

CRYSTALLIZATION AND MULTI-MELTING BEHAVIOR OF POLY (ETHYLENE TEREPHTHALATE) MODIFIED BY SODIUM SALT OF 5-SULPHO-ISOPHTHALIC ACID

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ABSTRACT

The crystallization kinetics of the copolyester, poly(ethylene terephthalate) (PET) modified by sodium salt of 5-sulpho-isophthalic acid (SIPM), was investigated by means of differential scanning calorimeter. The experimental results and polarizing-microscopy observation all showed that the introduction of SIPM did not affect the nucleation of crystallization. Within the temperature range between their glass transition temperature T_g and melting point T_m , the crystallization rate of the copolyester sample decreased with increasing content of SIPM. The relative crystallization rate constant Z of SIPM/DMT (dimethyl terephthalate) 4mol % sample was about 1% pure PET's Z value. For isothermal crystallized copolyester samples, DSC heating curves displayed multi-melting behavior. This was interpreted by molecular weight fractionation during crystallization and premelting-recrystallization mechanism. This interpretation showed why the second melting point T_{m2} will change according to Hoffman-Weeks(H-W) equation^[1] and the first melting point T_{m1} will increase with increasing SIPM. The principal cause of these phenomena is the high temperature crystallization rate decreases rapidly with increasing SIPM.

Random copolymer of PET by SIPM was reported as a typical cationic dyeable polymer^[2]. The melt of the copolymer was characterized by high viscosities at low shear rate^[3]. Crystallization and melting behavior of the modified copolyester were different from pure polyester PET. By means of DSC, we studied crystallization and multi-melting behavior of the random copolyester, and discussed forming mechanism of multi-melting.

EXPERIMENTAL

The samples of random copolyester of PET with SIPM were prepared by the method of general polycondensation. Intrinsic viscosities^[4] of these copolyester chips were 0.57—0.60. SIPM/DMT mol % of four measured samples were 0.0, 1.0, 2.0, and 4.0 respectively. DSC curves were recorded on a Perkin-Elmer DSC-2C. Sample weight was about 8mg. The chips were cut into fine grains (diameter 0.5mm), then were put into aluminum pans. A gold pan was used as reference material; pure nitrogen as furnace atmosphere. We used metal In to calibrate temperature and energy, and the Data Station 3500 control measurements and treat the data.

DSC heating and cooling curves

For eliminating cooling history differences, the samples were heated to 563.2K at heating rate 320K/min in DSC cell, then were isothermally retained for 5 minutes, we took out the pans rapidly from the furnace and quenched on ice block. After above process, the pans were put into the furnace, DSC curves from ambient temperature to 20K above melting point were measured at

heating rate 20K/min. After retaining isothermal at 20K above melting point for 10 minutes, cooling DSC curves were obtained at cooling rate 10K/min.

We used T_m , H_m , T_{ic} and H_{ic} to denote the melting point, heat of fusion, cold-crystallization temperature and exo-heat of cool-crystallization on heating DSC curves respectively. T_g was mid-point of glass transition. T_{ab} and H_{dc} were the melt-crystallization temperature and exo-heat of meltcrystallization on cooling DSC curves respectively.

Isothermal melt-crystallization DSC curve and multi-melting peaks

The sample in the pan was heated to 20K above melting point at heating rate 320/min, then was retained isothermal for 10 minutes to obtain full fusing copolyester. Then, the sample was rapidly cooled to pre-determined isothermal crystallization temperature T_c and kept isothermally crystallized for 10 minutes to obtain isothermal melt-crystallization DSC curve.

After isothermal crystallization, the pan was rapidly cooled to ambient temperature. Post-obtained heating DSC curve at rate 20/min displayed multi-melting peak.

Spherulite observation

Optical micrograph between crossed polarizer and analyzer was observed on OPTON polarizing microscopy. Temperature process of the sample was the same as in isothermal crystallization treatment.

X-ray diffraction photography

X-ray diffraction photograph of thin sheet, which was got after isothermal crystallization treatment, was carried on TFXC-2 fiber diffraction camera(made by our laboratory). Cu K α ; Ni filter; 36kV, 18mA, Exposed for 5 hours.

