Structure and structure formation of a main chain thermotropic polymer

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Random copolymers containing 58% 4-hydroxybenzoic acid and 42% 2-hydroxy-6-naphthoic acid are able to display a three dimensional order with a degree of crystallinity of more than 60%. The crystals are far from being perfect: their enthalpy and entropy of transition are 10–20 times smaller than expected for a perfect crystalline state and the volume change on transition is negligible. The crystallization occurs in two steps: the first, which is completed within seconds, leads to a degree of crystallinity of ~30%. The second, very slow, step, which corresponds apparently to postcrystallization, occurs over more than 10^7 s of annealing time and causes the degree of crystallinity to exceed 60%.

(Keywords: rigid rod-like polymer; thermotropic properties; crystallization; postcrystallization; crystal structure; thermodynamic properties)

INTRODUCTION

The crystallization behaviour of flexible chain molecules such as polyethylene or poly(ethylene terephthalate) has been the subject of numerous publications, reviewed in refs. 1 and 2. The crystallization process can be quite rapid, despite the strong interpenetration of chain molecules in the melt, because the overall chain conformation remains approximately unchanged during the crystallization whereas the local chain conformation is altered. Copolymers consisting of a crystallizable and a noncrystallizable building unit may crystallize quite rapidly also, even if the noncrystallizable units are rejected from the crystalline regions and even if the copolymers are random copolymers[1-4]. It is obvious that the chain sequences are able to adjust in a way which allows the crystal to grow, owing to the great flexibility of the chain.

Semiflexible chain molecules and even rigid rod-like chain molecules have recently been synthesized[5-7], which frequently display a nematic melt. The aim was to obtain polymers with extended chains which can easily be oriented in the molten state and which keep their orientation during the transition into the solid state. Such types of polymers are expected to display a large strength and a large stiffness provided that the mechanical load is applied along the direction of the chain orientation. The requirement for good mechanical properties is, of course, the occurrence of a transition of the fluid nematic state into a solid state, i.e. either a nematic glassy state or a crystalline state. The chain parallelism characteristic of the nematic phase will of course facilitate a lateral crystallization of the chains. Crystallization in the third direction, i.e. along the direction of the chain is less simple. This is not a serious restriction for the crystallization process provided that just homopolymers are considered. Translational steps over distances corresponding to the length of a monomer unit are sufficient for the structure formation process to take place. This is no longer the case for random copolymers. These have the advantage that their melting point is well below the temperature above

which the chain molecules decompose. They have, on the other hand, the disadvantage that large scale translational motions have to occur during crystallization. Consider the situation in which an appropriate sequence of a particular chain is incorporated into a growing crystalline region. The consequence is that other sequences are no longer able to diffuse to the surface of a crystal growing at some other location. This paper is concerned with calorimetric, volumetric and X-ray scattering studies on the structure and the structure formation process in a rigid random copolymer.

Experimental

Specimens of the copolymer containing 58% 1-4-hydroxybenzoic acid (HBA) and 42% 2-hydroxy-6-naphthoic acid (HNA) were supplied by Celanese Research Company, Summit, NJ, USA, in form of pellets. Isotropic samples were obtained by pressing films from the pellets at a temperature of 300°C. Oriented samples were obtained by extrusion, using a capillary rheometer equipped with a converging die. The thermal properties of the material were investigated with a Perkin–Elmer DSC 4. The X-ray analysis was carried out with a Siemens wide-angle diffractometer and a flat film camera, using either a photographic film or a position-sensitive detector to record the X-ray scattering.

RESULTS AND DISCUSSIONS

Structure of the nematic melt

The copolymer is known to display a nematic melt at elevated temperatures. The X-ray scattering diagram both of the macroscopically oriented and of the unoriented state were investigated. The X-ray diagram characteristic of the oriented state is displayed in *Figure 1*. It shows a broad halo on the equator and several arc-like reflections along the meridional direction. The broad halo on the equator resembles closely that observed for flexible chain molecules in the molten state. Its maximum value occurs

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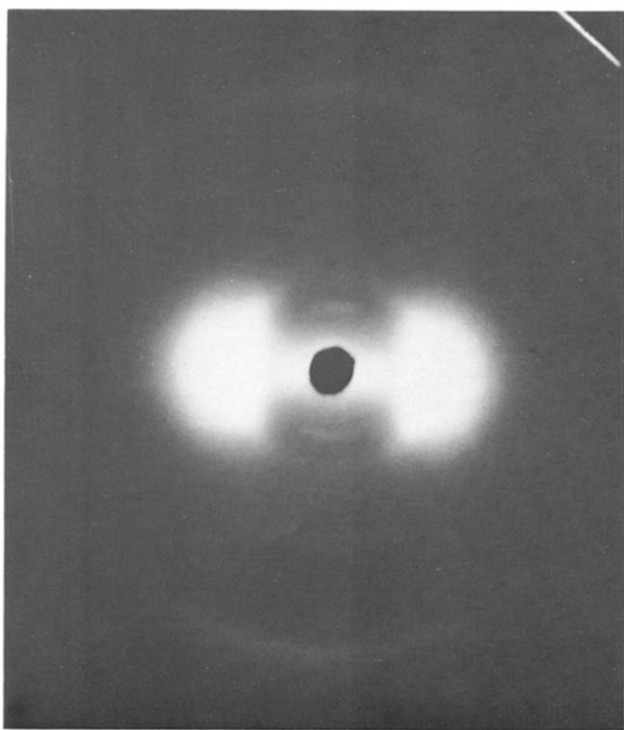
Figure 1 X-ray diagram of the oriented nematic melt at 300°C. The fibre axis is along the vertical direction

at $2\theta = 18.9°$ and its half-width is about 7.5° (the wavelength of the Cu Kα radiation was 1.5418 Å). The shape of the halo along the equator, displayed in *Figure 2*, is characteristic of a short range positional order in the direction perpendicular to the long axes of the chains.

