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Studies on the Molecular Structure and Crystallization Kinetics of Polytrimethylene Terephthalate

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Abstract : Making use of infra-red spectra and ^1H NMR spectra, we characterized the molecular structure of polytrimethylene terephthalate (PTT) which was synthesized by ourselves, and compared the resulting PTT with polybutylene terephthalate (PBT) and polyethylene terephthalate (PET). The crystallization kinetics for PTT was compared with those for PBT and PET. The crystallization activation energies of these three polyesters were weakened in the order of $\text{PET} > \text{PTT} > \text{PBT}$. It seems that the difference in the flexibility of molecular chains influences the crystallization activation energies.

1. Introduction

Polytrimethylene terephthalate (PTT), a new kind of polyester, was introduced by Shell Chemical Co. (USA) in 1995 for use as a premium carpet fiber. At the same time, the polymer was also actively pursued by Du Pont Co. (USA) and Degussa Co. (Germany). PTT has been known for many years but was not considered commercially feasible until Shell Chemical recently discovered the technology that makes it possible to produce 1,3-propanediol (PDO) via the hydroformylation of ethylene oxide and to commercialize PTT at a competitive price. Shell Chemical is now working to put its PTT into other market applications where it can be added value, such as spunbond and needlepunch non-woven fabrics, monofilament, engineering thermoplastics and films. It is predicted that PTT will be developed on a large scale before long [1,2].

PTT, polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) differ in the $-\text{CH}_2-$ number in their macromolecular chain element although all of them are a linear polyester. This article discusses their differences in molecular structure and the crystallization kinetics of PTT by comparing with those of PET and PBT.

2. Experimental

2.1 Samples

PTT was synthesized by ourselves from pure terephthalic acid (PTA) and 1,3-propanediol (PDO) by direct esterification and polycondensation. In the polycondensation reaction, the catalyst system used is the titanium (Ti) compound and the thermal stabilizer added is the tribenzene phosphate. PET and PBT were prepared by Yi Zheng Chemical Fibers Company. The main properties of three polyesters are shown in Table 1.

Table 1 The main properties of PTT, PBT and PET

Polyesters	Properties			
	$H_u (10^3 \text{ J/mol})$	$[\eta] / \text{dl} \cdot \text{g}^{-1}$	$T_m / ^\circ\text{C}$	$T_g / ^\circ\text{C}$
PTT	25.23	0.86*	223	61
PBT	22.57	0.91	224	24
PET	21.49	0.66	254	81

*The intrinsic viscosity was measured in an Ostwald viscometer using orthochlorophenol as a solvent at 25°C .

2.2 Infra-red Spectra

Infra-red spectra of the polyesters were recorded with a NICOLET-560 infra-red spectrometer. Scanning times: 12, Resolution: 2 cm^{-1} .

2.3 Nuclear Magnetic Resonance (NMR) Spectra

¹H NMR spectra of the polyesters were run on a Bruker Am 500 spectrometer. Each of the polyesters was dissolved in a mixture CDCl₃/CF₃COOD 3:1 v/v. Tetramethylsilane (TMS) is the standard reference material for ¹H NMR when organic solvents are used.

2.4 Crystallization Kinetics Analyses

The overall crystallization kinetics from the melt of the polyesters was analyzed with a Perkin-Elmer DSC-7 differential scanning calorimeter.

2.4.1 Measuring Conditions

The entire operating procedure was carried out in nitrogen atmosphere so that the polyesters (about 5 mg) can be protected from oxidative degradation. The reference material is Al₂O₃.

PTT samples were heated to 260°C at a rate of 20°C/min and maintained for 10 min at 260°C until the complete disappearance of any residual crystallinity in the melt. Then they were quickly cooled at 200°C/min. As soon as the desired crystallization temperature was attained, the values of the crystallization percentage with change of the crystallization time (t) were recorded.

The t and the crystallization percentage of PBT and PET samples could be acquired by the same way for PTT except that they were heated to 270°C and 280°C at 20°C/min, respectively.

