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Crystallization kinetics and multiple melting point phenomena of polybutylene naphthalate terephthalate (PBNT) copolyesters

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Summary

The melting behavior and crystallization kinetics of PBNT copolyesters were studied using differential scanning calorimetry (d.s.c.) The Avrami exponent, n, increased from 2.5 to 3.0 with increasing of annealing temperature between 161℃ and 170℃. The Avrami rate constant K increased with naphthalene content while activation energy decreased with naphthalene content. PBNT copolyesters showed three melting peaks, namely minor, lower and upper peaks respectively. The minor peak and lower peak grew with the increasing annealing temperature and holding time, while upper peak decreased. When scanning rate increased, minor peak and lower peak shifted to high temperature but upper peak decreased.

Introduction

The crystallization kinetics and melting behaviors of polymers are nowadays a subject of considerable importance. Many instruments have been used to study the crystallization kinetics of polymers, such as dilatometry, calorimetry, microscopy, light depolarization and scattering, density, however, the differential scanning calorimetry (d.s.c.) has been proven to be a convenient technique because of the small size of sample required, speed of operation and possibility of quickly reaching thermal equilibrium. Recently, we have reported on the preparation and characterization of copolyesters derived from 2,6-dimethyl naphthalate, 1,4-dimethyl terephthalate and 1,4-butandiol[1,2], which are thermally more stable than PBT and cost less than PBN. We have also discussed the sequence distribution of PBNT copolyesters and reported that the reactivity of BHBT (bishydroxybutyl terephthalate) and BHBN (bishydroxybutyl naphthalate) were about the same[3]. However, the crystallization kinetics and multiple melting point phenomena of PBNT copolytesters were not discussed. In this paper, crystallization kinetics and multiple melting point phenomena will be studied using d.s.c.

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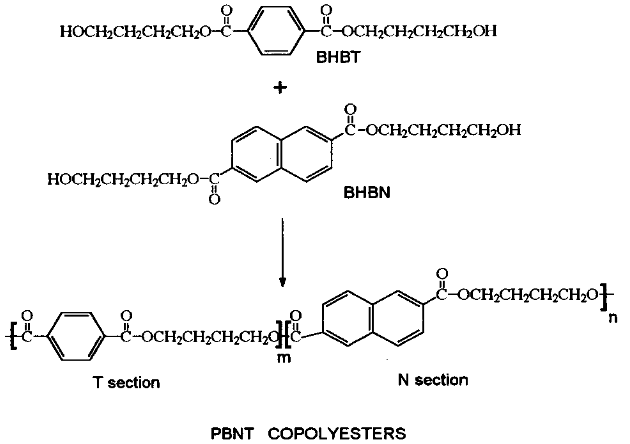
Experimental

PBNT copolyesters were prepared according to our previous papers.[1,2] The polycondensation reaction is shown in Scheme 1 and the compositions of resulted copolymers were determined by NMR[3] as shown in Table 1. The kinetics of isothermal crystallization was determined using a Perkin-Elmer d.s.c.-7 operating in nitrogen atmosphere. Temperature calibration was carried out using pure samples of In and Zn. The apparent enthalpies were determined using the conventional method, comparing the areas under the d.s.c. curve with the corresponding areas of a standard sample of Indium, taking $\triangle H_f$=28.45 Jg^{-1}.

Isothermal crystallization

Experiments for crystallization kinetics have been performed following the usual method. In order to melt all crystals completely, the samples were heated to a temperature about 40℃above their melting temperature, and then standing at that temperature for 6 min before quenching to the crystallization temperature at a rate of 300℃/min. At the desired crystallization temperature, the crystallization exotherms were recorded as a function of time until no change was observed.



Scheme 1 Polycondensation of PBNT copolyesters.

Table 1. The sample code and polymer composition of PBNT copolyesters.

