Kinetics of Mesophase Transitions in Thermotropic Copolyesters. 1. Calorimetric Study

Stephen Z. D. Cheng

Institute and Department of Polymer Science, The University of Akron, Akron, Ohio 44325.
Received December 15, 1987

ABSTRACT: Nonisothermal and isothermal kinetic studies of copolyesters with different 1,4-dihydroxybenzoic acid (HBA) and 2,6-dihydroxynaphthoic acid (HNA) compositions were carried out by differential scanning calorimetry (DSC). Different transition behavior is observed in the nonisothermal experiments among those copolymers, and it is strongly dependent on crystallization conditions (cooling rate) and chemical structure of their counits. It has been observed that crystals of macromolecules have a tendency to reject noncrystallizable counits. In isothermal experiments, two types of transition processes have been distinguished for the copolymers of 75/25 and 30/70 (HBA/HNA): a fast process which is characterized as solidification and a slow process which is close to a normal crystallization process of the polymers. The transitions may be described as a "condis" crystal transition from a nematic liquid. Microscopic structural formation has been discussed. The metastability and annealing effect of the crystals are analyzed. Thermodynamic data of the two copolymers (75/25, 30/70) at metastable equilibrium have also been estimated. The Avrami treatment still holds for the slow process, but with low values of the Avrami parameter, n. An explanation has been attempted.

Introduction

Macromolecular crystallization behavior has been extensively studied during the last 30 years.[1] For many crystallizations of flexible, linear macromolecules from a melt, heterogeneous nucleation is found, followed by spherulitic, chain-folded crystal growth. The macroscopic, overall crystallization process can be described by an Avrami equation:[2]

$$1 - V^c = \exp(-Kt^n) \tag{1}$$

with $n = 3$. V^c is the volume-fraction crystallinity, K is a temperature-dependent nucleation, and t represents time. In the case of time-dependent nucleation, n is usually equal to four. For two-dimensional morphologies n decreases by one. Quite often, one also observes fractional exponents or two sequential expressions like eq 1 with different values of n due to secondary crystallization or crystal perfection. Typical examples for the Avrami kinetics are polyethylene (PE),[1,3] poly(ethylene terephthalate) (PET),[1,4] and poly(aryl ether ether ketone).[5] A survey of over 50 polymers has shown that all of their Avrami crystallization kinetics have values of n above two, except for crystallization of fibrous and drawn samples which usually have lower exponents in the Avrami equation. Even in flexible random copolymers, e.g., ethylene terephthalate and ethylene sebacate (80/20 in molar ratio), the Avrami parameter n was found to be close to three.[1] However, without parallel knowledge of the microscopic, independently proven mechanism, the macroscopic, experimentally derived Avrami equation and Avrami parameters are only a convenient means to represent empirical data of crystallization.

A microscopic mechanism of polymer crystal growth was proposed shortly after the discovery of chain-folded crystals.[6] Practically all present efforts to describe the crystal growth are based on the activated state theory making use of surface free energy as the main hindering effect. Additional progress has been made based on molecular segregation[7] and continuous crystal growth related to morphological changes of growing crystal surfaces.[8]

For the discussion of crystallization of flexible random copolymers, it is of basic importance to find degree of isomorphism possible between various repeating units. If copolymers consist of crystallizable A and noncrystallizable B units, the nature of the crystalline state must lie between two extremes: the crystalline phase is composed entirely of A units, and is in metastable equilibrium, with a mixed amorphous phase of A units and noncrystallizable B counits (comonomer exclusion); and the crystalline phase is a solid solution of A and B units, the B counits produce defects in the crystalline A lattice and both crystalline and amorphous phases have the same composition (uniform comonomer inclusion). A theory of flexible random copolymer crystallization has been developed for the depression of melting point,[9–12] the kinetics of crystallization,[10–12] and the amount of noncrystallizable counit that is incorporated into the crystalline phase.[11] Qualitatively, the faster the crystal growth rate, the greater is the inclusion of B counits. However, some experimental results disagree with such a theoretical prediction.[13]

Recently, it has been interesting to introduce transition studies of random copolymers with rigid chain molecules, which frequently display a nematic melt. Structural formation during such a transition is basically different from crystallization of flexible copolymers. Rigidity of the molecules leads to an impossibility of chain folding and an anisotropic molecular motion in the supercooled nematic melt. Mesophase transitions usually occur via aggregation of the rigid chain molecules. Special attention has been paid to a series of copolyesters with different 1,4-dihydroxybenzoic acid (HBA) and 2,6-dihydroxynaphthoic acid (HNA) compositions. The X-ray structures of the copolymers were reported by Blackwell et al. and Stamatoff.[14] A high degree of axial orientation and three-dimensional order have been observed. The meridional maxima are aperiodic.[14,17] The transition enthalpies and entropies of the copolymers were found to be surprisingly low.[15–17] A recent report on one of the copolymers, 58/42 (HBA/HNA), has claimed an unexpected high crystallinity (60% or even higher) and occurrence of cocrystallization of two repeating units in its crystals during the transition. A criticism has been made to the copolymer crystallization theory put forward by Sanchez and Eby for flexible macromolecules.[15] Special models have been developed also for the crystallization of those copolymers.[17,18] The basic crystal was suggested to be with rotational disorder due to conformational mobility, proven by mechanical and dielectric relaxation.[19] The morphology of the superimposed crystals was proposed to be based on a matching of order between adjacent molecules.[18]

In this paper, as the first one in this series, nonisothermal and isothermal transition kinetics of the copolyesters are reported in a calorimetric study. We may now extend

0024-9297/88/2221-2475$01.50/0

our knowledge to explain in more detail the mesophase transition behavior and structural formation of rigid macromolecules.

Experimental Section

The random copolymers used in this study are composed of HBA and HNA with molar ratios of 75/25, 58/42, and 30/70 (HBA/HNA). The molar masses of the average repeating units can be calculated to be 132.5, 144.1, and 170.2 g/mol, respectively. All samples were kindly supplied by the Celanese Research Co. The preparation of the copolymers is described in detail by Calundann.[20] The copolymers were characterized by Celanese through their inherent viscosities in pentafluorophenol at 333 K (7.8, 5.1, and 9.2 dL/g, respectively). The chain length of similar molecules has been estimated to be about 140 repeating units.[14]

The pelletized samples provided were pressed into films with about a 1-mm thickness at a temperature of 580 K. To avoid any influence of previous thermal history, every sample was used only once.

Two instruments, a Du Pont thermal analyzer (990) coupled to a DSC cell and a Perkin-Elmer DSC2 connected to a newly established microlaboratory thermal analysis system on IBM PC computer, were used for scanning calorimetry. Both temperature and heat flow scales were calibrated with high-purity melting standards (naphthalene, benzoic acid, indium, lead, and tin) in a wide heating rate range (0.31–40 K/min). All thermal analyses were run under dried nitrogen.

The nonisothermal crystallization samples were heated to above their metastable equilibrium melting temperature, $T_d°$ (see below), and held for 15 min. Then, the samples were cooled to 320 K at different cooling rates. The DSC cooling traces were recorded. Heating experiments were then performed to $T_d°$. If a cooling rate of larger than 10 K/min had been used, the same heating rate must be used in order to avoid a possible annealing effect. The isothermal crystallization samples were held for 15 min above $T_d°$ as before. They were cooled to the predetermined crystallization temperature, T_c, as quickly as possible, and kept there for different fixed time periods, t_c. The samples then were heated again to $T_d°$ with (−10 K/min) or without cooling, and the DSC heating traces were recorded. If measurements of heat capacities were necessary, such as in the nonisothermal crystallizations, the base line of both empty pans and a standard sample for heat capacity, sapphire, were also performed.

The sample-weights were controlled in a range of 15–20 mg. All pan weights were within a deviation of ±0.002 mg. The standard heating rate is 10 K/min, unless otherwise specified.