The measurement of isothermal crystallization rate

The primary isothermal crystallization process of melt followed Avrami-Eroffeev equation^[5]

$$1 - C = \exp(-Zt^n) \quad (1)$$

C —relative crystalline fraction at moment t , i.e. exothermal area fraction before moment t , relative to whole exothermal area of isothermal process. If X_w was crystalline fraction, arrived by isothermal crystallization process, $k = Z X_w$ was crystallization rate constant. Z —relative crystallization rate constant. n —Avrami index. The $\ln[-\ln(1 - C)] \sim \ln t$ graph was plotted from the observed data. Linear fitting of these data provided n and Z . n was a characteristics for crystal nucleation, growth and morphology. We used fitting correlation coefficient r to judge the agreement of crystallization behavior with equation (1).

RESULTS AND DISCUSSION

Heating and cooling DSC curves of the 4 samples are shown in Fig.1 and Fig.2 respectively. Calculated thermal analysis parameters are listed in Table 1.

Table 1 Some thermal analysis parameters of four PET/SIPM copolyester

SIPM/DMT (mol %)	T_g (K)	T_m (K)	T_{ic} (K)	ΔH_{ic} (cal/g)	ΔH_m (cal/g)	T_{dc} (K)	ΔH_{dc} (cal/g)
0.0	355.1	527.1	410.6	8.39	10.9	485.8	11.1
1.0	355.5	522.8	435.0	8.32	8.88	467.4	10.5
2.0	357.8	520.3	449.3	7.21	7.31	460.8	9.1
4.0	358.8	513.2	469.5	—	—	449.7	—

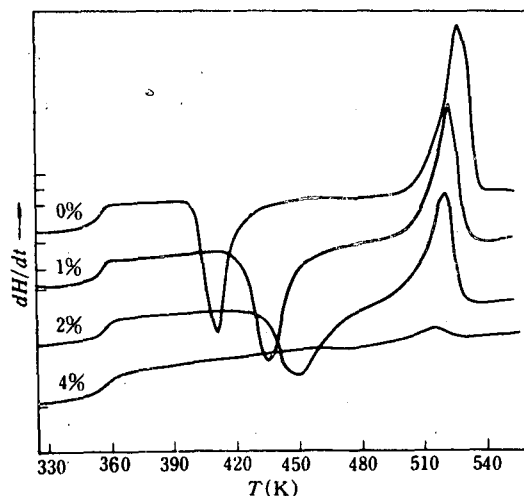


Fig.1 Heating DSC curves of SIPM/DMT
4 mol % copolyester

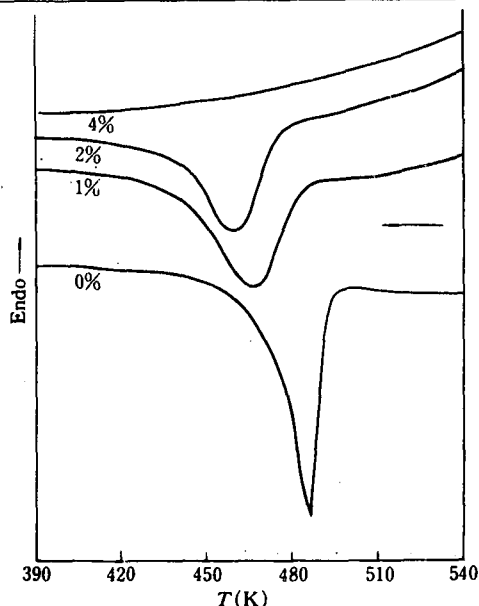


Fig.2 Cooling DSC curves of SIPM/DMT
4 mol % copolyester

T_g slightly increases with increasing SIPM in the copolyester. Moore et al.^[6] showed that T_g decreases with increasing isophthalate in PBT/PBI (polybutylene terephthalate/polybutylene isophthalate) copolyester. In view of Edgars stiffness factor^[7], substitution DMI for DMT don't change the segment mass, but DMI causes non-linear stereo-configuration of the molecules and increases the number of chain conformation. From this, we can comprehend Moore's result. In PET/SIPM copolyester, local aggregation of $-\text{SO}_3^-$ and Na^+ groups on molecular chains leads to temporary crosslinks of ionic groups^[3]. These lead to T_g increasing.