2.4.2 Data Treatment

The kinetics of the isothermal crystallization from the melt of all polyesters is usually analyzed on the basis of the Avrami equation [3-5]:

$$1 - X(t) = \exp(-kt^n) \quad (1)$$

n is Avrami exponent that depends on the type of nucleation and on the geometry of growing crystals. k is the overall kinetics rate constant that relates to rates of nucleation and crystal growth. X(t) is the weight fraction of crystalline regions at a time t and is determined according to the equation:

$$X(t) = \int_0^t (dH/dt) \int_0^\infty (dH/dt) dt \quad (2)$$

where t = 0 is taken at the moment of attainment of thermal equilibrium and t = ∞ at the end of crystallization [3]. And the first integral, namely, the numerator of equation (2) is the heat generated up to a certain time t and the second integral, namely, the denominator of equation (2) is the total heat of crystallization up to t = ∞. H is the heat evolved by

the crystallization. Then, X(t) values as a function of t at various crystallization temperatures (T_c) were acquired from the DSC measurements. Taking logarithms, equation (1) can be arranged in the following form:

$$\log \{-\ln[1 - X(t)]\} = n \log t + \log k \quad (3)$$

Here, "log" and "ln" denote the common and natural logarithms, respectively. The plot of $\log \{-\ln[1 - X(t)]\}$ vs. $\log t$ should yield a straight line with the slope n and intercept $\log k$. The crystallization rate (V_c) may be expressed by a reciprocal of the half-time of crystallization (t_{1/2}). That is to say, $V_c = 1/t_{1/2} = 1/(\ln 2/k)^{1/n}$ when $1 - X(t) = 1/2$ in equation (1).

According to the equation proposed in the book written by Mandelkern [6], the activation energy (ΔE_a) for transport across the liquid-nucleus interface can be estimated as follows:

$$\ln V_c + [1 + (n-1)\bar{a}] k' (T_m)^2 / [n T_c (\Delta T)^2] = A - \Delta E_a / RT_c \quad (4)$$

where R is the gas constant and is 8.314 J/mol · K, A is a constant, T_m is the equilibrium melting temperature and ΔT = T_m - T_c, n is the Avrami exponent, $\bar{a}$ is the factor indicating that the critical free energy required to form a secondary nucleus is less by $\bar{a}$ than that for primary nucleation (here, $\bar{a}$ is speculated to be equal to 1 for all of three polyesters if we assume only a primary, homogeneous nucleation process) and k' is a certain constant and can be calculated by the following equation [6]:

$$k' = 8\pi(\sigma_u)^2 \sigma_e / R(\Delta H_u)^2 \quad (5)$$

here, σ_e is interfacial free energy at the cylindrical edge of the molecular chains per molecule and σ_u is interfacial free energy of side surface per molecule. (σ_u)²σ_e for all PTT, PBT and PET can be assumed to be about 50 ergs³/cm⁶ [6]. ΔH_u is the heat of fusion and may be obtained from Table 1 for the polyesters. In addition, we assume that the cross sectional area of one molecule is 0.5 nm × 0.5 nm, and that the length of monomer unit is also 0.5 nm. Therefore, ΔE_a can be estimated from the plot of $\{\ln V_c + [1 + (n-1)\bar{a}] k' (T_m)^2\} / [n T_c (\Delta T)^2]$ vs. 1/T_c.

3. Results and Discussion

3.1 Molecular structure of PTT synthesized in this study

Fig. 1 indicates the infra-red absorption peaks of

Fig. 1 Infra-red spectra of PTT, PBT and PET.

PTT, PET and PBT between 1200 and 1800 cm^{-1} (wave number). As can be seen from Fig. 1, there is a little difference among the spectra of three polyesters. The stretching and contracting vibration peaks of their carbonyl groups ($\text{C}=\text{O}$) can be easily observed (about 1720 cm^{-1}). The absorption peaks at 1200-1300 and 1580/1500 cm^{-1} are assigned to vibrations of $\text{C}-\text{O}$ in carboxyl ($-\text{COOH}$) and of $\text{C}=\text{C}$ in benzene ring, respectively. The

absorption peaks of $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{CH}$ in a macromolecule are located at 1300-1500 cm^{-1} . As for $-\text{CH}_2-$ peak at $1460 \pm 10 \text{ cm}^{-1}$, the peak of PET is of the lowest and those of PTT and PBT are almost equal in height.