In this paper, peak temperatures for both heating and cooling traces were used. The width of transition peaks for the nonisothermal experiments was defined as a temperature difference at half-peak height, $\Delta T_c(1/2)$. The onset starting temperature was also used in the cooling experiments during the transitions, it was determined by the intersection between base line and extrapolation of peak line at the high-temperature side. When two melting peaks were observed during heating, their temperatures are determined to be $T_d(h)$ for the high melting peak and $T_d(l)$ for the low melting peak. The corresponding heats of transition for the peaks are $\Delta H_d(h)$ and $\Delta H_d(l)$, respectively.

Results

Nonisothermal Experiments. Figure 1 shows nonisothermal DSC cooling traces (heat capacity measurements) of the three copolymers from their nematic melts at different cooling rates. Surprisingly enough, for the copolymer of 75/25, a broadening of the exothermic peak is observed with decrease in cooling rate. Meanwhile, the peak and onset starting temperatures had shifted to higher temperatures as listed in Table I. On the other hand, the widths of the exothermic peaks do not change for the copolymers of 58/42 and 30/70 in the whole cooling rate range here studied. Only their onset starting and peak temperatures shift to lower temperatures with increasing cooling rate. These data can also be found in Table I. Nevertheless, broadening of the melting peak during heating with increasing heating rate is similar for the three copolymers. The heating DSC traces of those transitions at different heating rates are quite close to those of a normal crystal-melting process despite the width of the melting peaks which only changes about 2–3 K within the heating rate range here studied, instead of a considerable broadening (10–20 K) in the process of extended chain–crystal melting (polyoxymethylene) under the same heating condition.[21]

Table I
Nonisothermal Transition Properties of the HBA/HNA Copolyesters

cooling rate, K/min	T_c, K[a]	$\Delta T_c(1/2)$, K[b]	T_m, K[c]	ΔH_d, kJ/mol[d]
		75/25 HBA/HNA		
5	518.8	50	564.5	0.91
10	514.4	35	564.0	0.66
20	512.4	19	563.7	0.48
40	508.6	13	563.1	0.45
		58/42 HBA/HNA		
0.31	493.4	6.0	521.7	0.61
1.25	487.8	6.1	521.6	0.58
10	477.3	5.0	521.4	0.58
20	473.0	5.1	521.1	0.55
		30/70 HBA/HNA		
2.5	548.8	8.2	580.0	0.86
5	543.3	7.9	579.5	0.85
10	536.5	8.1	579.3	0.84
40	528.9	7.9	579.1	0.82

[a] Exothermic peak temperatures during cooling. [b] Temperature width of the exothermic peaks at half-peak height. [c] Endothermic peak temperatures during heating. [d] Heats of transitions measured during heating.

In Table I, the heats of transition of the copolymers are also listed. It is interesting that for the copolymer 75/25, the heat of transition increases with decreasing cooling rate. For the other two copolymers, however, it changes very little in the cooling rate range studied.

Isothermal Experiments in Low-Temperature Regions. Two temperature regions have been divided based on the nonisothermal experiments described in the previous section. The low-temperature region lies below the exothermic peaks shown in Figure 1a,c, and another, above the peaks. For the two copolymers of 75/25 and 30/70, the boundaries between the two temperature regions are 512 and 530 K, respectively (see below).

Figure 2a shows, as an example, a set of DSC heating traces for the copolymer of 75/25 crystallized at 505 K without cooling after different fixed time periods, t_c. It has been found that there are two distinguished endothermic melting peaks. Quantitative analysis reveals two different transition processes as shown in Figure 2b (for two isothermal temperatures: 485 and 505 K). One is contributed by the high melting peak (square symbols), which shows a linear relationship between the heat of transition, $\Delta H_d(h)$, and logarithmic crystallization time, $\log t_c$:

$$\Delta H_d(h, T_c, t_c) = A(T_c) \log t_c + B \qquad (2)$$

where $A(T_c)$ is the parameter which characterizes the velocity of the transition. Another is from the low melting peak (triangle symbols). The heat of transition, $\Delta H_d(l)$, increases with time. From Figure 2b, one can find that the high melting peak forms very fast, and in fact, it grows before reaching isothermal condition. The low melting peak, on the other hand, corresponds to the slow process. The overall changes of ΔH_d with respect to the time ($\log t_c$) at T_c = 480 and 505 K are also plotted in Figure 2b (sphere symbols). Relationships between transition temperature, T_d, and time, $\log t_c$, for both high and low melting

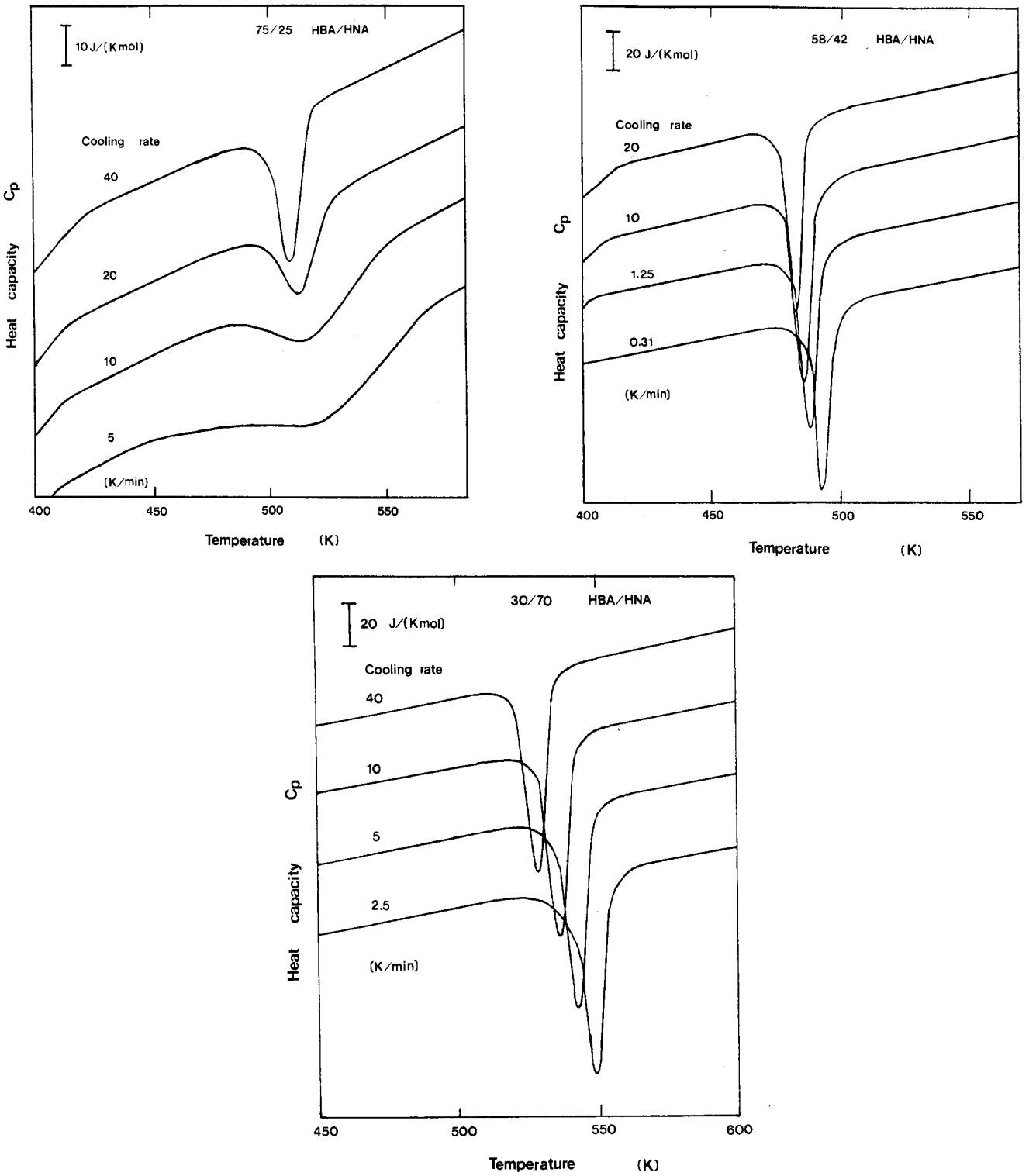

Figure 1. A set of DSC cooling traces (heat capacity measurements) of nonisothermal experiments for the copolymers from nematic states at different cooling rates: (a, top left) 75/25; (b, top right) 58/42; (c, bottom) 30/70.

peaks are shown in Figure 2c (for isothermal temperatures: 485, 495, and 505 K). Indeed, $T_d(h)$ does not change much with increasing time, t_c. However, $T_d(l)$ increases linearly with log t_c at different T_c:

$$T_d(l, T_c, t_c) = C(T_c) \log t_c + D \quad (3)$$

where $C(T_c)$ indicates the changing rate of crystalline metastability. It decreases with temperature [$C(T_c)$ = 20.8 at 485 K and 15.3 at 505 K].

