

Phase transitions in mesophase macromolecules: The transitions of poly(*p*-acryloyloxybenzoic acid)

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Poly(*p*-acryloyloxybenzoic acid) has been obtained in twelve single and two-phase physical states, which include the amorphous glassy and liquid states, the mesomorphic glassy and the mesomorphic liquid states and in addition eight two-phase semicrystalline states (crystal forms I and II). Using mainly differential scanning calorimetry, the transition temperatures, energies and heat capacity changes at the glass transitions have been studied. The time dependency of the glass transition has also been determined. The strongly heating rate dependent amorphous glass transition occurs at 348K (20K min⁻¹ heating rate, $\Delta C_p = 39 \text{ JK}^{-1} \text{ mol}^{-1}$), the mesophase glass transition, at 408K (also at 20K min⁻¹, $\Delta C_p = 43 \text{ JK}^{-1} \text{ mol}^{-1}$). The latter is less heating rate dependent. The amorphous to mesophase transition occurs between 375 and 475K ($\Delta H = -4.5 \text{ KJ mol}^{-1}$); the peaks of melting transitions, which are also strongly heating rate dependent, were observed at 573K and 553K (20 K min⁻¹ heating rate) for crystal forms I and II, respectively. The heat of fusion of crystal form I is estimated to be 22 KJ mol⁻¹. There seems to be no partially amorphous-partially mesomorphic state.

INTRODUCTION

The solid state of flexible, linear macromolecules is commonly not in equilibrium. The study of the solid-liquid phase transitions allows an analysis of this non-equilibrium state¹. Through analysis of crystallization and melting, the defect nature of the crystalline state becomes clear. The crystals are usually small and defective, which is reflected in a broadened melting region extending below the equilibrium melting temperatures. Observation of incomplete crystallization, detected by reduced heats of fusion, has led to the development of the crystallinity model. Only by extrapolation, or through measurement on specially prepared samples, are equilibrium melting data available². The glass transition can, through its hysteresis behaviour, be used to study the thermal³ and mechanical⁴ history of amorphous solids. By extrapolation of the heat capacity of the amorphous glass and the liquid to the (rate dependent) glass transition temperature, it is possible to establish reliable values of the change of the heat capacity on devitrification⁵.

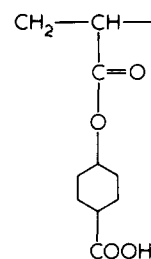
More recently an increasing number of mesomorphic macromolecules have been observed. Three of the questions that arise in connection with this state of intermediate order which will be addressed in this publication are:

(a) Can mesomorphic polymers be considered to be single phase equilibrium or metastable states, or do they also contain, simultaneously, amorphous regions such as those found in semicrystalline polymers?

(b) What is the nature of the transitions between amorphous, mesomorphic and crystal states?

(c) Is the glass transition behaviour of the mesophase on solidification different from that of an amorphous phase?

Up to the present there are at least three publications which address these questions⁶⁻⁸. Here we analyse the transition behaviour of poly(*p*-acryloyloxybenzoic acid) (PABA).



Two crystal forms have been reported for PABA^{9,10}. One of these (I) was proven to have a monoclinic structure, the other (crystal modification II) was identified as smectic *E_r*. It will be shown in this paper that PABA may exhibit, besides the just mentioned smectic *E_r* form, another, highly mobile mesophase state which can be cooled to a glass. In order to avoid confusion, the previously described smectic *E_r* state will be called crystal modification II (as it was in References 9 and 10). In accordance with this nomenclature, crystal form II showed a reasonable melting transition and no glass transition. The newly discovered, mobile mesophase is probably nematic. It is produced by melting of crystal forms I or II or out of the amorphous PABA above the glass transition. Below the melting temperature of crystal form I, it is metastable. Throughout this paper it will be called 'mesomorphic phase'.

PABA is used as an example for the study of phase transitions of side chain mesomorphic polymers. A similar

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study of mesophase transition behaviour due to main chain structure is underway using the copolymer system poly(ethylene terephthalate-co-*p*-oxybenzoate)^{11,12}. The first glass transition results on this latter mesophase copolymer system (40/60 mol%) are published as part I of this series of investigations on phase transitions in mesophase macromolecules⁸.