Sample code	polymer composition determined by NMR (%)	
PBN	N section=100	T section=0
PBNT I	N section=62.9	T section =37.1
PBNT II	N section =55.5	T section =44.5
PBNT III	N section =45.6	T section =54.4
PBT	N section = 0	T section =100

Results and Discussion

Isothermal crystallization

Figure 1 shows the second run cooling scan(20℃min^{-1}) of PBNT copolyesters. The order of crystallization temperature(Tc) is PBN> PBT> PBNT I≒ PBNT II≒PBNT III.

The reduced crystallinity, X(t), at a given time and crystallization temperature for a polymer can be calculated from its d.s.c. thermogram.[4] base on Eq.1.

$$X(t) = \int_0^t (dH/dt)/\int_0^\infty (dH/dt) = A_t/A_\infty \text{ ----------- } (1)$$

A_t is the area under the d.s.c. curve from t=0 to t=t, and A_∞ is the total area under the crystallization curve. A typical plot of X(t) vs. time for the PBNT I is shown in Figure 2 at different isothermal crystallization temperatures. From the slope of plot in Figure 2, the rate of crystallization (Vc) was calculated. We take Vc as the rate of crystallization corresponding to the straight section of the curve.[4,5,6] The activation energy associated to the overall process of crystallization has been evaluated from the rates of crystallization by using the following equation:[4,5,6]

$$Vc = A \exp(-Ec/RT) \text{------------------------} (2)$$

where A = a constant ,T= the crystallization temperature, Ec= activation energy and R= gas constant. Plotting lnVc vs. 1/T, Ec can be obtained from the slope. The Vc and Ec values of PBNT copolyesters were listed in Table 2. The crystallization half times ($t_{1/2}$) was defined as the time required to reach X(t)=0.5. The activation energies of PBNT

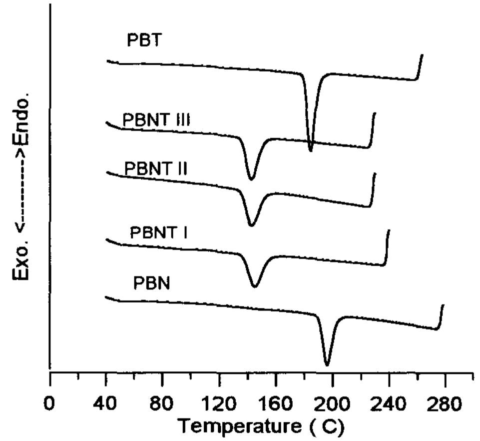


Fig. 1.Second-run d.s.c. cooling curves of PBNT copolyesters (scan rate 20 ℃min^{-1})

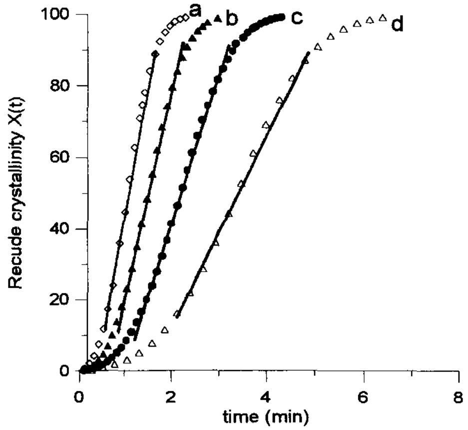


Fig. 2. Reduced crystallinity as a function of time plot for PBNT I (a)anneal at 161 ℃ (b) anneal at 164 ℃ (c) anneal at 167 ℃ (d) anneal at 170 ℃

copolyesters, evaluated from the crystallization rates Vc were high, and decreased with increasing naphthalene content in PBNT at the temperature range of 161-170℃.