In this region, three temperatures were chosen for isothermal experiments: 485, 495, and 505 K. Every experiment was repeated 3 times, and they are within very good reproducibility (±1.2% for ΔH_d, and ±0.1% for T_d).

For the copolymer 30/70, similar results were obtained. Figure 3a shows a set of DSC heating traces after different fixed time periods at T_c = 525 K. Figure 3b indicates changes of the heat of transition of the 30/70 sample for both fast (squares) and slow (triangles) processes, as well as the overall changes (spheres). Relationships between the transition temperature and time are plotted in Figure 3c. The values of $C(T_c)$ change from 16.8 at 480 K to 14.1 at 525 K. However, several special features of the 30/70 sample need to be noticed. First, the change of $\Delta H_d(l)$ of the 30/70 copolymer is generally slower than that of the

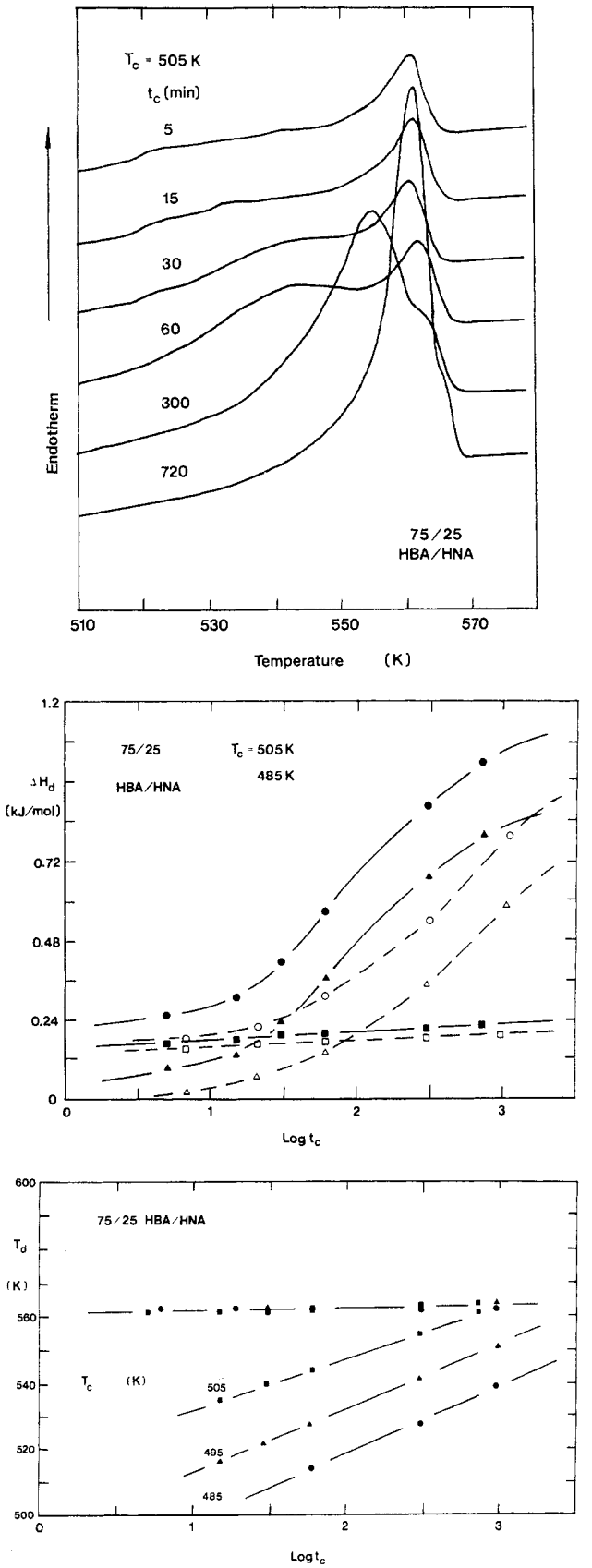

Figure 2. Isothermal experiments for the copolymer of 75/25 in the low-temperature region: (a, top) a set of DSC heating traces at T_c = 505 K in different time periods; (b, middle) relationship between ΔH_d and log t_c at T_c = 485 K (open symbols) and 505 K (closed symbols), in which square symbols (□, ■) represent the fast transition process, triangular symbols (△, ▲) represent the slow transition process, and circular symbols (○, ●) represent the overall change of ΔH_d; (c, bottom) relationships between T_d and log t_c at T_c = 485, 495, and 505 K.

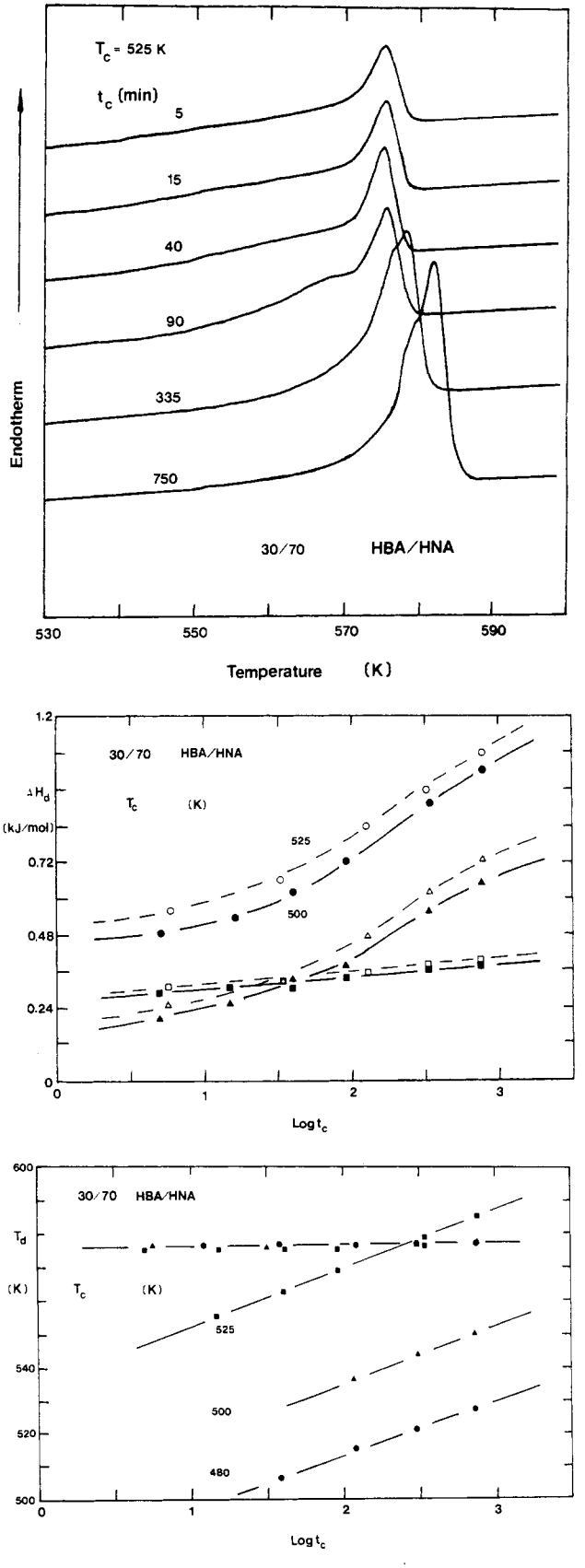

Figure 3. Isothermal experiments for the copolymer of 30/70 in the low temperature region: (a, top) a set of DSC heating traces at T_c = 525 K in different time periods; (b, middle) relationship between ΔH_d and log t_c at T_c = 500 K (closed symbols) and 525 K (open symbols), in which square symbols (□, ■) represent the fast transition process, triangular symbols (△, ▲) represent the slow transition process, and circular (○, ●) represents the overall change of ΔH_d; (c, bottom) relationship between T_d and log t_c at T_c = 480, 500, and 525 K.

