

STUDY ON SOLID STATE POLYCONDENSATION OF POLYETHYLENE TEREPHTHALATE COPOLYMERS*

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ABSTRACT

The kinetic data of solid state polycondensation of PET and its copolymers are determined. It is shown that the reaction rate of copolycondensation is higher than that of PET polycondensation, and increases with the comonomers content. But the reaction rate of copolycondensation in melt state of this kind of copolymers is lower than that of PET. It is considered that the chemical reactivity of comonomer is the main factor which affect the polycondensation in melt state, whereas the aggregative structure of the polymer is the main factor in solid state. The crystallinity and crystallite size of the copolymers have been measured by X-ray method.

INTRODUCTION

The effect of crystalline structure on solid state polycondensation of polyethylene terephthalate (PET) was studied by some authors.^[1-4] The influence of crystallinity of PET on the reaction kinetics in solid state polycondensation was reported by T. M. Chang.^[1] His result indicated that the higher the crystallinity of the polymer, the lower the reaction rate. The influence of crystallinity on diffusion of small molecules (e. g. ethylene glycol or water) was considered. S. Y. Chang's study^[2] also indicated that in solid state polycondensation of PET the kinetics depends on the precrystallization condition, and the diffusion of small molecules is affected by the increase of crystalline region. But another result was reported by Bamford^[3], in his study, similar rate constant of solid state polycondensation of PET was obtained for the samples before and after heat treatment.

In this paper the solid state polycondensation of PET and its copolymers are studied and the results indicate that the major factor influencing reaction rate in solid state polycondensation is the aggregative structure of the polymers.

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EXPERIMENTAL

Materials

Bishydroxyethylene terephthalate (BHET) was prepared by direct esterification of terephthalic acid (TPA) with ethylene glycol (EG).

Modified BHET was prepared by direct esterification of TPA and isophthalic acid (TPA) with EG (BHET-I), or by TPA and adipic acid (AA) with EG (BHET-A).

The catalysts of polycondensation $\text{Co}(\text{OAc})_2$ and Sb_2O_3 are commercial products, they were added in the stage of direct esterification.

Synthesis

Polycondensation of monomers (BHET, BHET-I, or BHET-A) was carried out in 0.5 L stainless steel reactor, the temperature of reaction was 280°C . Remaining pressure of the system is 70 Pa.

Solid state polycondensation was carried out in glass ampoule at controlled temperature. The reaction temperature was 215°C . Remaining pressure of the system is 40 Pa. Samples for solid state polycondensation are PET and its copolymers obtained by melt state polycondensation and chipped in size of $\phi 1.5 \times 5\text{mm}$.

Analysis

Intrinsic viscosity $[\eta]$ of samples was measured at 25°C using the solvent of phenol-tetrachloroethane (1 : 1 w/w) mixture with U-viscometer. Since the comonomer content is small, in the calculation of $\bar{M}_n$ of copolymers with Mark-Houwink's equation, the values of K , α were chosen as the same values as that for homopolymer.

X-ray analysis was carried out by using D/Max-rA diffractometer (Japan Physical Electrical Machine Company). Amorphous films ($35 \times 13 \times 0.042\text{mm}$) of PET and its copolymers were taken to undergo precrystallization (160°C , 1hr.) and solid state polycondensation (215°C , 2hr.), and then the films were examined by X-ray analysis. The method used was computer separating peaks, and calculated with Scherrer's equation.

RESULTS AND DISCUSSIONS

In this study two kinds of PET copolymers were used for solid state polycondensation. The results are shown in Fig. 1. It can be seen that in solid state polycondensation the reaction rate of PET copolymers is higher than

that of PET and increases with comonomer content. But contrary result occurs in melt state polycondensation (see Fig. 2), where the reaction rate constants of copolycondensation of BHET-I, or BHET-A is decreased obviously in comparison with the polycondensation of BHET.

This can be explained by the difference of chemical structure of comonomers. When comonomer IPA is introduced into copolymer chain, it becomes difficult for the hydroxyl group of BHET or polymer chain end to attack the carbon atom in carbonyl group of this comonomer because of its steric hinderance. So the reaction rate of copolycondensation of BHET-I is decreased. It can be shown schematically on next page.

