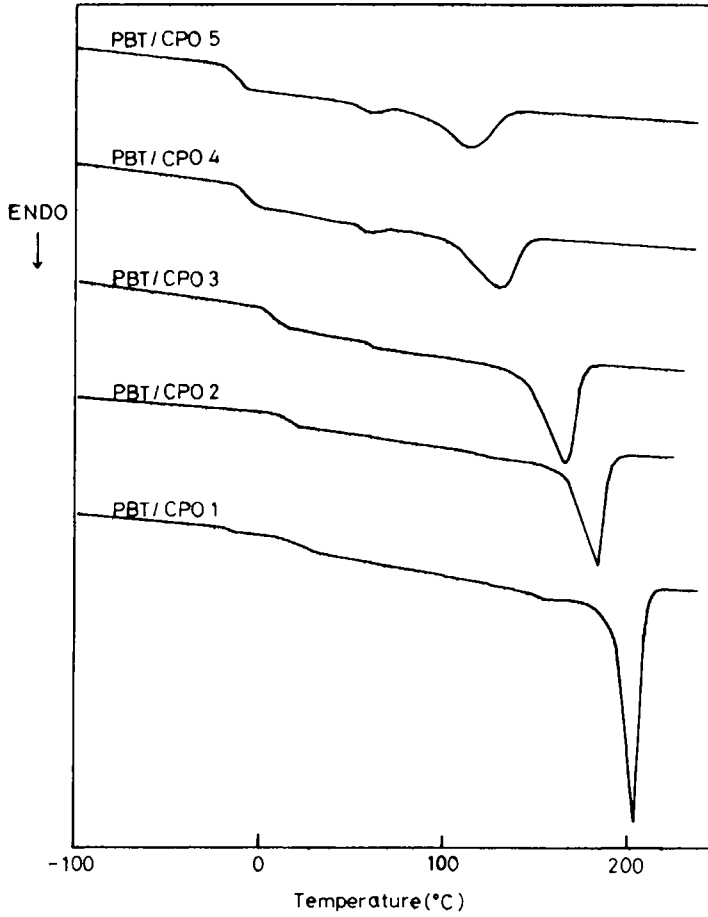


Fig. 3. Typical DSC thermograms of the copolyesters.

TABLE III
Thermal Properties of the Copolyesters

Notation	T_m (°C)	T_g (°C)	Crystallinity ^a
PBT/CPO1	202	23	29.7
PBT/CPO2	182	13	21.5
PBT/CPO3	164	7	18.6
PBT/CPO4	128	-9	14.1
PBT/CPO5	114	-17	10.0
PBT/CPO6	202	26	28.9
PBT/CPO7	183	15	24.1
PBT/CPO8	167	9	19.8
PBT/CPO9	134	-4	14.9
PBT/CPO10	184	15	25.3
PBT/CPO11	183	16	24.6

^aCrystallinity was obtained by dividing the heat of fusion of each copolyester by that of full crystalline PBT (34.5 cal/g).⁸

TABLE IV
Tensile Properties and Hardness of the Copolyesters

Notation	Tensile strength (kg/cm ²)	Modulus (kg/cm ²)	Elongation (%)	Hardness (Shore D)
PBT/CPO1	410 ± 10	6100 ± 200	40 ± 20	77
PBT/CPO2	210 ± 10	2800 ± 200	40 ± 20	67
PBT/CPO3	190 ± 10	2100 ± 100	160 ± 40	62
PBT/CPO4	100 ± 5	900 ± 50	400 ± 150	47
PBT/CPO5	70 ± 5	600 ± 50	250 ± 150	37
PBT/CPO6	410 ± 20	5800 ± 200	25 ± 10	77
PBT/CPO7	250 ± 20	3000 ± 200	50 ± 20	70
PBT/CPO8	220 ± 10	2600 ± 200	400 ± 150	63
PBT/CPO9	110 ± 5	1050 ± 100	250 ± 100	49
PBT/CPO10	300 ± 20	3400 ± 200	60 ± 30	71
PBT/CPO11	250 ± 30	3200 ± 200	40 ± 20	70

The DSC thermograms of some copolyesters are shown in Figure 3. The melting temperature (T_m), glass transition temperature (T_g), and crystallinity of the copolyesters are listed in Table III. Since the copolyesters were found to be random copolymers, T_m decreased as the content of caprolactone unit increased due to copolymerization effect. The crystallinity decreased as the content of caprolactone unit increased as well. There was no significant difference in T_m for the copolyesters prepared by the two methods with the same charged composition because the chemical structure and composition were almost the same.

Since T_g of CPO (-60°C) was lower than that of PBT (30°C), T_g of the copolyesters also decreased as the content of caprolactone unit increased.

The tensile mechanical properties and hardness of the copolyesters are shown in Table IV. The tensile strength and modulus decreased as the caprolactone content increased and the trend was consistent with the crystallinity (Table III). The elongation at break became very high as the mol % of caprolactone unit reached about 35%: this contributed to the more flexible caprolactone unit.

CONCLUSION

The copolyesters of poly(butylene terephthalate) and polycaprolactone were prepared by two methods from either caprolactone or polycaprolactonediol. The copolyesters from the two methods were found to be random copolymers through analysis of proton NMR spectra. The reason for almost the same structure was due to transesterification in the synthesis stage. Because the caprolactone unit was more volatile than the terephthalate unit. The mol % of the caprolactone unit of the copolyesters was considerably lower than the charged value. The thermal properties, tensile properties, and hardness were determined. T_m and T_g decreased as the content of caprolactone unit increased due to copolymerization effect; so did the crystallinity. The tensile strength, modulus, and hardness decreased as the caprolactone unit content increased, consistent with the trend of crystallinity of the copolyesters.

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