EXPERIMENTAL

Material

The monomer *p*-acryloyloxybenzoic acid and the crystal modification I of the polymer (PABA) was kindly supplied to us by Dr. Blumstein. The monomer was prepared by condensation of acryloyl chloride with *p*-hydroxybenzoic acid⁹. Crystal modification I of PABA was obtained by Blumstein *et al.*⁹ on slow polymerization in a thin layer of the molten monomer. Crystal modification II of PABA was produced by us using solution polymerization of the monomer in DMF as described in ref 9 for preparation of amorphous PABA (see Discussion section). The described polymer samples were identified as crystal modifications I and II by X-ray diffraction⁹. Amorphous PABA was prepared by quick thermal polymerization of the dried monomer (see Discussion section).

The mesophase form of PABA was produced from the low melting crystal modification II by quick quenching a few kelvin above the melting point before decomposition became noticeable. The liquid crystalline character of the product was verified by optical microscopy.

Techniques

Thermal analysis was performed with a duPont 990 Thermal Analyzer coupled to a 910 DSC-module and a 950 Thermogravimetric Analyzer. For scanning calorimetry, heating rates of 2, 5, 10, 20, 50 and 100K min⁻¹ and cooling rates between 0.5 and 50K min⁻¹ were used. The sample weights were between 2 and 10 mg, according to rates used. The temperatures scale was corrected for instrument lag by calibration with high purity metal standards (Ga, In, Sn, Pb, and Zn). No further correction was applied to peak temperatures and ends of melting. Thermogravimetry was also performed at various heating rates (5 to 100K min⁻¹). Typical sample masses were 1–2 mg. All thermal analyses were run under nitrogen atmosphere.

Glass transition temperatures are taken at the temperature of half unfreezing at the given heating rate.

Optical microscopy was carried out with a Leitz polarizing microscope, equipped with a Mettler FP2 hotstage, calibrated to ± 0.2 K, capable of 0.2–10K min⁻¹ heating rates. The normal magnification for visual observation was 400 \times .

X-ray diffraction patterns for identification were taken with a Picker X-ray diffractometer with nickel-filtered CuK α radiation.

Infra-red spectra for identification were recorded on a Perkin-Elmer 621 spectrometer. Samples were run as KBr pellets, prepared at 1.0 GPa pellet pressure from approximately 10 mg sample in 200 mg anhydrous KBr.

RESULTS AND DISCUSSION

Amorphous polymer

The suggested procedure⁹ for preparing amorphous PABA using solution polymerization followed by pre-

cipitation was attempted. It did not, however, result in completely amorphous PABA. Instead, as was verified by X-ray diffraction and thermal measurements, a considerable amount of crystal modification II PABA was obtained. Amorphous PABA could, however, be prepared by quick thermal polymerization. The dried monomer (400K, 30 min) was heated in the d.s.c.-cell at 100K min⁻¹ heating rate to 570K¹³, then quenched by inserting the pan containing the sample into liquid nitrogen. It should be mentioned that this method of preparation of amorphous PABA is not always successful, sometimes partially crystalline polymers were obtained even by this method. In many cases, however, the sample was shown to be optically isotropic, and thermal analysis confirmed the amorphous state by revealing a glass transition and no crystalline melting (see below). An explanation for the formation of amorphous PABA by quick thermal polymerization was given in our earlier work¹³. The partially crystalline samples arose probably whenever the monomer was not sufficiently dried before polymerization. In this case a small amount of oligomer of poly(*p*-oxybenzoate) is formed, which is liquid crystalline or crystalline depending on its molecular weight. As the acryl-polymerization proceeds, poly(*p*-oxybenzoate) crystals may act as seeds for crystallization of PABA¹³.

A typical d.s.c. trace for amorphous PABA is shown in Figure 1. There is a strongly heating rate dependent heat capacity increase of 39 J K⁻¹ mol⁻¹ at about 350K (for 10, 20 and 50K min⁻¹ heating rates at temperatures of 338, 348 and 355K, respectively). A similar temperature (363K) was suggested earlier for the glass transition of amorphous PABA⁹. This increase in heat capacity seems to be reasonable when compared to other polymers which commonly have a ΔC_p of 11.3 JK⁻¹mol⁻¹ of small, mobile backbone atoms, and double or triple this amount for larger constituent groups such as phenyl groups.