Meridional reflections of this kind have been attributed to the specific scattering properties of an aperiodic linear array by Gutierrez et al.[8], Chivers et al.[9] and Stamatoff[10]. The chains of the rod-like random copolymer considered here correspond to this array, the comonomer units being the points on this aperiodic array. The characteristic distances along the chain axis were found to be 7.19, 2.85 and 2.00 Å, in good agreement with the theoretical predictions which were 7.19–7.40, 2.98–2.99 and 2.10–2.11 Å, depending on the method used. The fact that the meridional reflections are spread out perpendicular to the meridional direction and are arc-like has to be attributed to disorientation of the chains and to shifts along the long axes of the molecules that are, however, far from random. Random shifts would have resulted in layer lines extending to infinity.

The distribution of the intensity of the amorphous halo at constant scattering angle as a function of the azimuthal angle can be used to determine the orientational order parameter, which for a homogeneous well aligned sample should correspond to the nematic order parameter. S is defined by $S = \frac{1}{2}\langle 3\cos^2\phi - 1\rangle = \int f(\phi)((3\cos^2\phi - 1)/2)d\Omega$, where ϕ characterizes the deviation of the molecular long axes from the preferred direction and the orientational distribution function, $f(\phi)$, is proportional to the azimuthal intensity distribution[11,12]. The value obtained was $S = 0.81$, which is in agreement with the values expected for a rigid chain molecule in the nematic melt. The orientational order as represented by the orientational order parameter S, is determined in a polydomain melt by the nematic order parameter within each nematic domain as well as by the director

distribution. Therefore, a nematic melt may be macroscopically isotropic, provided that random director distribution occurs. The only conclusion that will be drawn at this point is that the orientational order within each domain will not be less than the macroscopically observed one, so that the nematic order parameter is equal to, or larger than, ~ 0.8. This value is rather large compared with values observed for side chain liquid crystalline polymers or low molecular liquid crystals in the neighbourhood of the isotropic–nematic transition T_{ni}. However, no information is obtainable on the magnitude of the reduced temperature $(T - T_{ni})/T$ for the polymer considered here, so that any further discussion on the absolute magnitude of the order parameter has to be postponed until some estimate of the nematic transition temperature becomes available.

It is of interest to note that the macroscopic orientational order of the melt was invariant for several hours, although no external magnetic, electrical or mechanical field was applied.

Quenched samples

Starting from the nematic molten state a structural transition was observed on cooling; the exothermic peak in the d.s.c. diagram (*Figure 3*) is quite narrow. Also, there is a gradual decrease of the specific heat at lower temperatures (*Figure 3*). This variation can be attributed to the glass transition process[13,14]. On reheating the sample there is a gradual increase of the specific heat, which is due to the glass transition (cf. *Figure 4*), and an endothermic peak occurs at higher temperatures.

Clearly, the latter is due to the melting of the structure that had been formed during cooling. The heat of fusion[14] is very low $\sim 4.0\,\mathrm{J\,g^{-1}}$ ($\sim 570\,\mathrm{J\,mol^{-1}}$). The location of the exothermic peak can be varied to a certain extent by
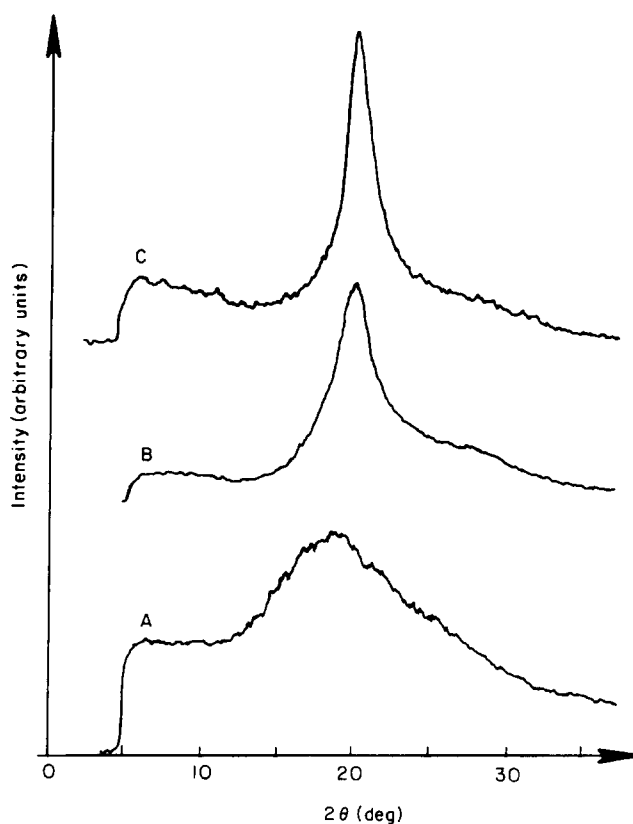
Figure 2 Intensity distribution along the equator. A, nematic state; B, quenched sample; C, well annealed sample
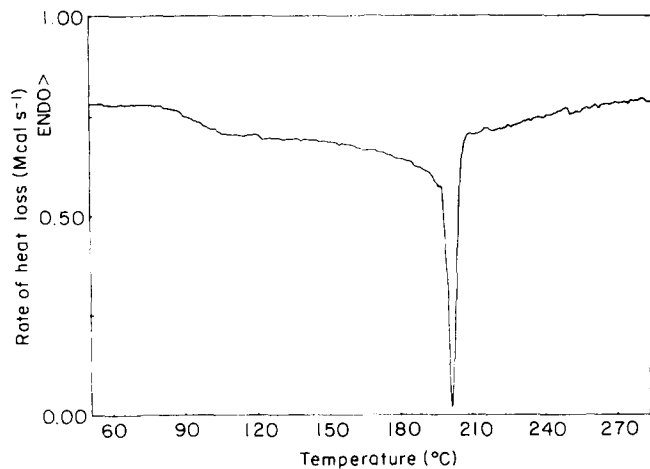
Figure 3 D.s.c. cooling diagram; cooling rate 15 K min^{-1}