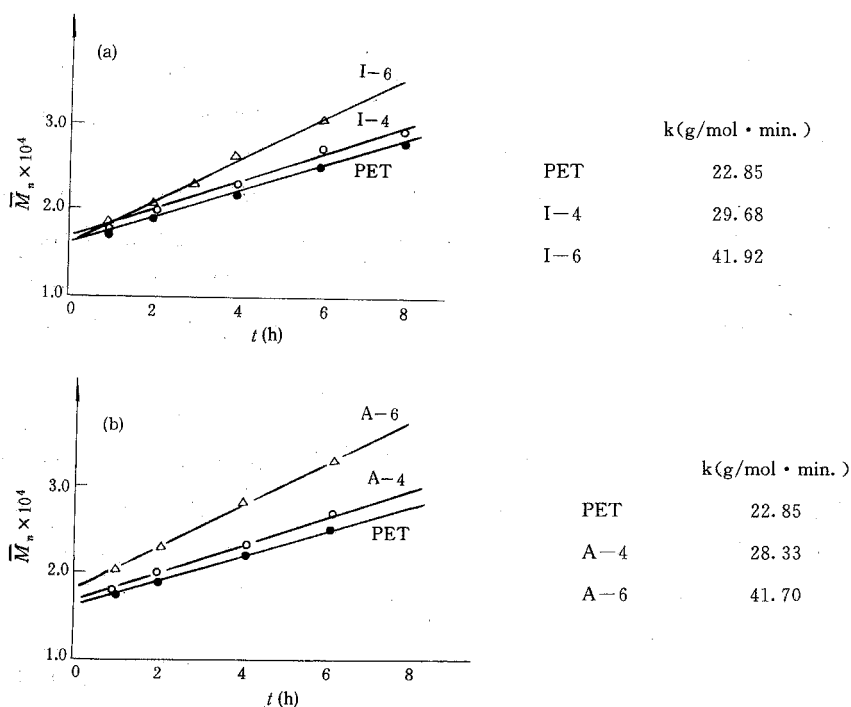
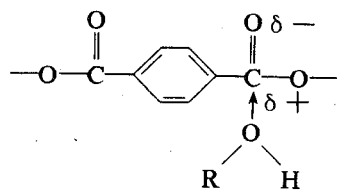
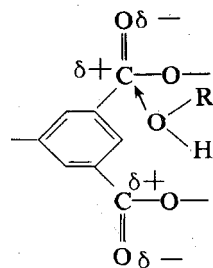


Fig. 1 Relationship between $\bar{M}_n$ and t for PET copolymer samples obtained by solid state polycondensation (a) I-4 4mol%IPA, I-6 6mol%TPA (b) A-4 4mol%AA, A-6 6mol%AA (mol% of comonomer is to TPA)

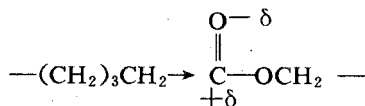
When the $-(\text{CH}_2)_4-$ segment of adipic acid (AA) comonomer is introduced into copolymer chain, the electropositivity of carbon atom in carbonyl group of AA monomer is decreased due to the electron donating effect of its methylene group as shown.



terephthalate



isophthalate



This is disadvantageous for the nucleophilic reaction between hydroxyl group of BHET or polymer chain end and carbonyl group of AA monomer. So the reaction rate of melt state copolycondensation of BHET-A is also decreased.

Hence in melt state polycondensation, the reaction rate of BHET-I and BHET-A are lower than that of BHET.

It is well-known that in solid state polycondensation there are two factors which influence the total apparent reaction rate: one is the chemical reaction happening between functional groups, and the other is the diffusion of by-products (such as EG and H_2O). The mobility of functional groups of copolymers chain end in solid state is obviously lower than that of in melt state. If the influence of chemical structure of comonomers on solid state polycondensation occurs as in melt state polycondensation, the solid state reaction rate should be lower, but the obtained result is in contrary. On the other hand, the diffusion of by-products (EG and H_2O) occurs mainly in amorphous region, which can be influenced by the changes of aggregative structure of obtained copolymer samples.