The glass transition is followed at higher temperature by an exotherm (between 390 and 470K for 50K min⁻¹ heating rate, Figure 1). The latent heat of the exotherm is $\Delta H = -4.5$ kJ mol⁻¹. It has been established by optical microscopy that the sample in this temperature region is becoming birefringent, but no endotherm was observed in the melting region of PABA at 50 K min⁻¹ heating rate (see below). Instead, after cooling the sample and reheating, the glass transition temperature shifts to about 410K which corresponds to the glass transition of the mesophase of PABA (see below). From this we conclude that

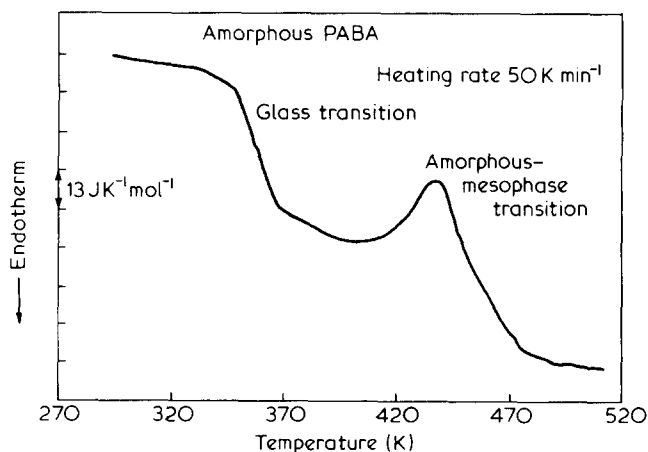


Figure 1 Typical d.s.c. trace for amorphous PABA

Table 1 Glass transition for semicrystalline PABA

Heating rate [K min ⁻¹]	Crystal form I and amorphous PABA		Crystal form II and amorphous PABA	
	T_g [K]	ΔC_p [JK ⁻¹ mol ⁻¹]	T_g [K]	ΔC_p [JK ⁻¹ mol ⁻¹]
2	324	—*	313	—*
5	326	—*	315	32.5
10	333	28.0	319	32.3
20	339	29.6	320	31.0
50	358	29.0	322	32.0

* The glass transition is followed by the amorphous to mesophase transition without attainment of a liquid heat capacity

Table 2 Glass transition data for semicrystalline and mesophase PABA at a heating rate of 50 K min⁻¹

Cooling rate [K min ⁻¹]	Crystal form I and mesophase PABA		Mesophase PABA	
	T_g [K] *	ΔC_p * [JK ⁻¹ mol ⁻¹]	T_g [K]	ΔC_p [JK ⁻¹ mol ⁻¹]
0.5	418	28.2	409	43.9
5	403	22.0	409	42.6
10	415	24.2	408	42.8
20	418	20.1	408	43.9
50	409	22.6	404	41.7

* Calculated using a mesophase—crystalline baseline extrapolated from close to the crystalline melting region (see text)

the observed exotherm corresponds to the amorphous to mesophase transition. At a lower heating rate (10 K min⁻¹) the mentioned exotherm is clearly double and an endotherm can be observed for these samples in the melting region of PABA, indicating the possibility of an amorphous to crystal transition at lower heating rates. Such partial crystallization of amorphous PABA was also reported in ref 9. The mesophase state was not described before.

Unfortunately, the glass transition of the amorphous polymer cannot be studied with regard to the hysteresis behaviour. Heating the amorphous polymer a few kelvin beyond the glass transition initiates the amorphous to mesophase transition with its parallel increase in the glass transition temperature. From the strong heating rate dependence of the glass transition, we conclude, however, that amorphous PABA has a normal hysteresis behaviour.

The semicrystalline states

The glass transition temperatures of the partially crystallized and partially amorphous PABA samples are listed in Table 1. They are observed at lower temperatures than for the purely amorphous and mesophase samples. Furthermore, T_g is somewhat lower for crystal modification II than for crystal modification I (see Table 1). It can be seen that the glass transition shows a strong heating rate dependence for crystal form I. Some rate dependence is also observed for crystal form II. It is reasonable, therefore, to suggest that the hysteresis phenomenon, which is based on a strong temperature dependence of the glass transition temperature, should be present for semicrystalline samples containing crystallites of crystal modification I. We have found recently that semicrystalline samples often show no hysteresis [examples: nylons, polycaprolactone, poly(ethylene

terephthalate) and poly(vinyl fluoride)]¹⁴. An example of a semicrystalline polymer with hysteresis is poly(ethylene oxide)¹⁴. Crystal form II of PABA is probably intermediate, with a minor hysteresis. We expect this behaviour to be governed by the interface morphology of the two-phase samples¹⁴.