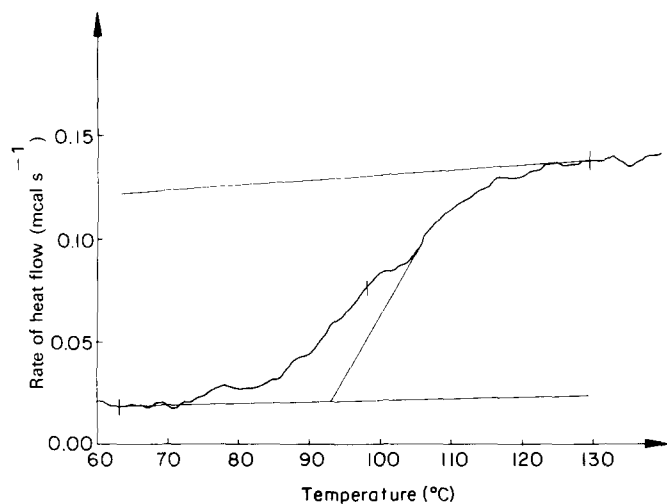**Figure 4** Variation of the specific heat at the glass transition temperature as displayed by d.s.c.; heating rate 15 K min^{-1}

changing the cooling rate (*Figure 5*). However, the shift of the peak position is small and the structural transition process cannot be suppressed by cooling the sample quickly into the glassy state. Subsequent heating runs revealed that the variation of the cooling rate did not appreciably affect either the transition temperature or the heat of transition. Experiments in which very thin films of the material were rapidly cooled to the temperature of liquid nitrogen between metal plates also showed that the structural transition process cannot be suppressed.

This finding is in agreement with our wide angle X-ray results. Samples that had been rapidly cooled down to room temperature were found to display the meridional reflections observed for the nematic phase (*Figure 6*). However, the halo along the equator was transformed into three sharp reflections that consisted of a doublet, which is often too narrowly spaced to be resolvable, and a third discrete reflection at larger angles. The distances corresponding to these reflections are 4.48, 4.29 and 2.51 Å respectively. Apparently they have to be attributed to a two dimensional long range order in the direction perpendicular to the long axes of the molecules. The meridional reflections observed correspond to distances of 7.19, 2.85 and 2.02 Å. However, off-meridional reflections are also observed, which are difficult to resolve unless background is subtracted. This has to be taken as an indication that a long range order exists along the

direction of the chain axes also. However, this order is far from being perfect, since higher order reflections were not observable. The layer distance, taken from the diagram of the oriented samples, amounts to ~12.4 Å.

Thus, it is obvious that the rapid structure formation process observed in the d.s.c. investigations corresponds to rapid lateral crystallization—as one might expect from the parallel arrangement of the chains in the nematic state–and some additional registry of neighbouring chains in the third dimension. The observed low heat of the transition might be taken as an indication that a small part only of the sample experiences the structural transition. The marked changes that occur in the X-ray diagram on cooling contradict this interpretation. The lateral peak observed for these polymers would correspond approximately to a degree of crystallinity of at least 30% for flexible chain molecules. This problem will be treated later in more detail. In the following sections the influence of annealing temperature and annealing time on the structure formation will be investigated.