In order to determine the changes of crystalline structure of copolyester during the solid state polycondensation the X-ray analysis was used. The WAXD curves of PET and the two kinds of copolyesters are shown in Fig. 3, Fig. 4, Fig. 5, and the crystallinity and crystallite size data are shown in Tab. 1.

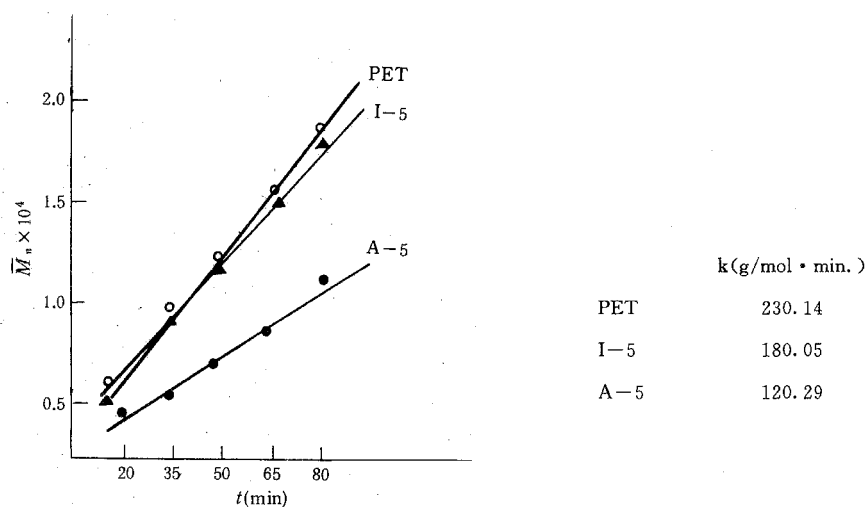


Fig. 2 Relationship between $\bar{M}_n$ and t for PET copolymer samples obtained by melt state polycondensation (I-5 5mol%IPA, A-5 5mol%AA) (mol% of comonomer is to TPA)

Table 1 Changes of crystallinity and crystallite size of PET and its copolymers during solid state polycondensation

Sample No.	Stage	Condition		Crystallinity%	Crystallite size(10^{-10}m)	
		Temperature($^{\circ}\text{C}$)	Time(min)		D010	d100
PET-1	Precryst.	160	0	52.3	55.5	35.9
PET-2	Precryst.	160	4	54.7	57.9	34.7
PET-3	Precryst.	160	10	51.7	56.4	37.8
PET-4	Polycon.	215	120	56.4	72.4	44.9
PET-I1	Precryst.	160	0	50.2	54.0	36.1
PET-I2	Precryst.	160	4	54.2	56.5	37.5
PET-I3	Precryst.	160	10	56.3	56.2	34.9
PET-I4	Copolycon.	215	120	54.9	80.3	59.7
PET-A1	Precryst.	160	0	47.7	54.7	37.6
PET-A2	Precryst.	160	4	57.3	56.4	36.0
PET-A3	Precryst.	160	10	51.3	56.1	34.9
PET-A4	Copolycon.	215	120	58.3	95.9	64.5

* Computer separating peaks and calculated with Scherrer's equation.

From Tab. 1 it can be seen that the crystallinity and crystallite size of samples are almost unchanged during precrystallization. This means that the crystallization of PET and the copolyesters is happened mainly at the heating up stage from room temperature to 160°C . From the WAXD curves and Tab. 1, it can also be seen that only after solid state polycondensation the

diffraction peaks become distinct, and the crystallite size increases obviously. This means that the crystal of these samples becomes more perfect during the solid state polycondensation, this is in accord with other authors.^[4] In WAXD curves there is obvious difference between PET and its copolymers. The diffraction peaks of copolyesters crystal faces (0 $\bar{1}$ 1), (010), (1 $\bar{1}$ 0), (100) become sharper and the diffraction peaks of ($\bar{1}$ 11), (1 $\bar{1}$ 1), ($\bar{1}$ 21) become more distinguished. The sharper diffraction peaks are not the result of obtained polymer chain segment from BHET-I(or BHET-A) because of small additive content of IPA (or AA) and its poor crystallization ability. But by introducing IPA and AA into polymer chain the crystal perfection of copolyester becomes easier than that of PET, and it can be found from the data for the increase of crystallite size (Tab.1).