X-ray diffraction analysis of high temperature crystallized thin sheet (SIPM/DMT 4 mol%) showed that only PET participate in crystallization but SIPM does not (Fig.3).

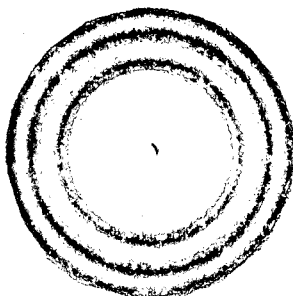


Fig.3 X-ray diffraction photograph of high temperature
crystallized thin sheet (SIPM/DMT 4 mol %)

For random copolymer, from Flory-Huggins equation

$$\frac{1}{T_m} - \frac{1}{T_{m0}} = -\frac{R}{H_u} \ln n_A - X(1 - V_A) \quad (2)$$

n_A —mol fraction of crystallizable unit A; T_m —equilibrium melting point of copolymer;

T_{m0} —equilibrium melting point of unit A homopolymer; X —interaction parameter; V_A —volume fraction of A, we may obtain estimation of X . Because the content range of SIPM in the copolymers is narrow, it is unsuitable for using the extrapolation method[1] to get the equilibrium melting point. We used T_m in Table 1 instead of T_m^* and by qualitative estimation it can be showed that the value of X is quite large. The ΔH_u value was from^[8]. The addition of SIPM intensified the molecular interaction. Clearly, T_m decreases with increasing SIPM.

The T_{ic} on heating process increases, i.e. $\Delta T_i = T_{ic} - T_g$ increases with increasing SIPM. This fact showed that cold-crystallization rate reduces with SIPM^[9]. The heating DSC curve of SIPM/DMT 4 mol % sample did not display any exo-peak because of the rate's reducing. The T_{dc} on cooling process decreases, i.e. $T_d = T_m - T_{dc}$ increases with increasing SIPM. This shows that high temperature crystallization rate reduces with SIPM^[9]. From above facts, crystallization rate decreases with SIPM at temperature between T_g and T_m .

Isothermal crystallization was studied quantitatively. We measured isothermal DSC curves of four samples at 465, 475 and 485K. The correlation coefficient r of all the $\ln[-\ln(1 - C)] \sim \ln t$ graphs were above 0.98. This showed that crystallization behavior of four samples agree with equation (1).

The Avrami indexes obtained were 1.7—2.1 and independent of SIPM content. This fact and polar-microscopy observation all showed that the addition of SIPM does not effect nucleation on melt-crystallization. Average size of spherulites in the samples retained isothermal at 480K for 3 minutes, was listed in Table 2. The size decreases with increasing SIPM. It also proved crystallization rate's reducing.

Table 2 Average size of spherulites. at 480K for 3 minutes

SIPM/DMT (mol %)	0.0	1.0	2.0	4.0
Diameter of spherulite (μm)	16	10	6	<4

The relative rate constants Z on isothermal process were listed in Table 3. The rate obviously decreases with raising T_c or increasing SIPM. The rate of the 4 mol % sample was about 1% of pure PET's. Because local aggregated ionic groups strongly interact with each other, the mobility of molecular segments is obstructed. From this, the crystallization rate is certainly reduced.

Table 3 The relative crystallization rate constants Z

Z	Crystallization temperature (K)		
	465	475	485
SIPM/DMT(mol %)			
0.0	0.9506	0.3836	0.0751
1.0	0.2127	0.1256	0.0572
2.0	0.0651	0.0478	0.0218
4.0	0.0073	0.0034	0.0021

The heating DSC curves of isothermal crystallized samples displayed multi-melting (Fig.4). Their melting peak temperature was listed in Table 4. The peaks are marked as T_{m1} , T_{m2} and T_{m3}

in the order of raising temperature. Three-melting peaks were displayed on DSC curves at $T_c = 465 \sim 475\text{K}$; two-melting peaks at $T_c = 485\text{K}$. The change of the melting peak temperature with SIPM was shown in Table 4. The change of the peak height with SIPM was shown in Figure 4: when SIPM content is increasing, the height of T_{m3} is decreasing, T_{m2} is increasing clearly and T_{m1} increasing only slightly. The premelt-recrystallization mechanism of two-melting peaks have been already accepted^[10,11,12]. Multi-melting peaks often appeared in the case of PET and its copolyester^[13,14,15].