Samples annealed at elevated temperatures

Nematic melts of the samples were rapidly cooled within the calorimeter to a temperature above that at which the rapid transformation process, described above, takes place, which was possible for starting temperatures above about 200°C. The samples were kept at this temperature for various times ranging between several seconds and several days. They were then heated again and the heat of transition and transition temperature were determined. The results of these investigations for two different annealing temperatures are depicted in *Figure 7*. It is clear that the transition process occurs at an annealing temperature of 215°C in two steps: a fast step, which is similar to that observed for normal transformation process, the time dependence of which agrees qualitatively with the one observed in a normal crystallization process, and a slow step. This slow transition process is characterized by a magnitude of the heat of transition which grows linearly as a function of the logarithm of the annealing time. Similar results were obtained for other annealing temperatures. *Figure 7* contains the results for an annealing temperature of 205°C. The rapid process has apparently already taken place within a very short time span, which cannot be resolved by this method. The second step of the transformation clearly corresponds to the slow one found for an annealing temperature of 215°C. The question then
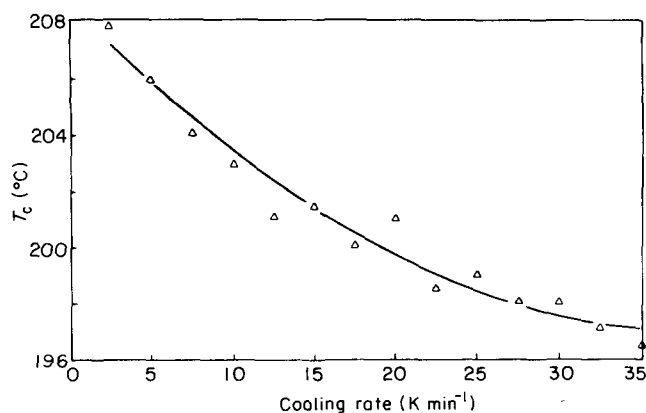

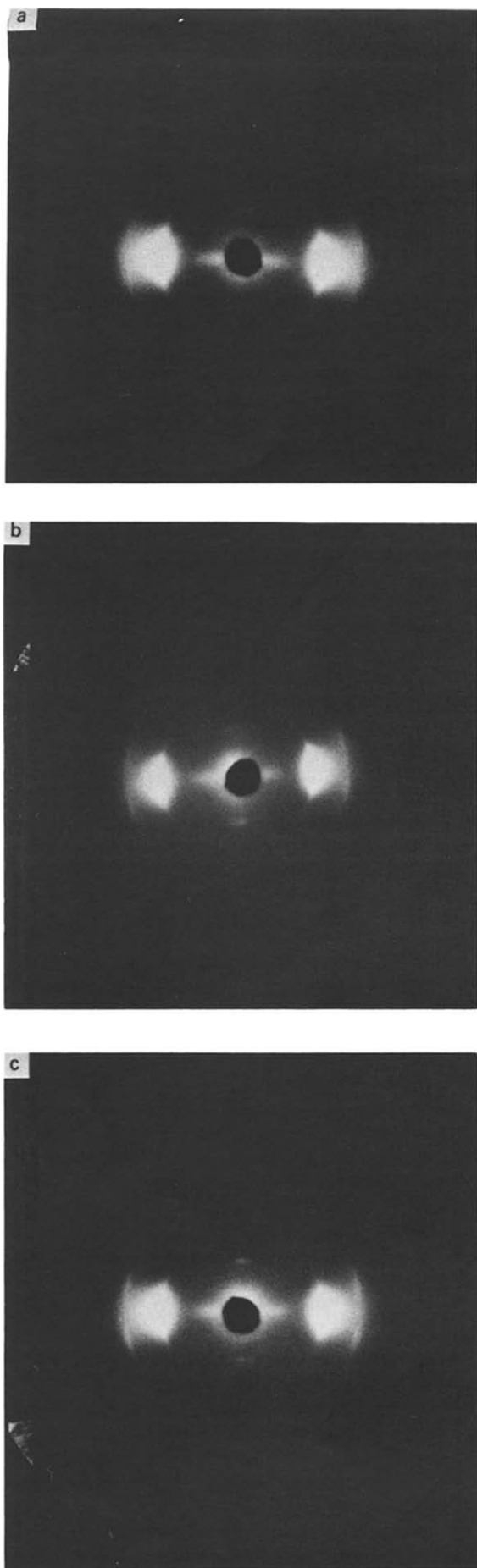**Figure 5** Location of the exothermic transition as a function of cooling rate
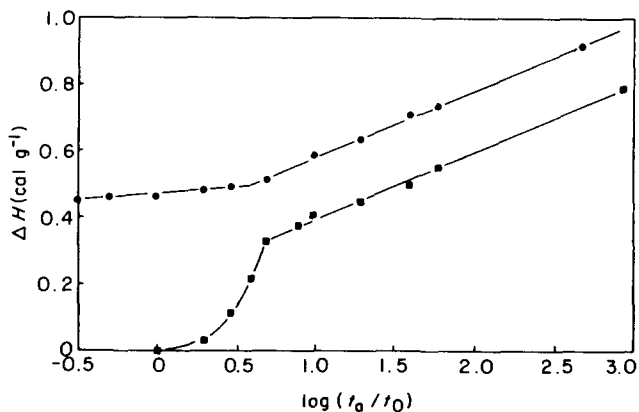
Figure 7   Variation of the enthalpy of fusion with annealing time. Annealing temperature: 205°C (●), 215°C (■)
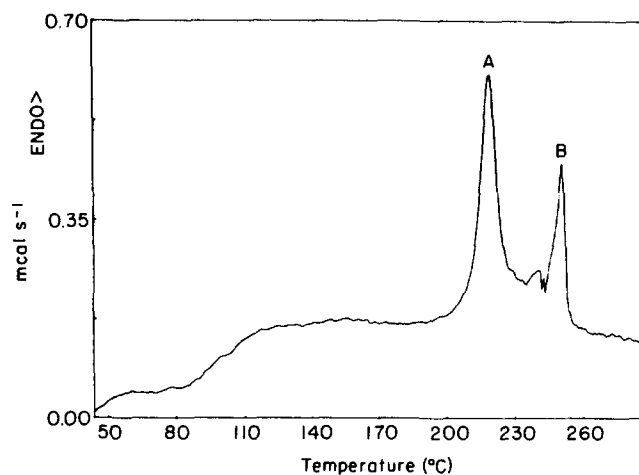