Tables 2-4 give the correlation between chemical shifts (δ) and various compositions observed in the ^1H NMR spectra [Figs.2 (a)-(c)]. By comparison of these relative integral values in Figs.2 (a)-(c), it is quantitatively shown that the $-\text{CH}_2-$ numbers of PBT are 2.04 times of PET and 1.34 times of PTT, and $-\text{CH}_2-$ numbers of PTT are 1.52 times of PET. As may be observed from Figs.2 (a)-(c), the relative mole ratio of $\odot / -\text{CH}_2\text{CH}_2\text{CH}_2-$ in PTT is 0.6122 and the relative mole ratio of $\odot / -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ in PBT is 0.4773. Thus the chemical constituent of the sample synthesized by ourselves was surely proved to be that of PTT.

3.2 Crystallization Kinetics

$X(t)$ which varied with time (t) was measured with DSC in isothermal crystallization at some temperatures which were lower than the melting point and higher than the glass transition temperature (T_g). The

Table 2 The correlation between chemical shifts (δ) and various compositions in the ^1H NMR spectra of PTT

PTT structure:		
$\text{+O-C(=O)-C}_6\text{H}_4\text{-C(=O)-OCH}_2\text{CH}_2\text{CH}_2\text{O+}_n$		
$\delta(\text{PPM})$	Compositions assignment	Remarks
11.65	residual H of $\text{CF}_3\text{CO}_2\text{D}$	
8.13	H of benzene ring	
7.24	residual H of CDCl_3	
4.63	$-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$	δ of underlined parts
2.39	$-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$	δ of underlined parts
0	TMS	

Table 3 The correlation between chemical shifts (δ) and various compositions in the ^1H NMR spectra of PBT

PBT structure:		
$\text{+O-C(=O)-C}_6\text{H}_4\text{-C(=O)-OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O+}_n$		
$\delta(\text{PPM})$	Compositions assignment	Remarks
11.65	residual H of $\text{CF}_3\text{CO}_2\text{D}$	
8.13	H of benzene ring	
7.24	residual H of CDCl_3	
4.53	$-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$	δ of underlined parts
2.50	$-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$	δ of underlined parts
0	TMS	

Table 4 The correlation between chemical shifts (δ) and various compositions in the ^1H NMR spectra of PET

PET structure:

δ (PPM)	Compositions assignment	Remarks
11.65	residual H of $\text{CF}_3\text{CO}_2\text{D}$	
8.13	H of benzene ring	
7.24	residual H of CDCl_3	
4.89	$-\text{OCH}_2\text{CH}_2\text{O}-$	
0	TMS

Fig. 2 ^1H NMR spectra of (a) PBT, (b) PTT and (c) PET.

isothermal crystallization parameters were obtained by plotting the crystallization curve according to equations (3) and (4).

3.2.1 Influence of crystallization temperature on the crystallization parameters

Table 5 shows that the crystallization rate (V_c), crystallization rate constant (k) and Avrami exponent (n) decrease with increasing crystallization temperature (T_c) and the crystallization half-time ($t_{1/2}$) increases with increasing T_c for all three polyesters.

Table 5 The parameters of isothermal crystallization kinetics for three polyesters

Samples	T_c ($^{\circ}\text{C}$)	$\Delta T = T_m - T_c$ ($^{\circ}\text{C}$)	$t_{1/2}$ (min)	V_c (min^{-1})	n	k (min^{-1})	ΔE_d (10^3J/mol)
PTT	167	56	1.05	0.96	3.5	5.92×10^{-1}	52.29
	170	53	1.22	0.82	3.3	3.62×10^{-1}	
	173	50	1.28	0.78	3.2	3.10×10^{-1}	
	176	47	1.49	0.67	3.1	1.97×10^{-1}	
PBT	170	54	0.69	1.45	4.4	3.58	19.23
	173	51	0.74	1.36	3.6	2.04	
	176	48	0.78	1.29	3.3	1.58	
PET	190	64	1.90	0.53	3.6	7.08×10^{-2}	75.00
	193	61	2.12	0.47	3.2	6.31×10^{-2}	
	196	58	2.45	0.41	3.0	4.75×10^{-2}	
	199	55	2.87	0.35	2.9	3.31×10^{-2}	