75/25 one during the isothermal experiments in this temperature region. Second, the heat of transition formed during cooling, $\Delta H_d(h)$, which is characterized by the high melting peak, for 30/70 is larger (in fact, almost double) than that of 75/25.

Isothermal Experiments in High-Temperature Regions. When the isothermal experiments were carried out in the temperature region above 512 K (see below) for the copolymer 75/25, the transition behavior changes. Only one endothermic melting peak was observed in the time scale studied here as shown in Figure 4a, revealing one transition process, even though a broadening of the melting peak with increasing time is clear. Changes of the heat of transition with respect to logarithmic time are plotted in Figure 4b at three chosen temperatures (515, 530, and 545 K). Such changes slow down with increasing temperature. The transition temperature increases linearly with logarithmic time, log t_c, as shown in Figure 4c at these three temperatures. Their slopes of the temperature with respect to log t_c, $dT_d/d(\log t_c)$, steepen with increasing temperature, T_c [$C(T_c)$ = 3.69 at 515 K; 7.39 at 530 K, and 9.12 at 545 K].

Similar results can be observed for the copolymer 30/70. Figure 5a shows a set of DSC heating traces in different time periods at T_c = 560 K. One found a broadening of the melting peak with increasing time, and finally, a second melting peak developed which is lower than the original one after a long isothermal time. Changes of the heat of transition with respect to logarithmic time at chosen temperatures (T_c = 550, 560 K) are plotted in Figure 5b. The contribution of the second melting peak to ΔH_d at 560 K is also included (see Figure 5b). Again, the transition temperature has a linear relationship with log t_c as shown in Figure 5c, and the change of slopes has the same tendency as in the case of 75/25 [$C(T_c)$ = 7.98 at 550 K, and 11.31 at 560 K].

The reproducibility of the experiments performed in this temperature region is equally as good as that in the low-temperature region described in the previous section.

$\Delta H_d°$ and $T_d°$ at Metastable Equilibrium. Based on the experimental data of the heats of transition and transition temperatures for both the copolymers, extrapolations were made to infinite crystallization time to obtain their thermodynamic properties at metastable equilibrium, $\Delta H_d°$ and $T_d°$. Figure 6a shows for the copolymer 75/25 and the extrapolation of reciprocal heat of transition $(\Delta H_d)^{-1}$ with respect to reciprocal logarithmic time, $(\log t_c)^{-1}$, at different temperatures, T_c. The extrapolated value at $(\log t_c)^{-1} = 0$ indicates the heat of transition for 75/25 at metastable equilibrium, $\Delta H_d°$ (3.68 ± 0.25 kJ/mol). A relationship between T_d and $(\log t_c)^{-1}$ leads to an extrapolated value of $T_d°$ at metastable equilibrium (610 ± 2 K) as shown in Figure 6b.

A parallel study was carried out for the copolymer 30/70. The heat of transition at the metastable equilibrium, $\Delta H_d°$, is 4.65 ± 0.30 kJ/mol. The transition temperature at equilibrium, $T_d°$, is 630 ± 2 K.

Transition Kinetics. It is now possible to look at overall transition kinetics based on the values of $\Delta H_d°$ at metastable equilibrium for both the copolymers. Equation 1 can be modified to the form

$$1 - \Delta H_d(T_c, t_c)/\Delta H_d° = \exp\{-K(T_c)t_c^n\} \quad (4)$$

For those transitions which do not show linear relationships between ΔH_d and log t_c, the Avrami treatment is usually a first test. Table II lists, according to eq 4, Avrami parameters n and $K(T_c)$ of both the copolymers crystallized at different temperatures. The results indicate that the values of n are in the range between 0.2 and 0.8.

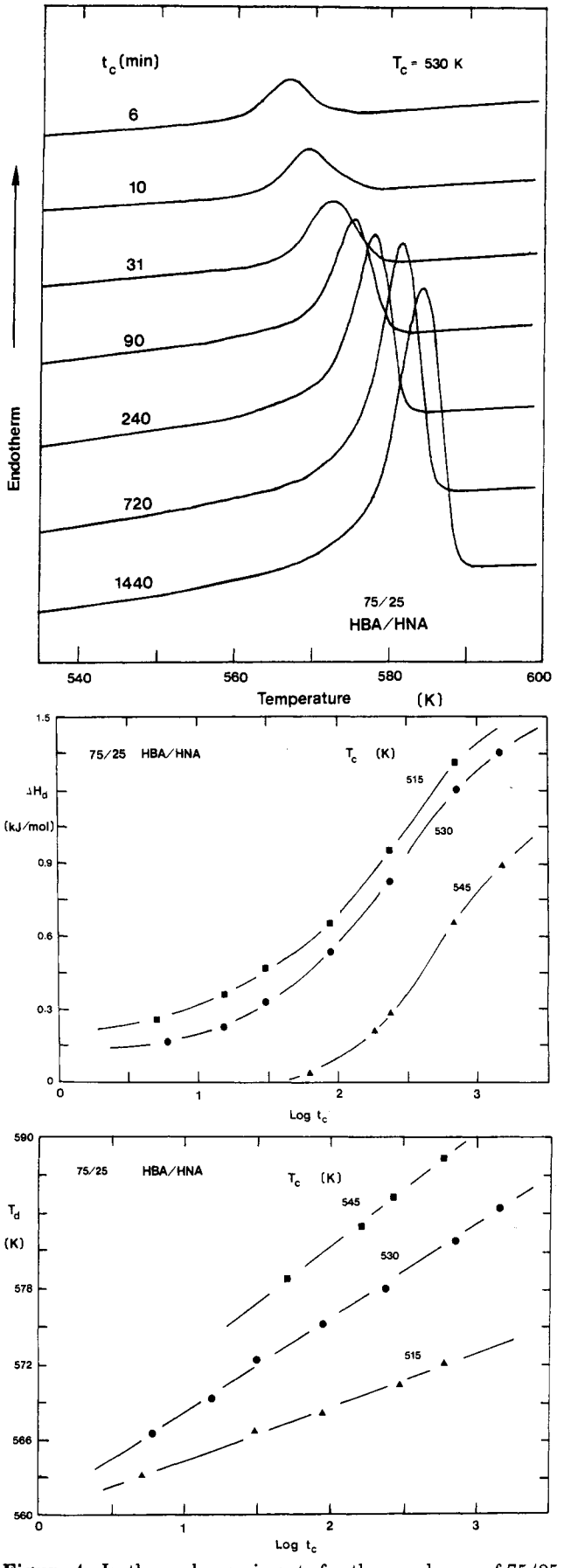

Figure 4. Isothermal experiments for the copolymer of 75/25 in the high-temperature region: (a, top) a set of DSC heating traces at T_c = 530 K in different time periods; (b, middle) relationships between ΔH_d and log t_c at T_c = 515, 530, and 545 K; (c, bottom) relationships between T_d and log t_c at T_c = 515, 530, and 545 K.