From the above results, it can be thought that at the condition of nearly the same percent crystallinity, the increase of crystallite size of PET copolymers leads to larger amorphous region (the part of amorphous region between crystallites becomes larger), as a result the diffusion of small molecules (EG, H₂O) in solid state polycondensation becomes easier and the reaction rate is increased. So the crystalline structure is the main factor affecting the reaction rate in solid state polycondensation of PET. The chemical reactivity of the functional groups of monomers is the main factor influencing the reaction rate in melt state polycondensation of polyesters.

CONCLUSION

From the comparison of the reaction kinetics of both PET and its copolymers in solid state polycondensation with that in melt state poly

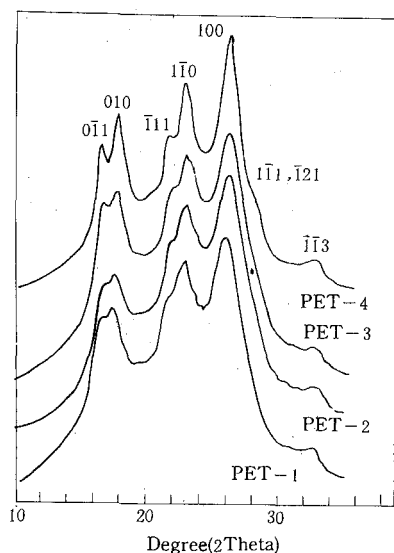


Fig. 3 WAXD curves for PET obtained by solid state polycondensation PET-1 PET-2 PET-3 samples after precrystallization (160°C, 40Pa) 0 min, 4 min, 10min; PET-4 sample after solid state polycondensation (215°C, 2 hr, 40Pa)

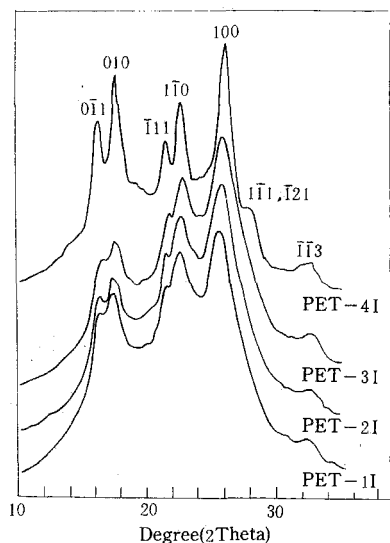


Fig. 4 WAXD curves for PET copolymer (with the content of IPA 6mol%) obtained by solid state polycondensation
PET-1I, PET-2I, PET-3I samples after precrystallization (160°C, 40Pa), 0 min, 4min, 10min; PET-4I sample after solid state polycondensation (215°C, 2hr, 40Pa)

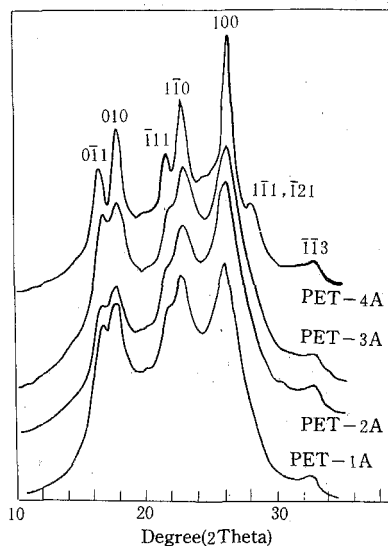


Fig. 5 WAXD curves for PET copolymer (with the content of AA 6mol%) obtained by solid state polycondensation
PET-1A, PET-2A, PET-3A samples after precrystallization (160°C, 40Pa) 0min, 4min, 10min; PET-4A sample after solid state polycondensation (215°C, 2hr, 40Pa)

condensation and X-ray analysis results, it is concluded that the primary factor influencing the reaction rate in solid state polycondensation of PET polymer is the aggregative structure of the samples.

Keywords:

Solid state polycondensation; PET copolymer; WAXD; Crystallite size

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