Figure 8   D.s.c. trace of an annealed sample for cooling rate 15 K min^{-1} (annealing temperature 190°C, annealing time 3 h). (A) peak T_{m1}; (B) peak T_{m2}

Figure 6   X-ray diagram of an oriented quenched sample (a), oriented annealed sample (b) and stepwise annealed sample (c)

arises if annealing of samples that had been cooled to low temperatures which in the course of the cooling cycle, had experienced the rapid transformation process are also able to show the second step of the transformation.

Samples annealed at lower temperatures

The annealing temperatures were chosen in a temperature range between the glass transition temperature and 220°C. The annealing time was varied between several seconds and ~10^3 h. Annealing gave rise to the formation of a second transformation peak (T_{m1}), in addition to the one originating from the rapid cooling process (T_{m2}). *Figure 8* shows a d.s.c. trace of a sample that had been annealed at a temperature of 190°C for 3 h. The heat of the transition characteristic of this peak (T_{m1}) was a function of both the annealing time and the annealing temperature. In addition, the transition temperature of this peak also depended strongly on the annealing temperature and annealing time. Both findings are displayed in *Figures 9–11*. The transition temperature, T_{m1}, increases linearly as a function of the logarithm of the annealing time at constant annealing temperature. If this straight line is extrapolated to short annealing times (seconds) the transition temperature always corresponds exactly to the annealing temperature. Apparently, a structure is formed that is unstable with respect to slight temperature increases. The stability of these structures grows with increasing annealing time. The slope of the
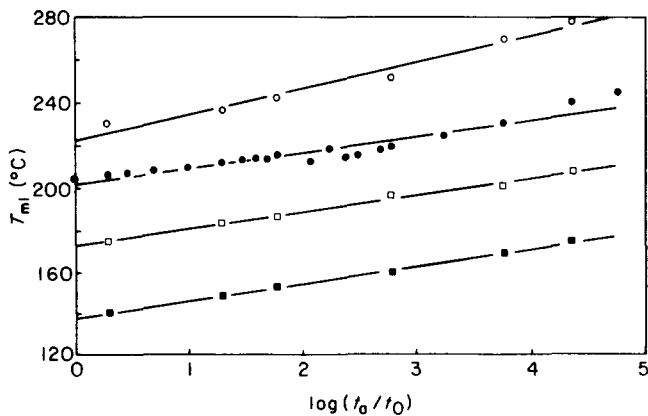
Figure 9 Variation of the transition temperature T_{m1} as a function of the annealing time t_a ($t_0 = 1$ min) for different annealing temperatures, T_a: 130°C (■), 160°C (□), 190°C (●), 220°C (○)
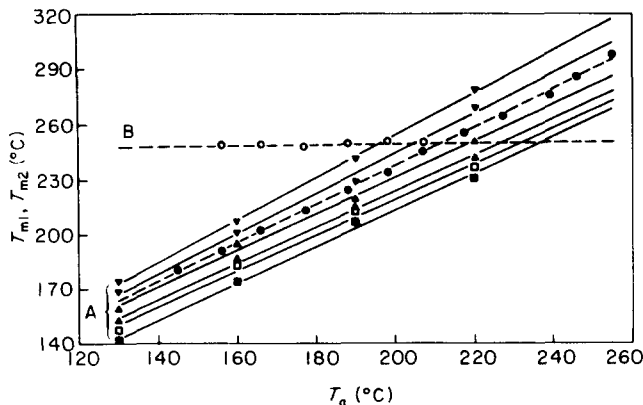
Figure 10 Variation of transition temperatures T_{m1} (A) and T_{m2} (B) as a function of the annealing temperature T_a for different annealing times, t_a: 2 min (■), 20 min (□), 1 h (▲), 10 h (△), 100 h (▼), 400 h (▽). (●), results for variation of the annealing temperature by 15 K every 24 h (see text)

straight lines representing the variation of the transition temperature, T_{m1}, with annealing time are identical for all annealing temperatures. Thus a master curve is constructable for the dependence of the transition temperature, T_{m1}, on the annealing temperature, T_a.