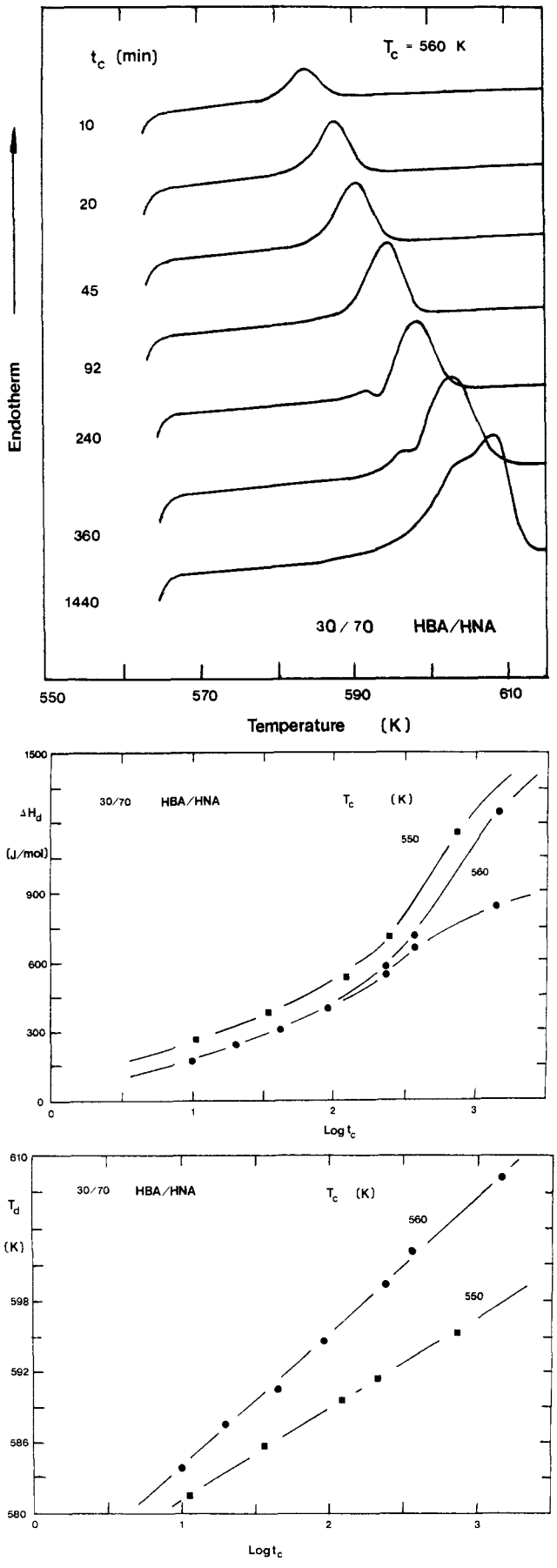

Figure 5. Isothermal experiments for the copolymer of 30/70 in the high-temperature region: (a, top) a set of DSC heating traces at T_c = 560 K in different time periods; (b, middle) relationships between ΔH_d and log t_c at T_c = 550, 560 K; (c, bottom) relationships between T_d and log t_c at T_c = 550, 560 K.

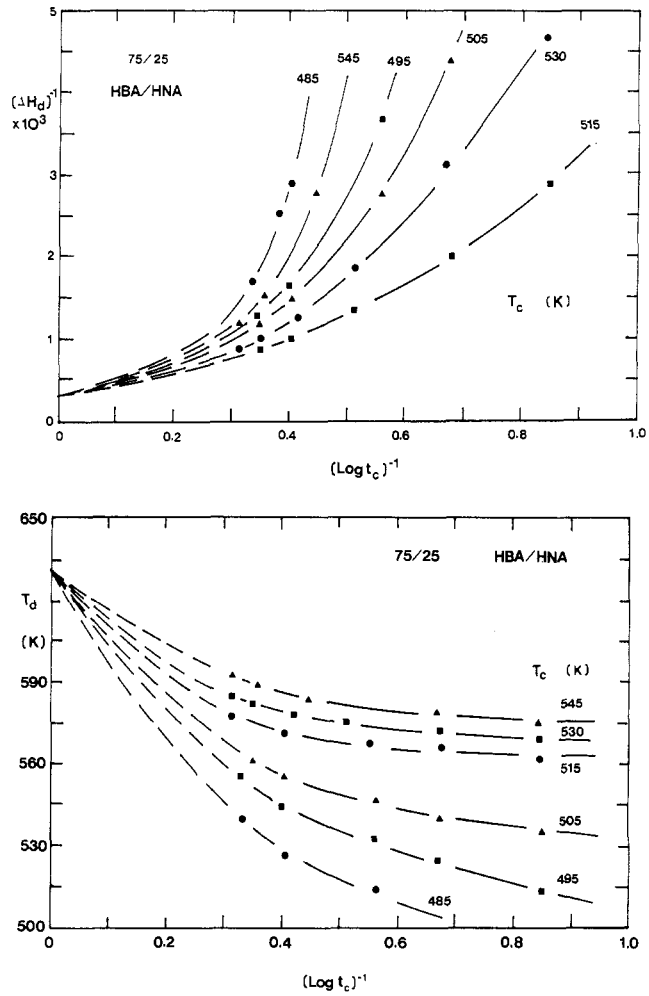

Figure 6. Thermodynamic data of the copolymer of 75/25 at metastable equilibrium: (a, top) extrapolation of $\Delta H_d°$ at different temperatures based on relationships between $[\Delta H_d]^{-1}$ and $[\log t_c]^{-1}$; (b, bottom) extrapolation of $T_d°$ at different temperatures based on relationships between T_d and $[\log t_c]^{-1}$.

Table II
Avrami Parameters of the Transition Kinetics of the 75/25 and 30/70 Copolyesters[a]

75/25 (HBA/HNA)			30/70 (HBA/HNA)		
T_c, K	n	log K	T_c, K	n	log K
485	0.67	−2.69	480	0.29	−1.62
495	0.54	−2.31	500	0.25	−1.55
505	0.49	−1.95	525	0.24	−1.51
515	0.34	−1.37	550	0.38	−1.66
530	0.45	−1.70	560	0.42	−1.85
545	0.73	−2.83			

[a] The Avrami parameters calculated here are based on eq 4 in the text.

Furthermore, relationships between temperature, T_c, and time, t_c, at different crystallinities $[\Delta H_d(T_c, t_c)/\Delta H_d°]$ for both the copolymers are shown in Figures 7. In Figure 7a two crystallinities of the copolymer 75/25 have been chosen: 10% and 20%. Relationships between log t_c and T_c at these two crystallinities show a similar kinetic behavior compared with a normal crystallization process (for details, see, for example, ref 1 and 2) if an overall crystallinity is taken into account; namely, this crystallinity must include both the fractions formed during cooling and isothermal experiments in the low-temperature region. A more or less symmetric shape with a minimum of log t_c at T_c = 512 for the copolymer 75/25 can be found, indicating that the fastest transition occurs at 512 K, and the tran-

