Relationship between Physical Properties and Chemical Structures of Poly(ethylene terephthalate-*co*-ethylene isophthalate)

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ABSTRACT: A series of copolyesters based on different ratios of polyethylene terephthalate (PET) to polyethylene isophthalate (PEI) have been synthesized. With the involvement of PEI, the copolyesters become less crystallizable and even amorphous when PEI content is above 20%. The WAXD profiles of the crystallizable copolyesters infer that the crystals come from PET homopolymer. DSC cooling runs indicated that the copolyesters with PEI no more than 15% are easily crystallizable, while the copolyester with 20% PEI is not easily crystallized at a cooling rate above 5°C/min. Heating runs indicated that the copolyesters with PEI below 20% show melting processes. Nonuniform results were provided by WAXD and DSC, however, the effect of PEI on the ability of crystallization was deduced similarly from WAXD and DSC. Glass transition temperatures have been measured by DSC. Due to the flexibility of PEI chain, glass transition temperatures of the copolyesters decrease linearly with increasing composition of PEI as predicted by the principle of additive contribution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1191–1195, 1999

Key words: copolyesters; polyethylene terephthalate; polyethylene isophthalate; glass transition temperature

INTRODUCTION

Polyethylene terephthalate (PET) is one of the advanced polymers with excellent thermal and chemical resistance and mechanical properties. It is exclusively used as films for packaging such as bottles for beverages, as seen in routine life, and laminate layer in inner and outer layers of cans for beverage. Although it has higher melting and glass transition temperatures, its drawback lies in the brittleness of its final products,[1] so that it is of necessity to improve its flexibility.

Copolymerization is a good way to modify its physical properties.[2] In this study, copolyesters based on different ratios of polyethylene terephthalate to polyethylene isophthalate have been synthesized. The effects of PEI content on physical properties have been discussed herein. The ability of crystallization were examined by WAXD and DSC, and glass transition temperatures (T_g) were explored by DSC.

EXPERIMENTAL

Materials

The copolyesters were prepared as outlined in Scheme 1, where x and y refer to the molar ratios of PET to PEI, when $x = 1$, the polymer is a PET homopolymer. The intrinsic viscosities of the copolyesters have been listed in Table I. In the following, the ratio of PET to PEI will be used to

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Scheme 1

denote the copolyesters, for example, 100/0 and 0/100 are used to refer to PET and PEI homopolymers, respectively.

DSC Measurement

DSC measurements were conducted on a Seiko differential scanning calorimeter (Model DSC-220CU). The specimens weighed 4 to 6 mg. During the measurement, a dried N_2 gas was purged at a constant flow rate. First, the specimens were

Table I   The Viscosities of the Copolyesters

Copolyester	Intrinsic Viscosity[a]
100/0	0.563
90/10	0.537
85/15	0.502
80/20	0.503
75/25	0.531
70/30	0.547
60/40	0.524
50/50	0.504
40/60	0.542
30/70	0.451
20/80	0.389
10/90	0.380
0/100	0.372

[a] The intrinsic viscosity was measured in the solution of trifluoroacetic acid at 30°C by means of a Ubbelohde viscometer.

heated to 300°C at a rate of 20°C and held for 10 min to remove the residue thermal history. The first cooling and second heating runs were recorded. The cooling or heating rates will be mentioned in the specified circumstances.

WAXD Measurement

The specimens for WAXD measurements were prepared by melt pressing at 280° with a thickness of 1.5–1.7 mm. The melts were cooled to room temperature simultaneously. WAXD measurements were performed at room temperature using a Rigaku vertical diffractometer (MODEL RINT 2500) with a rotating anode X-ray generator. The CuKα radiation source was operated at 30 kV and 40 mA. A divergence slit of 1° was employed, together with two receiving slits of 0.15°. All the measurements were carried out in $\theta/2\theta$ mode. The specimens were scanned in the range of 4–70°, with an interval of 0.01° at a scanning speed of 0.1°/min.

RESULTS AND DISCUSSION

Figure 1 illustrates WAXD patterns of the copolyesters. It is easily noted that the copolyesters with PEI less than 20% show crystalline peaks. The relevant crystalline positions (2θ) are the same as those of the PET homopolymer. As a conseqence,

Figure 1 WAXD patterns for the copolyesters 100/0, 90/10, 80/20, 70/30, and 0/100.

Temperature (°C)

Figure 2 DSC thermograms of copolyesters 100/0, 90/10, and 85/15. (The cooling rate is 5°C/min; the heating rate is 10°C/min.)

it can be deduced that the crystals come from the PET homopolymer. The copolyesters with more than 20% PEI are amorphous. This result confirms that the copolyester becomes less crystallizable with involvement of PEI. Similar results have been demonstrated by DSC, however a nonuniform conclusion is reached because of the difference between the two characterization methods. Molecular motions on WAXD determination are prohibited; on the other hand, molecules in a speciment during DSC measurement are active. In this sense, WAXD is relative static, while DSC is dynamic.