The kinetic analysis of the isothermal crystallization was carried out on the basis of the Avrami equation.[7]

$$X(t)=1-\exp(-Kt^{n}) \text{---------------------------} (3)$$

Taking logarithms of Eq 3 and rearranging results into in Eq. 4

$$\ln [-\ln (1-X(t)]=\ln K + n \ln t \text{----------------} (4)$$

A typical Avrami plot for the PBNT I at different crystallization temperatures was shown in Figure 3. From the slope and intercept of the Avrami plot, the Avrami exponent n and rate constant K were obtained. Another approach to the Avrami rate constant K was calculated from Eq.3 by taking X(t)=0.5, then

$$K=\ln 2/t_{1/2}^{n}. \text{---------------------------------} (5)$$

The value of n, K, K(Eq. 5) for PBNT copolyesters were also summarized in Table 2. From Table 2, the Avrami exponent is 2.5-3.0 and increases slightly with increasing crystallization temperature. The Avrami exponent n, shown in Table 2, seems to be independent on the compositions of PBNT copolyesters. This may be due to the long butylene segment reduced the difference between BHBN and BHBT, and also the flexible and long butylene segment had made this molecule to adopt a configuration that would fit into a lattice structure easily, and thus the PBNT copolyesters tended to crystallize as in the isomorphism state. A good agreement between the K(Eq. 5) and K values from the intercept of the Avrami plot is shown in Figure 4. The K values increased with increasing naphthalene content in PBNT and approached the maximum as the crystallization temperature decreased.

Table 2. Crystallization parameters for PBNT copolyesters

Sample	Tc(℃)	Vc(min^{-1})	$t_{1/2}$(min)	K(min^{-n})	n	K (Eq.5)	Ec(KJ mol^{-1})
PBNT I	161	0.765	1.08	$5.97*10^{-1}$	2.5	$5.73*10^{-1}$	169.6
	164	0.602	1.51	$2.36*10^{-1}$	2.7	$2.26*10^{-1}$	
	167	0.429	2.21	$7.34*10^{-3}$	2.9	$7.13*10^{-2}$	
	170	0.297	3.40	$1.99*10^{-3}$	3.0	$1.87*10^{-3}$	
PBNT II	161	0.613	1.41	$3.08*10^{-1}$	2.5	$2.94*10^{-1}$	221.5
	164	0.450	2.10	$9.17*10^{-2}$	2.8	$8.88*10^{-2}$	
	167	0.288	3.35	$2.41*10^{-2}$	2.8	$2.36*10^{-2}$	
	170	0.178	5.60	$5.41*10^{-3}$	2.9	$5.13*10^{-3}$	
PBNT III	161	0.565	1.62	$1.90*10^{-1}$	2.7	$1.86*10^{-1}$	273.1
	164	0.383	2.52	$4.73*10^{-2}$	2.9	$4.58*10^{-2}$	
	167	0.216	4.17	$1.14*10^{-2}$	2.9	$1.11*10^{-2}$	
	170	0.124	7.86	$1.32*10^{-3}$	3.0	$1.26*10^{-3}$	

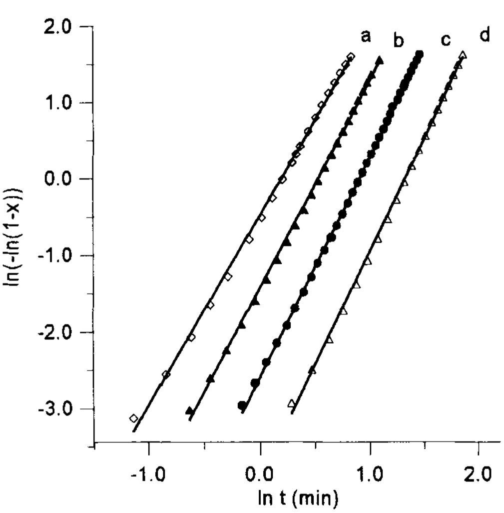


Fig. 3. A typical Avrami plot for PBNT I (a)anneal at 161 °C(b) anneal at 164 °C (c) anneal at 167 °C(d) anneal at 170 °C

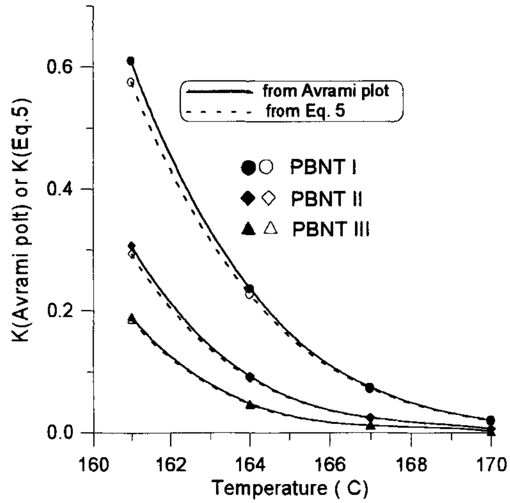


Fig. 4. The Avrami rate constants (K and K(Eq. 5) values of PBNT copolymers with temperature.