The heat of transition was also found to be a linear function of the annealing time (*Figure 11*). However, the slopes of these lines were dependent on the annealing temperature. The time variation of the heat of transition is represented by:

$$\Delta H_m(T_a, t_a) = a(T_a)\ln(t_a/t_0)$$

The quantity $a(T_a)$, which is a measure of the velocity of the transformation, depends on the annealing temperature (*Figure 12*). Extrapolation to the glass transition temperature yields a value of $a(T_a)$ that is close to zero, which is, of course, reasonable. However there is no temperature variation of the transition rate that can be represented in terms of a Williams–Landel–Ferry (WLF) mechanism or a thermally activated process. The surprising result is that the transition rate stays within the same order of magnitude for a temperature interval of about 100 K, starting just above the glass transition temperature and approaching the melting temperature. Usually there is an increase of the transition rate by several orders of magnitude to a maximum value as the temperature is increased above the glass transition

temperature, followed by a marked decrease as the melting temperature is approached. It is also surprising that the structure formation process at constant T_a occurs in a time span of many decades while still obeying the same kinetic law and apparently obeying the same mechanism. A crystallization process usually is completed within one or two decades of the crystallization time. The nature of this transition process will be discussed in more detail below. It should be pointed out at this stage that the higher temperature transition, corresponding to the rapid process of structure formation, is independent of the annealing temperature and annealing time.

The X-ray diagram of the annealed samples corresponded roughly to that of the quenched samples. However, the intensity of the reflections along the equator increased relative to the background with increasing annealing time, which is indicative of further structural improvements (*Figure 2*). Studies on oriented samples showed, in agreement with reports in the literature, that the reflections along the equator decreased slightly in width. This was also observed for the first layer line along the meridian and for the off-meridian reflections. No changes were observed for the remaining layer lines along the meridian. The X-ray diagram of well annealed samples, which had been heated to higher temperatures, showed a gradual variation of the scattering behaviour as the temperature approached that of the lower of the two melting temperatures. The diagram corresponded approximately to that of the quenched samples.
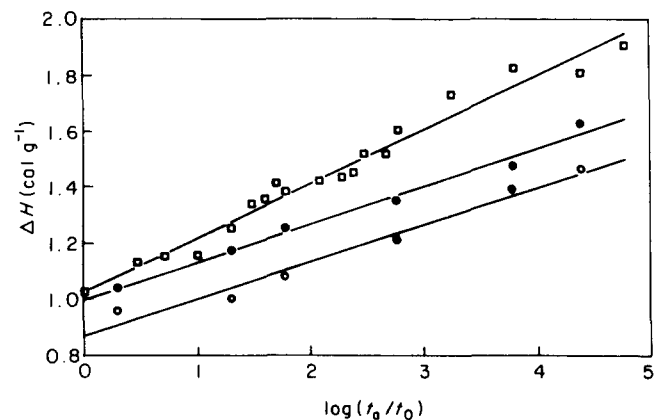
Figure 11 Variation of the heat of transition ΔH as a function of the annealing time, t_a ($t_0 = 1$ min) for different annealing temperatures, T_a: 130°C (○), 160°C (●), 190°C (□)
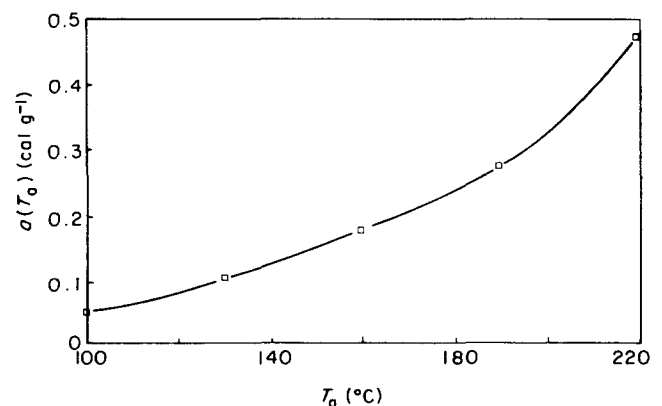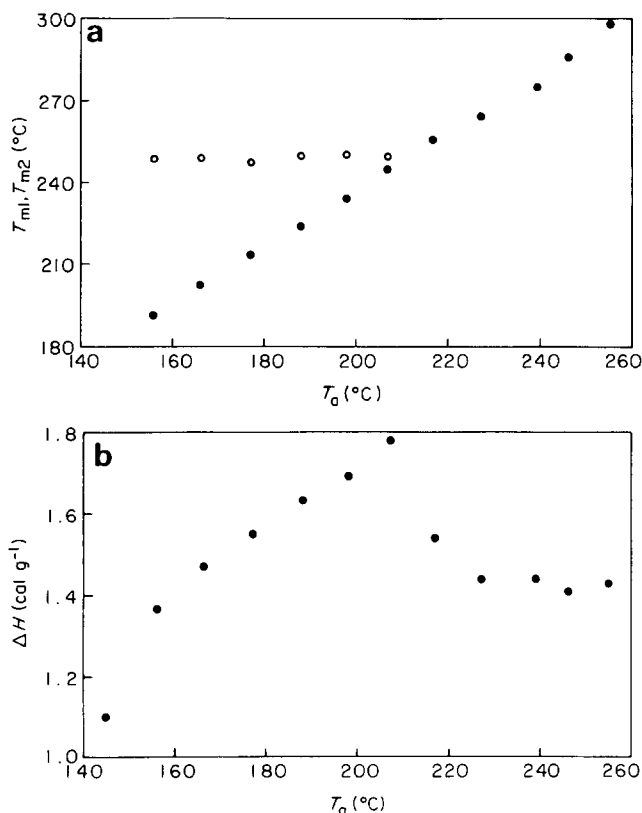