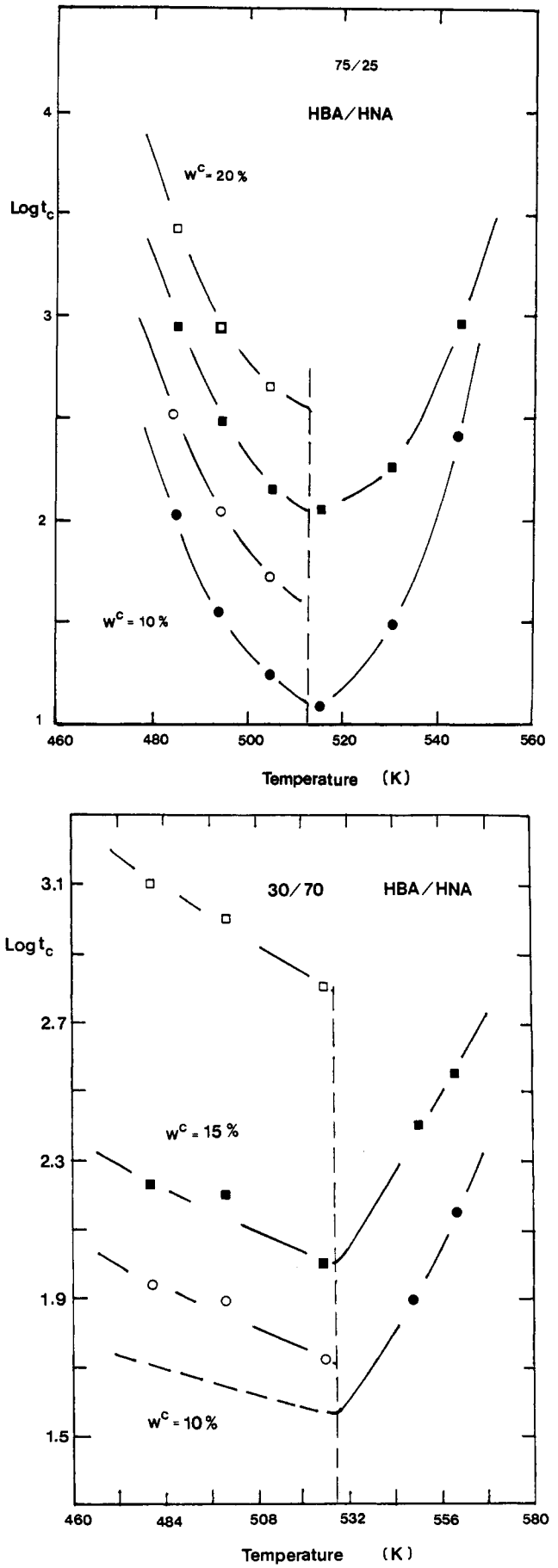

Figure 7. Relationships between log t_c and temperature for (a, top) W^c = 10% and 20% of the copolymer of 75/25 and (b, bottom) W^c = 10% and 15% of the copolymer of 30/70 (dashed line is expected data for W^c = 10%).

sition slows down with both increasing and decreasing temperature. However, a discontinuity is observed (Figure 7a, opened symbols) when one only considers the net formation of the crystallinity under isothermal condition in the low-temperature region, revealing that the isothermal transition below T_c = 512 K is much slower compared symmetrically to its correspondingly high-temperature side. From Figure 2b, one has found that the contribution to the crystallinity during cooling is about 4–6%.

Figure 7b shows similar results for the copolymer 30/70. Two crystallinities have been chosen to be 10% and 15%. A minimum of log t_c at T_c = 530 K can be found, but less symmetric shape of the curve is seen. A discontinuity is also observed in Figure 7b if only the net formation of crystallinity under isothermal condition in the low-temperature region is considered. Since the crystallinity during cooling is about 10% for the copolymer 30/70, one cannot precisely determine log t_c in the low-temperature region for the overall crystallinity of 10% in Figure 7b. It has been shown by a dashed line as predicated values.

Discussions

Solidification and Cooperativity during the Mesophase Transitions. For a normal nonisothermal crystallization process, such as PEEK[5] and PET,[22] true supercooling of a metastable melt is caused by the necessity of nucleation.[1] A decrease of the peak temperature and broadening of the peak width with increasing cooling rate during crystallization are explained by the fact that transition kinetics is slow relative to the experimental cooling rate.[21]

For the copolymer 58/42, an almost constant width of its exothermic peaks in the cooling rate range between 0.31 and 40 K/min (Figure 1b) reveals that the transition process of the copolymer is rather faster (usually within several seconds or even shorter) than the rate at which heat can be released to the surroundings by conduction. Such a process is usually described as a *solidification* that is dominated by heat transfer.

On the other hand, for the copolymer 75/25 the peak width is broadened with decreasing cooling rate from a solidification (Figure 1a). One may expect that only a gradual change of the heat capacity during the transition should be observed when the cooling rate is sufficiently slow. It is preliminarily explained that during the transition the cooperativity of chain molecular motion is gradually lost.[23] More and more molecules individually cross over the phase boundary and aggregate with others. To observe such a phenomenon, a long enough crystallization time (slow cooling rate) compared with the time needed for molecular motion is necessary. A prerequisite is the chemical structure of counits in the copolymers. Only with a matching of order between adjacent molecules can the crystals grow.[17,18] For the copolymer 75/25, rich in phenylene groups, and statistically represented, three phenylene groups and one naphthalene group consist of one corepeating unit. It has a relatively high possibility to form crystals with matching counits. Nevertheless, for the copolymer 58/42, one may predict that phenylene and naphthalene groups are almost alternated randomly. Such a possibility of matching the counits becomes lower. On the other hand, if the chemical structure of the counits becomes regular, the nonisothermal transition behavior will be close to that in cases of normal crystallization.[24] Therefore, for the phase transition of copolymers, three different nonisothermal transition behaviors can be seen.

An interesting example is the copolymer 30/70 which is rich in naphthalene groups. An expected broadening of the transition peak with decreased cooling rate, similar

to the case of 75/25, is not observed. In contrast, the nonisothermal transition behavior of 30/70 is close to the case of 58/42 (Figure 1b,c). It will be explained in the next section.

For the solidification of the copolymers during their transitions, the heats of fusion, ΔH_d, should be almost constant in the cooling rate range here studied (Table I). However, a clear increase of ΔH_d for the copolymer 75/25 with decreasing cooling rate has been observed (Table I), indicating that metastability of the crystals does improve when the transition peak becomes broad during cooling.

In the isothermal experiments of the copolymers, the fast transition process could also be explained as a solidification process during cooling before isothermal conditions are reached.

Structural Formation of the Transitions. Transition of rigid copolymers occurs, which is basically different from crystallization of flexible linear macromolecules, via aggregation from an anisotropic molten (nematic here) state where chains are already extended, parallel, free of entanglements, and in proper sequence for crystallization.[25] During the transition two types of macromolecular motion must at least be included: first, a translational motion along the chain direction and, second, a rotational motion with respect to chain axis in order to adjust chains into register on a counit scale (matching of molecular and crystal dimension). The macromolecules may thus form a two-dimensional lattice perpendicular to the direction of chain axis and to some registry along chain direction. Therefore, during the transitions there are at least three possible hindering effects: translation, rotation, or/and nucleation (aggregation) of the macromolecules. Overall kinetics of the transition most likely results from a combination of the three effects, which are largely dependent on crystallization condition and chemical structure of the counits.

Experimental evidence has provided some insights, but certainly not all at this moment, to distinghish a few effects from this combination. The nonisothermal crystallization of the copolymer 30/70 shows similar behavior as the 58/42 one rather than that of 75/25, indicating that presumably the naphthalene groups in the copolymer 30/70 cannot rotate as easily as the phenylene group in the copolymer 75/25 since the rotation of 2,6-naphthalene group causes a twist of the chain molecules. It thus increases the rotational energy barrier. A larger cross-section and higher concentration of the naphthalene groups may also, on the other hand, introduce a larger friction during the translational motion along the chain direction in the copolymer 30/70. It increases the translational energy barrier and becomes another hindering factor.

In the case of 75/25, the nonisothermal experiments indicate a change in molecular motion from slow cooling (translational motion is possible) to quenching (local aggregation). Rigid macromolecules in the copolymers thus still have a tendency to reject noncrystallizable counits during the transition, even though such a comonomer exclusion is far from a metastable equilibrium.

In the low-temperature regions of isothermal experiments, a nonnegligible amount of crystals formed by solidification hampers further crystal formation. It leads to the discontinuities for both the copolymers as shown in Figure 7. They largely hinder the translational motion along the chain direction. It proves that the translational motion is one of the main effects during the transition. A similar observation can also be found in the high-temperature region of isothermal experiments. A broadening of the melting peaks (Figures 4a and 5a), especially for the copolymer 30/70, reveals that previously formed crystals hamper further crystal growth.

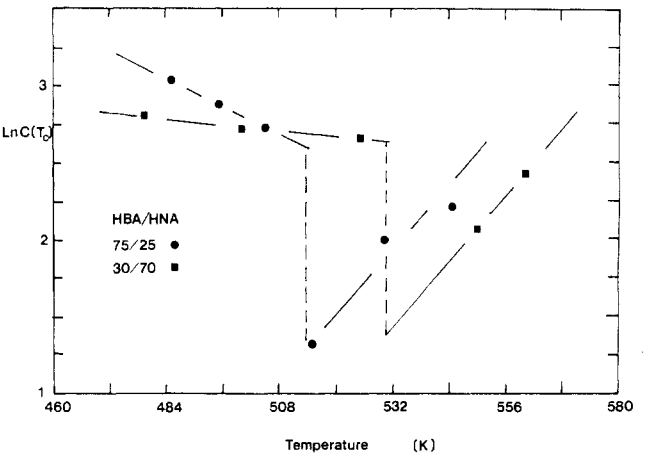

Figure 8. Relationsips between ln $C(T_c)$ and crystallization temperature for the two copolymers 75/25 and 30/70.