The d.s.c. curves for the semicrystalline samples show similarity to the curve of Figure 1. All show an exotherm above the glass transition which is mainly due to a change of the amorphous phase to mesophase. The enthalpy of this exotherm which varied from -3.1 to -5.4 kJ mol⁻¹ cannot be used for the determination of crystallinity of the samples, since it varies somewhat with heating rate. The probable reason for this change with heating rate is additional annealing or reorganization of the crystals during the transition of the amorphous portions.

Heating the semicrystalline samples beyond the glass transition followed by cooling, leads to samples which consist of mesophase and crystals. On a second heating, the glass transition of the mesomorphic portion of PABA is higher than that of the amorphous portion. Data are shown in Table 2. This increase in T_g on change of the amorphous phase to mesophase is similar to the experiments initially carried out on completely amorphous PABA. Comparing these results with earlier data for the glass transition of semicrystalline PABA (398K), it becomes clear that Blumstein *et al.* reported the glass transition temperature for partially crystalline—partially mesophase samples⁹. A d.s.c. trace for a semicrystalline PABA containing mesophase, instead of amorphous phase, is shown in Figure 2. In this case the baseline after T_g cannot be easily selected because of excessive curvature. Moreover, the hysteresis behaviour in heat capacity, which should manifest itself in an endothermic peak in the glass transition region for the chosen cooling and heating rates, is absent. Conversion of the amorphous phase to mesophase is, in this case, the condition for suppression of hysteresis.

The directly measured jump in C_p of the semicrystalline samples at the glass transition, observed between 360 and 420K at a cooling rate-independent temperature of half-unfreezing of 409K, corresponds to about 15 JK⁻¹mol⁻¹ when the baseline curvature, mentioned above, is neglected. This value of ΔC_p is low. Blumstein *et al.*⁹ reported 40% as the highest value for the form I crystallinity of

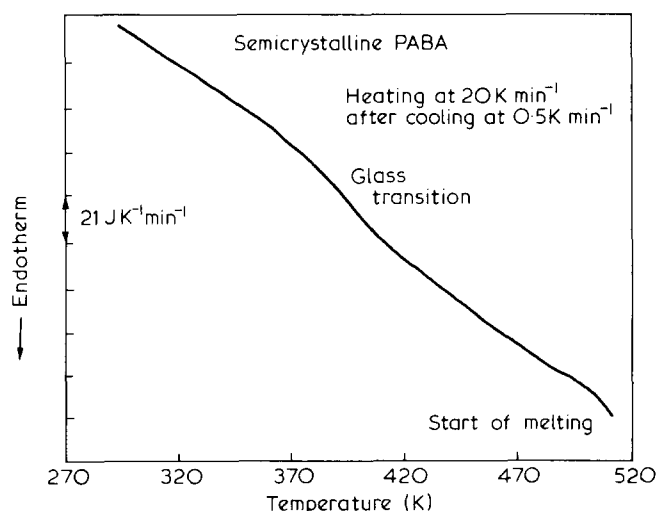


Figure 2 D.s.c. trace for a semicrystalline PABA

Table 3 Melting transition data for semicrystalline PABA* of crystal forms I and II

Heating rate [K min ⁻¹]	Crystal form I			Crystal form II		
	T_m^{**} [K]	T_{peak} [K]	ΔH_f [kJ mol ⁻¹]	T_m^{**} [K]	T_{peak} [K]	ΔH_f [kJ mol ⁻¹]
2	556	548	19.5	525	514	16.6
5	563	558	19.0	534	523	14.5
10	576	566	18.5	548	541	10.1
20	585	573	12.5	561	553	8.4
50	598	585	8.7	578	570	5.8
100	611	594	7.1	597	589	4.4

* Second phase is mesophase

** End of melting

PABA. Using $\Delta C_p = 43 \text{ JK}^{-1} \text{ mol}^{-1}$ for the mesomorphic polymer, the heat capacity change at the glass transition for the semicrystalline polymer would therefore be expected to be about $25 \text{ JK}^{-1} \text{ mol}^{-1}$. Assuming the baseline curvature above the glass transition temperature is still part of the glass transition, one can see that there is a higher temperature region before the beginning of melting, where the baseline seems to be linear. Extrapolating this linear baseline to the glass transition temperature leads to the more reasonable glass transition data shown in Table 2. Because of the long extrapolation, the data fluctuate somewhat, but T_g is still approximately constant at $412.6 \pm 6.5 \text{ K}$ and ΔC_p is $23.4 \pm 3.0 \text{ JK}^{-1} \text{ mol}^{-1}$, close to the expected value for a typical crystal form I crystallinity. Obviously, in this case, as for other semicrystalline polymers¹⁴, the qualitative baseline method for determining ΔC_p values of T_g is difficult to apply to the glass transition characterization, absolute heat capacity measurements are necessary¹⁵. We hope to deal with these questions in more detail at a later time.