Figure 12 Variation of the rate of transition $a(T_a)$ as a function of the annealing temperature, T_a

Samples subjected to a stepwise variation of annealing temperature

In addition to the annealing studies described above the annealing temperature was varied stepwise for samples that had previously been quenched to room temperature from the nematic melt. The temperature was increased stepwise by about 15 K, starting from a temperature of 130°C. The samples were kept at each annealing temperature for 24 h. One of the samples from the total set of samples was removed from the oven after each annealing step and was subjected to a d.s.c. run. It seems that a stepwise increase of the temperature resulted each time in a complete loss of the previous annealing history. This means that the d.s.c. diagram obtained agreed exactly with the one obtained for samples without previous annealing. This is true both for the transition temperature T_{m1} as well as the heat of transition, as is obvious from *Figures 10* and *13*. The position of the endothermic peak was found to increase continuously after each temperature variation. Changes in this behaviour occurred, however, if the annealing temperature approached ~200°C, apparently because the structure that had been formed during the rapid structure formation process partially melted. This process leads to a reduction of the total heat of transition, which is clear in *Figure 13*.

The X-ray diagram of the samples that had been subjected to a stepwise increase of the annealing temperature agreed with that obtained for a sample which had been annealed at only one temperature. The equatorial reflection showed two maxima and the off-meridian reflections were strongly developed. No structural transition had taken place but the structure had become more highly ordered than that of the once annealed samples.

Magnitudes of the heats of transition and the volumes of transition

It has already been pointed out that the heats of the transitions are very small compared with the corresponding values of flexible chain molecules, and also that this low heat of transition cannot be attributed to a low degree of ordered structure in the solid state, because of the well defined scattering diagram, which indicates a degree of crystallinity of up to 60%[15]. The degree of crystallinity was obtained from the wide angle X-ray diffraction pattern, using well established techniques[16]. For a polymer composed of the same comonomer units and containing 40 wt% HBA and 60 wt% HNA units, Blundell reported a degree of crystallinity of about 21% for slowly cooled (unannealed) samples[17]. The fact that the degree of crystallinity may surpass 60% despite the irregular chemical structure of the chain molecules, has to be taken as an indication that conventional copolymer theories fail to account for the structure formation in these polymers[15]. It is not certain what the origin of this high degree of crystallinity is. There is evidence for the occurrence of cocrystallization[15] and it seems that the crystallizable units are less selective with respect to geometric and energetic variation of the chain units than is usual. More recently, Bechtoldt, Wendorff and Zimmermann[20] have formulated a new structural model that takes these puzzling observations into account. They have proposed that the crystalline state is distorted with respect to the rotational disorder. However, additional studies are required in order to gain a detailed understanding of the structure formation process of this class of polymers.

Therefore it has to be concluded that the structure formation is characterized by a very low internal heat of transition and consequently, because of the rather low melting temperature, by a low entropy of transition[15]. A transition from a nematic to a crystalline state is not necessarily characterized by low entropies and enthalpies of transition, as is known from low molecular weight liquid crystals or polymeric side chain liquid crystals[18,19]. The transformation from the nematic into the solid crystalline state is characterized by volume changes of the order of several parts per cent. This is, however, not the case for the polymer considered here. The densities of the samples that exhibited different heats of fusion were very close to each other, i.e. in the range of 1.394 ± 0.002 g cm^{-1}. These aspects were discussed in a separate paper[15].

Model considerations on structure formation

A detailed understanding of the structure of these chain molecules and of the structure formation process requires additional investigations such as dynamical studies that the authors are currently performing. Nevertheless, at this point the authors would like to describe their current view.

The nematic phase is found to be characterized by parallel orientaion of the molecules, the macroscopic order parameter, S, being ~0.81. The positional order in the direction perpendicular to the chain direction is short-ranged and apparently similar to that found in flexible

Figure 13 D.s.c. results obtained for a stepwise variation of the annealing temperature (annealing time 24 h): (a) transition temperatures, T_{m1} (●) and T_{m2} (○), as a function of the annealing temperature, T_a; (b) heat of transition as a function of the annealing temperature, T_a

chain molecules. The chains are shifted relative to each other in the direction of the chain axes. However, the shifts are far from being random. Cooling the nematic phase down to lower temperatures results in the onset of a rapid structural transition process. This transition comprises the formation of a two dimensional lattice perpendicular to the direction of the chain axes and to some registry in the third dimension, as is clear from the off-meridional reflections. The order is, however, disturbed in this direction as just one reflection characteristic of a regular structure along the chain axes is observed. The shift of the chain molecules relative to each other is less than in the nematic state.