It is generally believe that the cause of forming T_{m3} is due to the melting of perfect and large crystallites, which are formed during the heating process of DSC measurement. The dependence of T_{m3} on T_c and heating rate is slight, as shown in Table 4. If T_{m3} would be the contribution of larger crystallites and T_{m1} would be the contribution of other crystallites, then this result showed that the portion of crystallite is decreasing.

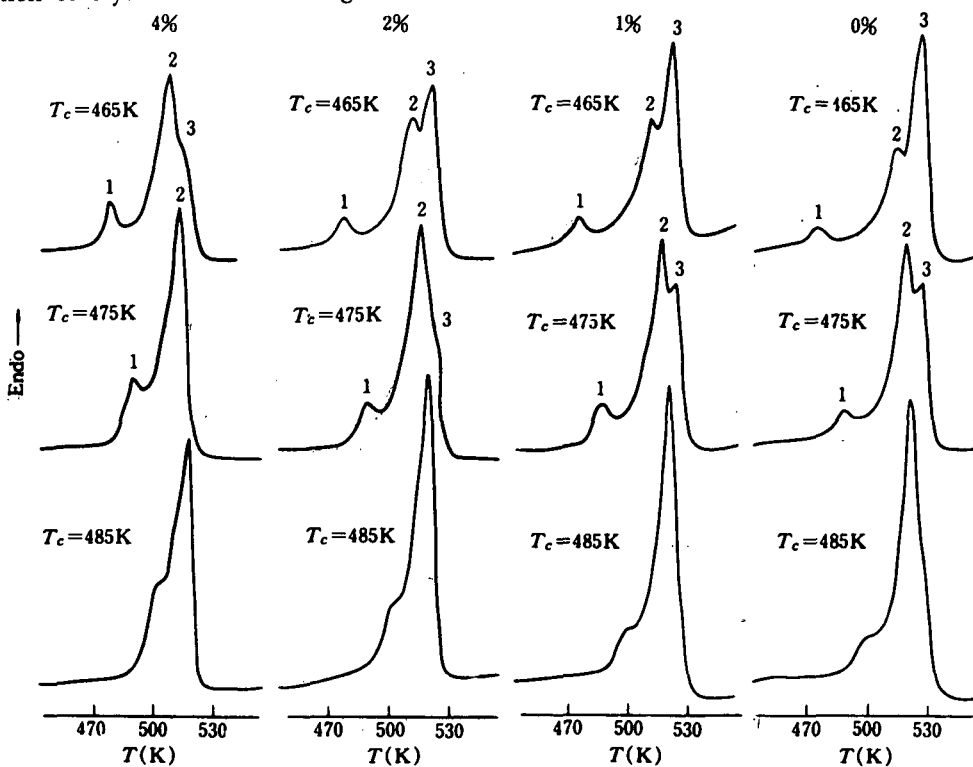


Fig.4 Heating DSC curves of various SIPM/DMT mol % isothermal crystallized samples (Heating rate 20K/min)

Interpretation of the forming cause of T_{m1} and T_{m2} is difficult. First, at the end of isothermal experiment, we did not quench the samples to ambient temperature but directly measured heating DSC curves, there was T_{m1} peak on the direct DSC curve. However T_{m1} was not the contribution of quench process. Marrs et al.^[13] suggested that T_{m2} was the contribution of high molecular weight (MW) folding crystallites and because of MW fractionation^[15], MW in non-crystallite region was lower when high MW molecules have crystallized. In continual crystallization, low MW crystallites with higher concentration of end-group defect were formed. T_{m1} just was the melting of these low MW crystallites. It is known that MW distribution of melt random co-condensed polymer is nearly single-peak Flory distribution function. But we can see that T_{m1} and T_{m2} were

two separated peaks. Therefore, Marrs' interpretation is not perfect. Ikeda^[15] studied 3-melting of DSC curve on PET ($160^{\circ}\text{C} \leq T_c \leq 225^{\circ}\text{C}$). He suggested that during heating process of DSC measurement the folding crystallites at T_c melt and produce finite width ideal endo-peak. The width corresponds to the crystallites size distribution. At the same time, recrystallization, lamellar thickening and perfection contribute crystallized exo-heat. The ideal endo-peak are diminished by the exo-thermogram. So then, we observed T_{m1} and T_{m2} double peaks. But why only T_{m2} is in accordance with H-W equation^[11]? Ikeda's interpretation did not give a proper answer. However, folding crystal melting point, according to H-W equation, must be the peak temperature of the ideal melt endo-peak and not just T_{m2} .