Blumstein *et al.*⁹ raised the possibility that at 525K there is a true melting of the polymer. In order to investigate this process, we used optical microscopy and d.s.c. measurements combined with thermogravimetric analysis. Optical microscopy showed that the polymer melts approximately at 525K. This is not, however, a crystal to isotropic transition; but a mobile, liquid crystalline phase which is observed beyond the melting. From the texture under the microscope it can probably be classified as a nematic phase. Once either of the two crystal forms was melted, the obtained mesophase cannot crystallize on cooling, i.e. it is metastable.

Melting data obtained from d.s.c. measurements are summarized in Table 3. For the lowest heating rates, an endothermic process is observed close to the earlier suggested temperature region, but a certain amount of decomposition also occurs during the melting⁹. Thermogravimetry at a heating rate of 20 K min^{-1} showed, for example, 19% and 7% weight loss at the temperature which corresponds to the end of the melting endotherm for modifications I and II, respectively. From Table 3 it can be seen that the melting point of crystal modification II is lower than that of I, therefore, modification II can be melted with less decomposition than modification I. For modification II, there was a second endotherm observed (peak temperature 589K at 20 K min^{-1} heating rate). This endotherm is, however, irregular and typical for decomposition with loss of decomposition products. It is reasonably well separated from the melting peak. The melting temperatures of Table 3 show considerable super-heating at high heating rates. The heat of fusion data show also a strong heating rate dependence,

which indicates that the endotherm includes other heat effects. It is possible that annealing or reorganization of crystals could occur at decreasing heating rates, but its contribution should be minor, especially since no separate exotherm is noticeable at lower temperatures. It is more likely that decomposition enters as a major contribution at slow heating rates. Assuming the fastest heating rate value most free of decomposition, ΔH_f is 7.0 kJ mol^{-1} for crystal modification I. Taking into account the -4.5 kJ mol^{-1} heat of transition of the amorphous to mesophase transition and assuming 40% crystallinity suggested in ref 9 (X-ray data), a crystal to isotropic melting transition with $\Delta H_f = 22 \text{ kJ mol}^{-1}$ is obtained which is not much different from $\Delta H_f = 23.2 \pm 2.4 \text{ kJ mol}^{-1}$ of the monomer reported in ref 13. The entropy of fusion is thus about $40 \text{ JK}^{-1} \text{ mol}^{-1}$, a reasonable value when compared with other linear macromolecules². The transition to the mesophase, instead of the isotropic melt, reduces the entropy of fusion by about $8 \text{ JK}^{-1} \text{ mol}^{-1}$. (Only minor changes are expected in these values when true values for the equilibrium mesophase-melt transition temperature become available).

Mesophase transitions

Liquid crystalline PABA was obtained by melting semicrystalline PABA of crystal modification II, followed by quick quenching in liquid nitrogen. Subsequently, these samples were heated to 450K (above T_g) and cooled at different cooling rates to introduce reproducible thermal histories. For final analysis, the samples were heated at 20 and 50 K min^{-1} . The obtained d.s.c. traces are shown in Figure 3. The corresponding T_g and ΔC_p values are presented in Table 2.

It can be seen that the glass transition of mesophase of PABA is at a considerably higher temperature than the glass transition of amorphous PABA and, furthermore, it is heating rate independent. The increase in heat capacity at the glass transition temperature is similar to that of the amorphous polymer. Figure 3 reveals that the mesomorphic glass shows a strongly suppressed enthalpy relaxation. Furthermore, the glass transition in our mesophase PABA is followed by a small endotherm (see Figure 3). We could determine that this endotherm corresponds to some decomposition product which forms during the melting step. Semicrystalline PABA (modification II) was held for this purpose for several hours at 525K and the evaporating decomposition product was condensed on a cold surface. Analysis by d.s.c. showed an endothermic peak at 482K at 20 K min^{-1} heating rate with a latent heat of 115 J g^{-1} . From these data it can be concluded that our mesophase polymer contained about 1–2% impurities.