The rapid transformation process is replaced by a slow process that occurs on annealing at lower temperatures. It also occurs at higher temperatures as the second transformation step. The thermodynamic properties of the two kinds of structures, which are formed during the rapid and the slow transition processes, respectively, differ markedly, and the kinetics of formation differ. The transition temperature and heat of transition of the structure formed during the rapid process is independent of the annealing temperature and annealing time provided that the temperature is kept below $\sim 200°C$. The heat of transition and transition temperature of the structure formed during the slow transformation process depend heavily on the annealing conditions, i.e. both on the temperature and on the time. So the question arises, whether the observation of two thermodynamic transitions has to be attributed to some kind of heterogeneities, such as chemical heterogeneities, heterogeneities with respect to the physical structure, or kinetic heterogeneities.

Chemical heterogeneities. A nonrandom distribution of the comonomer units along the chains may lead to segregation effects that show up in structure formation. The observation that the location and the intensity distribution of the meridional reflections agree with those expected for a random copolymer contradicts this assumption.

Heterogeneities with respect to the physical structure. The formation of two kinds of structure, such as different crystal modifications, would lead to two d.s.c. peaks but also to clearly observable changes in the X-ray diagrams. It was found, however, that the only changes occurring on annealing were variations of the width of the reflections. Therefore it was concluded that annealing causes an improvement of the ordered structure both in terms of the degree of crystallization and in terms of an increasing registry of the chain molecules but nothing else.

Kinetic heterogeneities. Finally, the possibility is considered that the observed two step process of structure formation is due to a kinetic mechanism that occurs differently at different places within the sample. The reason could be that the crystallization process becomes severely restricted if, in the course of the crystallization, at least one part of each chain molecule becomes attached to one growing crystalline region (see *Figure 14*). The local orientational order and the local positional order in the remaining nematic regions are then fixed. Any further progress has to occur via translational and reorientational motions of chains that are attached to other crystals. The probability for this process to occur will depend on the number of chain units that are already
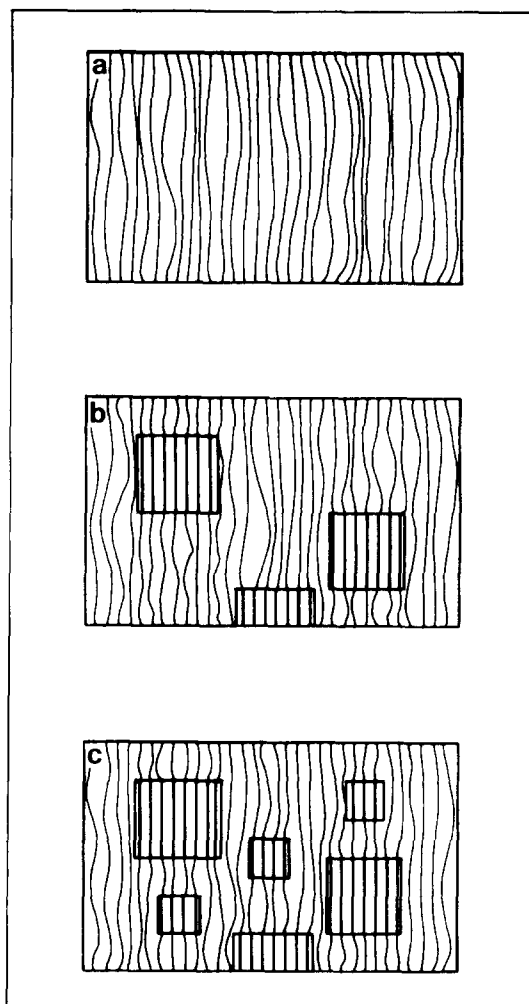
Figure 14 Structural model for the crystal structure formation. (a) nematic phase, (b) after rapid transition step, (c) during slow transition step

built into a crystalline region. This means that the structure formation process gets slower and slower as crystallization continues, in agreement with the observed logarithmic law. The authors are currently modelling this behaviour in terms of the ageing theory for amorphous glasses, where similar time laws exist.

The two step process thus comprises a rapid crystallization, which continues until the sample is physically 'crosslinked'. The remaining part of the sample can now be transformed into an ordered structure only by a slow diffusional process that corresponds to the second step of the transformation. This two step mechanism is similar to the crystallization and the subsequent postcrystallization known from structure formation in flexible chain molecules. Furthermore, the second transformation step acts on regions within the sample that do not correspond to those transformed during the first step. First of all, the degree of crystallinity is observed to increase on annealing. Also, the high temperature endothermic peak is not influenced by annealing whereas the second peak, the low temperature peak formed during the slow process, depends strongly on the annealing conditions. The low transition temperature of the endothermic peak and its marked variation with annealing temperature and annealing time are attributed to size effects. Small crystals that exhibit a low transition temperature may develop at lower temperatures within

the physically 'crosslinked' matrix. The size that grows most rapidly corresponds to that of the nuclei which become stable at this temperature. A stepwise increase of the temperature causes the small crystals to become unstable again and induces the formation of larger crystals. This process continues up to high annealing temperatures. The high temperature transition occurs as this structure becomes unstable, apparently also because of size effects.

However, annealing above this temperature leads to a structure identical to that obtained for lower annealing temperatures. The formation process occurs clearly along the same lines as at lower temperatures, which was shown by annealing studies performed at 205 and 215°C.

ACKNOWLEDGEMENTS

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