Multiple-Melting Phenomena:

Figure 5 shows second run heating scan(20 °C$\min^{-1}$) of PBNT copolyesters. Because all d.s.c. curves showed double melting phenomena, further study on melting behavior was made for PBNT copolyesters.

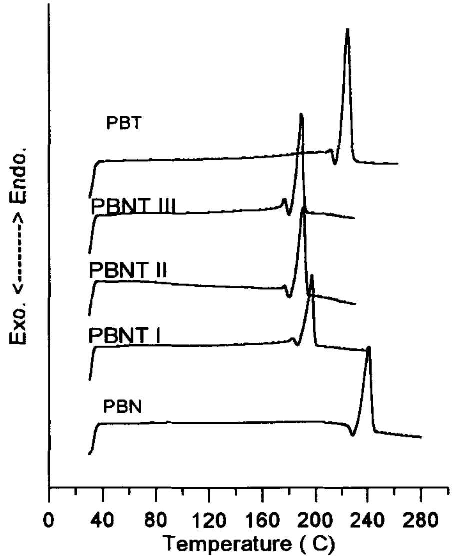


Fig. 5. Second-run d.s.c. heating curves of PBNT copolyesters (scan rate 20 °C$\min^{-1}$)

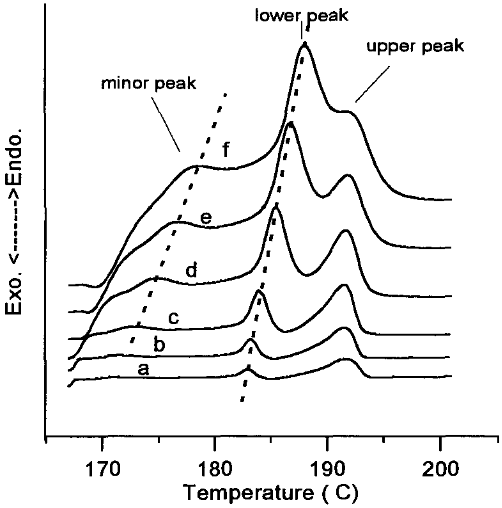


Fig. 6. Various d.s.c. heating rates of PBNT II crystallized at 167 ℃for 30 min (a)3 ℃min^{-1} (b)5 ℃min^{-1} (c)10 ℃min^{-1} (d)20 ℃min^{-1} (e)30 ℃min^{-1} (f) 40 ℃min^{-1}

Dependence of the melting peak on heating rate

Figure 6 shows d.s.c. curves of PBNT II under different heating rate(from 3℃min^{-1} to 40℃min^{-1}). The peak sizes of minor and lower peaks increased with increasing heating rate, whereas the upper peak decreased under similar conditions. The enthalpies of minor and lower peaks increased with increasing heating rate, but the enthalpy of upper peak decreased. This results implied that the lower peak and minor peak were attributed to melting of crystallites formed during primary and secondary crystallization, and the upper peak was due to melting of crystals formed during recrystallization of imperfect lamellae. When raising the heating rate the amount of recrystallization decreased because of the short time for melting and recrystallization. The faster the heating rate, the less the amount of recrystallization; thus, the upper melting peak ought to decrease.