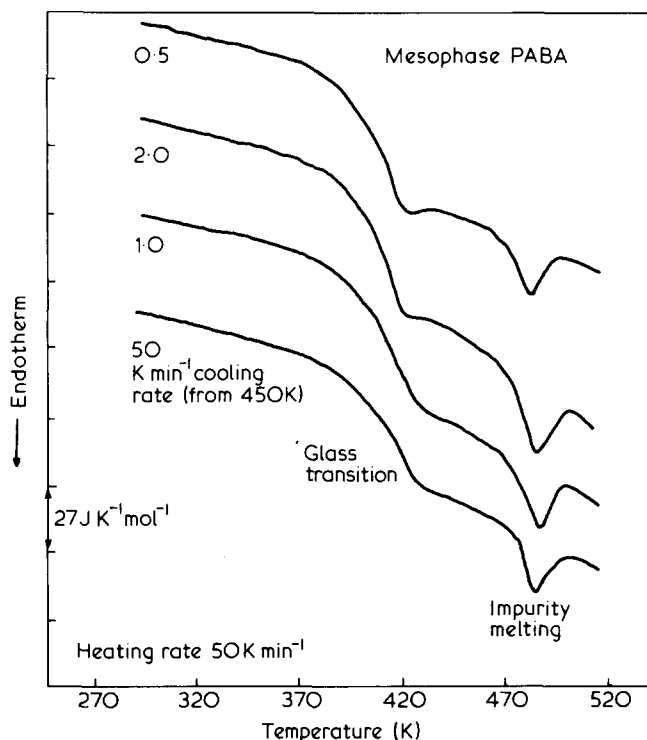


Figure 3 D.s.c. traces for mesophase PABA

The mesophase–isotropic liquid transition could not be observed because of the intervening decomposition. The mesophase did not show much tendency to crystallize, it is metastable. Crystallization was mainly observed during polymerization (crystal forms I and II)⁹ and on precipitation from solution (crystal form II). Question 'c' in the Introduction must thus remain unanswered relative to the mesophase to crystal transition (see ref 7 for such a study on a different mesophase polymer system).

CONCLUSIONS

(I) Poly(*p*-acryloyloxybenzoic acid) has been analysed in the following twelve single and two-phase physical states:

1,2 Amorphous (liquid or glassy) ($T_g = 348\text{K}$ at 20 K min^{-1} ; $\Delta C_p = 39\text{ JK}^{-1}\text{mol}^{-1}$);

3,4 mesophase (liquid or glassy) ($T_g = 408\text{K}$ at 20 K min^{-1} ; $\Delta C_p = 43\text{ JK}^{-1}\text{mol}^{-1}$);

5,6 semicrystalline (amorphous liquid or glassy + crystal modification I) ($T_g = 339\text{K}$ at 20 K min^{-1});

7,8 semicrystalline (amorphous liquid or glassy + crystal modification II) ($T_g = 320\text{K}$ at 20 K min^{-1});

9,10 semicrystalline (mesophase liquid or glassy + crystal modification I) ($T_g = 409\text{K}$, $T_m = 585\text{K}$ at 20 K min^{-1});

11, 12 semicrystalline (mesophase liquid or glassy + crystal modification II) ($T_g = 408\text{K}$, $T_m = 561\text{K}$ at 20 K min^{-1}).

(II) Considering that only one T_g could be observed in any of the samples, we may rule out a partially amorphous–partially liquid crystalline two-phase state. The probable answer for question (a) raised in the Introduction is that the PABA mesomorphic polymer can

be considered to be a single phase.

(III) A change from the amorphous state to the mesophase has a heat of transition of -4.5 kJ mol^{-1} . It raised the glass transition temperature, but causes little change in ΔC_p at T_g . Relative to question (b) in the Introduction, we find a first order transition between these two phases, each, however, retains a glass transition. The higher T_g for the mesophase indicates its limited mobility. Assuming the fully amorphous PABA to have a normal enthalpy relaxation (hysteresis behaviour, because T_g shows a strong rate dependence), there is a large reduction in the hysteresis behaviour on going to the mesophase, as a partial answer to question (c) in the Introduction.

(IV) The semicrystalline PABA samples (mesophase + crystalline) have broadened glass transitions without enthalpy relaxation (hysteresis). This can be considered normal, since the majority of semicrystalline polymers also show such behaviour.

(V) The extrapolated heat of fusion for crystal form I is 22 kJ mol^{-1} which leads to an approximate entropy of fusion of $40\text{ JK}^{-1}\text{mol}^{-1}$ and an entropy of $8\text{ JK}^{-1}\text{mol}^{-1}$ for the mesophase to isotropic melt transition.

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