It is also interesting to find that those earlier grown crystals, during the fast transition process, are annealed slowly at later times (see below) and are independent of the later growth during the slow transition process. It indicates that the earlier crystals as nuclei of further growth are being exhausted due to the difficulty of moving noncrystallizable counits away from their fronts of crystal surfaces.

Crystal Annealing. In the low-temperature regions of isothermal experiments, the crystals formed by solidification (fast process) were provided to have a chance for crystal annealing by the following isothermal condition. It has been found that the heat of transition for the crystals obeys a linear relationship with logarithmic time, log t_c (more precisely, annealing time, t_a), as described in eq 2. The increase of crystallinity $[\Delta H_d(h, T_c, t_c)/\Delta H_d^\circ]$ for both the copolymers is, however, very small. The change in the transition parameter, $A(T_c)$, with respect to temperature for both of the copolymers in their low-temperature regions is exponentially temperature dependent, meaning that the annealing process becomes relatively effective at higher temperature. Moreover, from Figures 2c and 3c, the transition temperatures of the crystals formed by the fast process keep almost constant in the time period here studied [$T_d(h)$ changes within 1 K], clearly indicating that perfecting a crystal *after* the transition (annealing) is more difficult than *during* the transition by a further "freezing" of the chains in the crystals.

It is also surprising to see that the crystals formed by solidification are more stable than those crystallized in the slow process at least in the early stage of isothermal experiments. Therefore, one may conclude that solidification occurs in relatively ordered domains during cooling from the nematic melt.

Linear relationships between $T_d(l)$ and log t_c (see Figures 2c and 3c) at different T_c in the low-temperature regions indicate perfection processes during the crystal growth for both the copolymers. An exponential decrease of $C(T_c)$ with increasing T_c, as shown in Figure 8, means that poorer crystals formed at lower temperature and shorter time period are easier to be perfected, mainly by decrease of defects and improvement of the surface structure, as well as the size change of the crystals.

In the high-temperature regions for the two copolymers, only one transition process can be observed during crystallization. However, despite the results reported on the copolymer 58/42,[15] the heats of transition formed under isothermal condition for both the copolymers do not show

a linear relationship between ΔH_d and log t_c. Excluding any hindering effect caused by previously formed crystals, the chain molecules in this temperature region have relatively high mobility. Linear relationships between T_d and log t_c are still found. However, in contrast to those in the low-temperature regions, the transition parameter, $C(T_c)$, surprisingly increases exponentially with crystallization temperature as is also shown in Figure 8. It may be explained by the fact that higher chain mobility and longer crystallization times at higher T_c lead to the formation of better crystals.

Thermodynamic Properties of the Transitions. Thermodynamic properties of the transitions, $\Delta H_d°$ and $T_d°$, have been obtained based on the extrapolations (Figure 6). It must be noticed that in the cases of random copolymers here studied, no true equilibrium data can be found. A metastable equilibrium may only be reached as described as the first extreme case in the Introduction.

According to the data of $\Delta H_d°$ and $T_d°$ for both the copolymers, entropy changes during the transitions can be calculated on the basis of $\Delta S_d° = \Delta H_d°/T_d°$. For the copolymer 75/25, $\Delta S_d° = 6.03 \pm 0.5$ J/(K mol), and for the copolymer 30/70, $\Delta S_d° = 7.38 \pm 0.5$ J/(K mol). The mesophase transitions here studied are thus characterized by very low enthalpies and entropies of the transitions [compared to $\Delta H_d°$ = 20–50 kJ/mol and $\Delta S_d°$ = 40–100 J/(K mol) in usual cases].[26] On the other hand, the observation of melting peaks at different heating rates indicates that the first-order transition is observed, revealing that the crystals do form during the transitions. It must, therefore, be concluded that the crystal packing of the rigid copolymers is far from perfect, and chain conformations do not change very much from their nematic melts except when transitional motion along the chain direction is stopped. The formed crystals can thus be better described as "condis crystals"[25,26] rather than rigid crystals.

An unexpected high crystallinity of 60% or higher for the copolymer 58/42 is still surprising to us even though cocrystallization has been claimed.[15] From our experimental data, the degree of condis crystallinity below 40% for both the copolymers 75/25 and 30/70 is found, based on the metastable equilibrium data. It seems reasonable to see a degree of crystallinity of about 21% for a slowly cooled (unannealed) copolymer which contains 40 wt % HBA and 60 wt % HNA counits[26] compared with the data reported here (see Table I).

Transition Kinetics of the Avrami Type. Turning to the discussion of Avrami treatment for a crystallization process of flexible linear macromolecules, one would like to review three assumptions which have to be made in order to describe an overall crystallization kinetics using eq 1: (1) isothermal transition conditions; (2) random nucleation; (3) growth rate of a new phase, dependent only on temperature and not on time (linear growth rate). It has also been asserted that for small molecules the Avrami treatment may be used as an approximation at least for an early stage of a diffusion-controlled growth transformation process for which assumption 3 may not rigorously hold.[28] For oriented rigid macromolecules growing longitudinally, the Avrami treatment can be satisfied as a two-dimensional growth if molecules are all parallel. The parameter n must thus be two in the case of predetermined nuclei.[29] Results of kinetics involving condis crystals have recently been reported in *trans*-1,4-polybutadiene (TPB) and polytetrafluoroethylene (PTFE).[30] Two sets of surprisingly low values of n for both the polymers have been observed. Furthermore, the value of n increases with crystallization temperature. From the experimental data listed in Table II, kinetics of the condis crystal formation for the two copolymers can also be cast well in an Avrami equation (eq 4) with low values of n (0.2–0.8), similar to the cases of TPB and PTFE.

A very simplified and possible explanation for the low values of n is that each individual crystal does not grow with constant radial growth rate as one assumed before (third assumption for the use of Avrami treatment). On the basis of eq 1, one may rewrite it to be

$$1 - V^c = \exp(-gN\upsilon^n t^n) \tag{5}$$

for the case of predetermined nuclei. Here υ is the radial growth rate, g is a geometrical factor (which is $4\pi/3$ for spheres), and N represents the number of nuclei per unit area. If υ is characterized to be a linear rate of crystal growth, eq 5 is now equivalent to eq 1 with $K = gN\upsilon^n$. However, if υ is not a constant radial growth rate, but can be expressed in a form of

$$\upsilon = \upsilon_0 t^m \tag{6}$$

eq 1 must thus be cast into

$$\log [-\ln (1 - V^c)] = \log g + \log N + n \log \upsilon_0 + n(m + 1) \log t_c = \log K^* + n(m + 1) \log t_c \tag{7}$$

where $K^* = gN\upsilon_0^n$ and $n(m + 1)$ is called as an *apparent coefficient*. For instance, one possible mechanism that would alter the linear crystal growth rate is a diffusion-controlled transition in which case the growth rate would scale as $t^{-0.5}$.[31] According to eq 7, the apparent coefficient becomes $0.5n$, and it would be 0.5, 1, and 1.5 for one-, two-, and three-dimensional growth, respectively. In general, the exponential number of eq 6, m, is smaller than zero if the radial growth rate slows down with respect to time ($m = 0$ when υ is a linear growth rate). The apparent coefficient in this case is, therefore, always smaller than the dimensionality n expressed in eq 1 for a linear crystal growth rate. Obviously, K in eq 1 and K^* in eq 7 have different meanings based on their definitions. There should be no reason to imagine that both K and K^* could have even close values.