Figure 2 presents examples of DSC diagrams of the copolysters. The copolyester 80/20 cannot be crystallized at a cooling rate higher than 2°C/min. Only at a very slow rate (e.g., 2°C/min) does the copolyester 80/20 show a very weak crystallization peak. When heated, melting processes were detected for the copolyester 80/20, even when it had been crystallized at a cooling rate higher than 2°C/min (e.g., 5°C/min as referred to in Fig. 3). Here it is proposed that during heating, molecular motions result in rearrangement so that the crystals may be produced.

T_c and ΔH_c are crystallization temperature and heat of crystallization during cooling runs, T_m and ΔH_m refer to melting temperature and heat of fusion during heating runs. Figure 4 shows dependence of T_m and T_c on PEI content. Figure 5 illustrates ΔH_c and ΔH_m changing with PEI content. Both T_c and T_m decrease with increasing PEI content. It suggests that the crystals grow imperfectly, as PEI content increases. It is noted that both ΔH_c and ΔH_m decrease when the content of PEI is high. The crystallinity (W_{ch}) of the

copolyesters can be characterized by the following equation:[3]

$$W_{ch} = \frac{\Delta H_m}{\Delta H_m^0} \tag{1}$$

Temperature (°C)

Figure 3 DSC thermograms of the copolyester 80/20. (a and b runs show DSC thermograms during cooling at the rate of 2 and 5°C/min, respectively. c and d runs represent DSC thermograms during heating at the rate of 10°C/min, following a and b runs respectively.)

Figure 4 Dependence of T_m and T_c on PEI content. (Up triangle and circle symbols refer to T_m and T_c, respectively; solid and open marks refer to the specimens formed at the cooling rates of 5 and 10°C/min, respectively.)

Figure 6 Correlation between T_g and PEI content. (●, experiment results; ○, predicted by principle of additive contribution; solid line refers to fitting for linear relation between T_g and PEI content based on experiment result, while dotted line refers to fitting based on the principle of additive contribution.)

where ΔH_m^0 refers to heat of fusion for the equilibrium crystal. As mentioned previously, the crystals originate from PET homopolymer, so that ΔH_m^0 for them refers to that of the PET homopolymer. As a result, the crystallinities of the polyesters 100/0, 90/10, 85/15, and 80/20 only depend on ΔH_m. It can be concluded that the crystallinity decreases with increasing PEI content.

With the involvement of PEI, the copolyesters become less crystallized, even amorphous, when PEI content is above 20%. The crystals become imperfect if PEI content is high.

Glass transition temperature (T_g) of the copolyester is also affected by PEI content. Although there are many factors that influence T_g, the most important factor is the heating rate.[4] In this article, to study the effect of PEI on T_g, the heating rate is fixed at 5°C/min.

In this case PEI shows a lower glass transition temperature than PET, due to flexible conformation, from the structural point of view. Figure 6 shows dependence of the glass transition temperature on PEI content. The experimental results fit those predicted by additive contribution[5] to the glass transition temperature. The glass transition temperature of the copolyesters decreases linearly with PEI content.

CONCLUSION

Polyethylene isophthalate (PEI), in a series of copolyesters based on different ratios of polyethylene terephthalate (PET) and polyethylene isophthalate (PEI), affects physical properties. With involvement of PEI, the copolyester becomes less crystallizable and even amorphous when PEI content is above 20%. The crystallinities of the crystallizable copolyester become lower, and the crystals grow imperfectly, when PEI content increases. The glass transition temperature of the copolyesters decrease linearly with PEI content, as predicted by the principle of additive contribution.

Figure 5 Dependence of ΔH_m and ΔH_c on PEI content. (Symbols are the same as those in Fig. 4.)

REFERENCES

1. Tsutsumi, N.; Nagata, M. In Encyclopedia of Polymeric Materials; Salamone, J. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1996, p. 6110, vol. 9; and reference therein.
2. Tirrell, D. A. In Encyclopedia of Polymer Science and Engineering; Kreschwitz, J. I., Ed.; John Wiley & Sons: New York, p. 194, vol. 14, 2nd ed.
3. Mo, Z.; Zhang, H. J Macromol Sci Rev Macromol Chem Phys 1995, C35, 555.
4. Plazek, D. J.; Ngai, K. L. In Physical Properties of Polymers: Handbook; Mark, J. E., Ed.; AIP Press: New York, 1996, p. 139; and references therein.
5. Van Krevelen, D. W. Properties of Polymers: Their correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions; Elsevier Science Publishing Company Inc.: New York, 1990, 3rd ed.