Dependence of the melting peaks on crystallization temperature and holding time

Figure 7 shows the d.s.c. scans at 10℃min^{-1} of various PBNT II samples that were quenched from the melt state and subjected to isothermal crystallization at (a)167℃20min, (b)170℃25min, (c)173℃35min and (d)176℃60min. In addition to the upper melting peak and lower melting peak, a minor endothermic peak can be clearly identified in each thermogram slightly above the respective crystallization temperature. Interestingly, the peak temperature of the upper melting endotherm appeared to be independent of the isothermal crystallization temperature, but the melting enthalpy decreased with increasing crystallization temperature and holding time. By contrast, the minor peak and lower peak temperatures were strongly dependent on the crystallization temperature used and holding time at that temperature. The minor peak temperature and lower peak temperature increased with

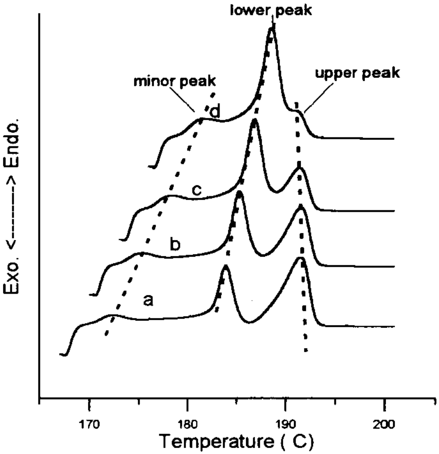


Fig. 7. D.s.c. heating scans (10℃min^{-1} of PBNT II crystallized at (a) 167℃ 20min(b) 170℃ 25min (c)173℃ 35min (d) 176℃ 60min

the crystallization temperature and holding time, the enthalpies of minor peak and lower peak also increased with crystallization temperature and holding time. These results implied that minor crystal lamellae and lower crystal lamellae could thicken with time when held at an isothermal crystallization temperature for long enough time. That is, when the crystallization temperature and holding time increase, the imperfect(thin) lamellae will become more perfect(thick) lamellae, so the upper endothermic peak due to melting of crystals formed during recrystallization of imperfect lamellae decreases with increasing temperature and holding time.

Figure 8 shows the d.s.c. scans at 10℃min^{-1} of the PBNT I crystallized at 167℃for various time. The d.s.c. curves of PBNT I did not show minor peak for 1 min and 1.5 min but change in its intensity and location with increasing time of crystallization after 5 min. The baseline became unhorizontal when the time reached 2 min . This implied the secondary crystallization occurred at this moment and grew with time. That is, the crystallization is two stage mechanism and the minor crystal lamellae grows with lower crystal lamellae in parallel when annealing time increases. Woo et. al.[8,9] described the secondary crystallization as a line growth mechanism(n=1) and Stein et. al.[10] and Okamoto et al[11] described PBT as three dimensional heterogeneous spherical crystal(n=3), the fractional n value (2.5-3.0) from Table 2 may be attributed to the secondary crystallization occurring during the crystal growth.

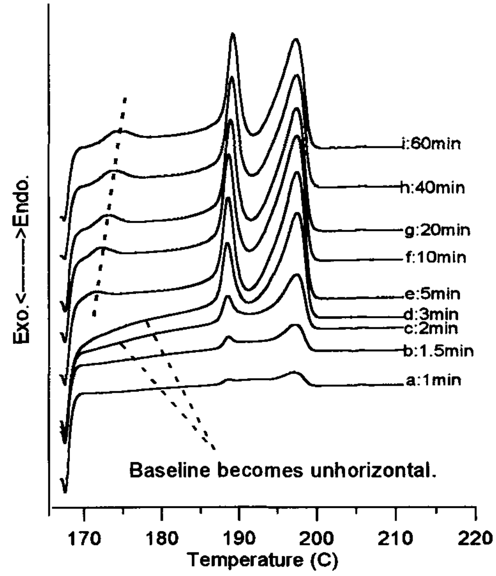


Fig. 8. D.s.c. heating scans (10 °Cmin^{-1}) of PBNT I crystallized at 167 °C for various times (a) 1 min (b)1.5 min(c)2 min (d)3 min (e)5 min (f) 10 min (g)20 min (h)40 min (I) 60 min

Acknowledgment

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