In the kinetics studied here, a possible reason for $m < 0$ and, thus, a lower apparent coefficient n may be the restriction of the crystal growth due to previously formed crystals, therefore reducing molecular mobility. The change of n with respect to temperature must be attributed to a combination of several rate-determining steps, and the minima of n formed in both copolymers is introduced. If the crystallization temperature is high enough, one may expect only nucleation (aggregation) as the rate-determining step, and the value of n must be close to two as previously reported.[32]

Finally, a change of $\Delta H_d°$ from an assumed value of 1.5 kJ/mol to 10 kJ/mol does not affect very much the value of n (±0.15), meaning that the determination of $\Delta H_d°$ at the metastable equilibrium is relatively insensitive to the kinetics. Possibilities of the combination described above, however, need to be proved by more evidence from other experimental observations in order to have further discussion. This is our purpose for this series of the papers.

Conclusions

Several conclusions can be drawn from our understanding of the kinetics of mesophase transitions for those copolymers presented in this paper. (1) Despite the different mechanisms of phase transition, crystals do form in the copolymers and consist of separate phases (microphase) in the bulk materials. They may be described better as "condis crystals". (2) Microscopically, the

structural formations may contain two specific molecular motions: translational motion along the chain direction and rotational motion with respect to chain axis. The chain molecules are able to reject noncrystallizable counits if the transitions are slow enough and the chemical compositions are favorable. (3) Two transition processes have been observed: a fast process, which can be characterized by solidification, and a slow process, which is close to a normal crystallization process. The experimental data of the latter case can be cast in an Avrami equation. However, the apparent coefficient n here is very low. It may be caused by the decrease of radial crystal growth rate due to the hindering of previously formed crystals and a reduction in molecular mobility. (4) Thermodynamic properties of the copolymers at their metastable equilibria have been estimated. Both low heats of the transition and entropies of the transition reveal that chain packing in the crystals is far from perfect, and chain conformations do not change very much during the transitions from nematic melts to condis crystals.

Acknowledgment. I express my special gratitude to Prof. B. Wunderlich for his helpful discussions. This work could also not be accomplished without the support of The University of Akron in establishing my new laboratory.

Registry No. (HBA)(HNA) (copolymer), 81843-52-9.

References and Notes

(1) Wunderlich, B. *Macromolecular Physics, Crystal Nucleation, Growth, Annealing*; Academic: New York, 1976; Vol. 2. For earlier review, see for example; Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1964.
(2) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103; **1940**, *8*, 212.
(3) Ergoz, E.; Fatou, J. G.; Mandelkern, L. *Macromolecules* **1972**, *5*, 147; and other related papers listed in ref 1.
(4) Villanova, P.; Ribas, S.; Guzman, G. *Polymer* **1985**, *26*, 423.
(5) Cebe, P.; Hong, S.-D. *Polymer* **1986**, *27*, 1183.
(6) Hoffman, J. D. *Polymer* **1982**, *23*, 656; **1983**, *24*, 3; **1985**, *26*, 803; *Macromolecules* **1986**, *19*, 1124.
(7) Cheng, S. Z. D.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 577, 595. Cheng, S. Z. D.; Bu, H. S.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.*, in press. Cheng, S. Z. D.; Wunderlich, B. *Macromolecules*, in press.
(8) Sadler, D. M. *Polymer* **1983**, *24*, 1401; **1984**, *25*, 1446; *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1533.
(9) Flory, P. J. *Trans. Faraday Soc.* **1955**, *51*, 848.
(10) Sanchez, I. C.; Eby, R. K. *J. Res. Natl. Bur. Stand., Sect. A* **1973**, *77A*, 353.
(11) Helfand, E.; Lauritzen, J. I., Jr. *Macromolecules* **1973**, *6*, 631.
(12) Sanchez, I. C.; Eby, R. K. *Macromolecules* **1975**, *8*, 639.
(13) Fischer, E. W.; Sterzel, H. J.; Wagner, G. *Colloid Z. Z. Polym.* **1973**, *251*, 980.
(14) Gutierrez, G. A.; Chivers, R. A.; Blackwell, J.; Stamatoff, J. B.; Yoon, H. *Polymer* **1983**, *24*, 937. See also: In *Polymer Liquid Crystals*; Blumstein, A., Ed.; Plenum: New York, 1984. Stamatoff, J. B. *Mol. Liq. Liq. Cryst.* **1984**, *110*, 75. Blackwell, J.; Biswas, A.; Gutierrez, G. A.; Chivers, R. A. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 73.
(15) Butzbach, G. D.; Wendorff, J. H.; Zimmermann, H. J. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 821; *Polymer* **1986**, *27*, 1337.
(16) Cao, M.-Y.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 521. See also: Cao, M.-Y. Ph.D. Thesis, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, 1988.
(17) Windle, A. H.; Viney, C.; Golombok, R.; Donald, A. M.; Mitchell, G. R. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 55.
(18) Hanna, S.; Windle, A. H. *Polymer* **1988**, *29*, 207.
(19) Bechtoldt, H.; Wendorff, J. H.; Zimmermann, H. J. *Makromol. Chem.* **1987**, *188*, 651.
(20) Calundann, G. W. U. S. Patent 4 161 470, 1980.
(21) Wunderlich, B. *Macromolecular Physics, Crystal Melting*; Academic: New York, 1980; Vol. 3.
(22) Ozawa, T. *Polymer* **1970**, *12*, 150.
(23) Buar, H. *Colloid Polym. Sci.* **1974**, *252*, 641.
(24) Cheng, S. Z. D.; Janimak, J.; Zhou, Z. L., manuscript in preparation.
(25) Wunderlich, B.; Möller, M.; Grebowicz, J.; Buar, H. *Adv. Polym. Sci.*, in press.
(26) Wunderlich. B.; Grebowicz, J. *Adv. Polym. Sci.* **1984**, *60/61*, 1.
(27) Blundell, D. J. *Polymer* **1982**, *23*, 359.
(28) Christian, J. W. *Theory of Transformation in Metals and Alloys*, 2nd ed.; Pergamon: Oxford, 1975.
(29) Keller, A. In *Polymers, Liquid Crystals and Low-Dimensional Solid*; March, N., Tosi, M. Eds.; Plenum: New York and London, 1984.
(30) Grebowicz, J.; Cheng, S. Z. D.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 675.
(31) Schultz, J. *Polymer Materials Science*; Prentice-Hall: Englewood Cliffs, NJ, 1974.
(32) Warner, S. B.; Jaffe, M. *J. Cryst. Growth* **1980**, *48*, 184.

Modulus of Polybutadiene Networks Made by Hydrosilation Cross-Linking

Mirta Inés Aranguren* and Christopher W. Macosko

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455. *Received September 10, 1987*

ABSTRACT: In this work we studied the effect of the topological interactions between polymer chains by measuring the small deformation modulus of polybutadiene networks. The networks were prepared by linking pendant double bonds (vinyls) on the polybutadiene with *p*-bis(dimethylsilyl)benzene catalized by platinum(II). Model reaction studies with a hexene and hexadiene mixture and a low molecular weight polybutadiene showed that this cross-linking reaction is complete and free of side reactions when the pendant double bonds are in excess. With silane in excess the backbone double bonds also react. Two monodisperse polybutadienes with different vinyl content and plateau moduli were linked with the same reaction. The small strain modulus measurements for the networks were better explained by including the effect of topological interactions along the contour of the network chains. The effect of interactions on the junction points was smaller that found by Dossin and Graessley for polybutadienes cross-linked by radiation.[1]

Introduction

While the basic concepts of the theory of rubber elasticity have long been well established, the effect of topological interactions between network chains (entanglements) is still a subject of controversy.[2-4]

It is generally accepted that topological interactions have a localized effect on the mobility of the junction points by suppressing the fluctuations of the cross-linking junction about its average position.[5] Following Graessley's work we can express the small deformation modulus as[1]

$$G = (\nu - h\mu)RT \quad (1)$$

where G is the modulus of the network at small deformations, ν is the concentration of elastically active strands,

0024-9297/88/2221-2484$01.50/0