In Table 4, T_{m1} and T_{m2} raise with raising T_c at the same mol % copolyester. This behavior is similar to PET/DMS^[13] and PBT/DMS^[14] systems. At the same T_c , T_{m2} drops with increasing SIPM as PET/DMS. But T_{m1} increases with increasing SIPM. Therefore, although the H-W equation can be used to random copolymer^[17], but Marrs' and Ikeda's interpretation still are not proper.

Prime and Wunderlich^[18] studied crystallization of extended chain on polyethylene under high pressure. They showed that, because of crystallized MW fractionation, the larger crystal dominates over the crystallites obtained when MW weight-distribution curve was not very unsymmetrical. Harland et al.^[16] also stated that MW distribution can effect folding crystallization of polyethylene in view of MW fractionation. We supposed, MW fractionation on crystallization may be adapted to other polymer. On homopolyester and copolyester, MW of fractionated crystal gradually decreases with growth time. The ideal melt thermogram would be a wide peak owing to lamellar thinning and chain-end defect increasing. Visco-average MW of our samples were about 43,000—37,000. Their MW distribution (Flory distribution) were nearly symmetrical. Therefore their ideal melt thermograms may be of unsymmetrical peak, with peak temperature nearly at the upper limit of the single peak (Fig.5). Then similarly to Ikeda's diminution, T_{m1} and T_{m2} double peaks have been produced on the DSC curves (Fig.5).

Table 4 Melting peak temperature of isothermal crystallized samples

SIPM/DMT mol %	Crystallization temperature T_c (K)		
	465	475	485
0.0	474.99	487.32	499.50
1.0	475.22	487.32	500.20
2.0	476.40	489.27	501.37
4.0	478.80	490.83	503.70
0.0	514.80	519.08	521.47
1.0	512.68	516.61	520.71
2.0	511.52	515.54	519.33
4.0	509.00	512.73	517.36
0.0	527.32	526.35	—
1.0	523.49	523.62	—
2.0	521.40	—	—
4.0	—	—	—

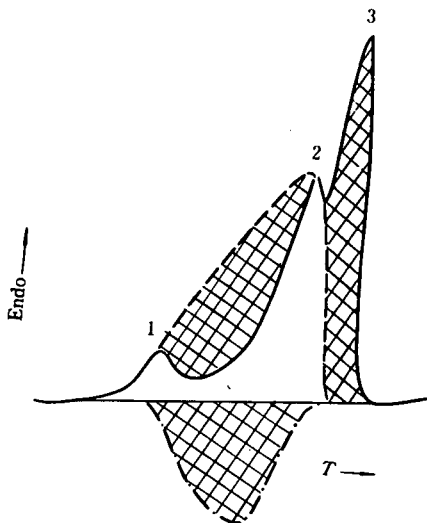


Fig.5 Mechanism of forming 3-melting peaks

—observed DSC curves; ----ideal melt thermogram; -.-recrystallized exo-thermogram.

The three shadow areas are of the same size

In view of above suggestion, owing to T_{m2} is nearly equal to ideal melt peak temperature T'_m , then T_{m2} can be adapted to the H-W equation. T_{m1} not only depends on temperature shift of the ideal melt thermogram but also depends on the temperature shift of recrystallized exo-thermogram more strongly. On the PET/DMS copolyester^[13], high temperature crystallization rate increases due to the introduction of flexible chains, then the exo-thermogram shifts to lower temperature during DSC measurement and T_{m1} is decreased. On our PET/SIPM copolyester, because of the crystallization rate rapidly decreasing with increasing SIPM, the downward shift of the ideal melt thermogram, characterized by T_{m2} , can not compensate the upward shift of the exo-thermogram. Therefore, T_{m1} increases with increasing SIPM.

Keywords:

Crystallization Kinetics; Multi-melting behavior

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