It is well known that the overall crystallization which includes both processes of the formation of crystal nuclei and their growth can be measured by DSC, and that the growth of crystal grain begins from the surface of crystal nucleus. In general, the polyesters will form spherulites under the high temperature, and the temperature dependence of the isothermal spherulite

growth rate (G) may be expressed by the Turnbull-Fisher equation [7]:

$$G = G_0 [\exp(-\Delta E_d/RT_c)] [\exp(-\Delta F^*/RT_c)] \quad (6)$$

$$\Delta F^* = KT_m / (\Delta H \Delta T) \quad (7)$$

Here ΔE_d is the activation free energy for the transport process of chain segment through the crystallization interface; ΔF^* is the free energy for the formation of a nucleus of critical size. G_0 usually reflects the macromolecular structure and molecular weight. ΔH is the melting enthalpy. K is a constant depending on the kind of polymers.

As for ΔE_d , we can obtain from equation (4). However, it is well known that the term $\exp(-\Delta E_d/RT_c)$ reflecting the spreading of chain segment plays a main role when the crystallization is carried out at a lower temperature, and that the term $\exp(-\Delta F^*/RT_c)$ reflecting nucleation occupies a main position when the crystallization is performed at a higher temperature. Our experiment corresponds to the latter situation because of the isothermal crystallization from the quenched melt. That is to say, the crystallization rate is mainly determined by ΔF^* . As can be known from equation (7), ΔF^* is inversely proportional to the degree of supercooling ($\Delta T = T_m - T_c$). With an increase of T_c , ΔF^* increases and hence G decreases. Finally the decrease of G results in the decrease of V_c and k .

Table 5 indicates that values of the exponent n in the Avrami equation vary from 2.9 to 4.4, for all samples studied, and decrease with increasing T_c . It is clear that the Avrami exponent n of all three polyesters is non-integral. This shows that the isothermal crystallization of PTT, PBT and PET might be ascribed to heterogeneous nucleation [8-12] because the foreign substances such as catalyst, stabilizer, etc exist in them.

From Figs.3-5, we see that all plots except those for PBT samples have a good linear relation within the range of T_c discussed. In Fig.4, most of the experimental data are in agreement with the Avrami equation except those at right end of the curve. In the case of PBT, deviation from the Avrami equation in the late period of crystallization can be considered as arising from significant secondary crystallization, which takes place after the growing-up spherulites bumped against each other and their boundaries intersected each other.

Fig. 3 Crystallization behavior of PTT at different temperatures.

Fig. 4 Crystallization behavior of PBT at different temperatures.

Fig. 5 Crystallization behavior of PET at different temperatures.

Since the data points spread at the beginning and at the end, these data were neglected during regression, that is, only the data points for $X(t) = 20-80\%$ were used.

3.2.2 Influence of macromolecular structure on crystallization rate and activation energy

Table 5 shows that the crystallization rate (V_c) decreased in the order of PBT > PTT > PET. The crystallization rate constant (k) of PBT is two orders of magnitude greater than that of PET, and k of PTT is one order of magnitude greater than that of PET. There are four, three and two methylenes in a chain unit of PBT, PTT and PET respectively and, therefore, the flexibility of their macromolecular chains decreases in the order of PBT > PTT > PET. The more flexible their molecular chains are, the more easily the chains are transported into crystal surfaces and in the better ordered state the chains are arranged.

From Table 5, the activation energies (ΔE_a) of these polyesters are different. The energies required for macromolecular chains to be transported from the melt to a crystal surface were weakened in the order of PET > PTT > PBT when the polyesters were crystallized. The difference in the flexibility of molecular chains seems to have influenced the crystallization activation energies. However, the

polyester materials used in this report have not been purified at all. Further intensive investigation is needed for purified materials.

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