

# Phase transitions in solutions of rigid polymers studied by synchrotron radiation

Y. Cohen

Chemical Engineering Department, Technion-Israel Institute of Technology, Haifa, Israel 32000

and S. Buchner and H. G. Zachmann

Institut für Makromolekulare Chemie, Universität, Bundesstrasse 45, D-2000 Hamburg 13, Germany

and D. Davidov

Racah Institute of Physics, Hebrew University, Jerusalem, Israel  
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Oriented liquid-crystalline solutions of the rigid heteroaromatic polymers poly(*p*-phenylene benzobisthiazole) and poly(*p*-phenylene benzobisoxazole) in polyphosphoric acid were transformed into crystalline phases by absorption of moisture. At moderate moisture levels crystal-solvate phases are formed by co-crystallization of the polymer and its solvent, whereas at high water content the crystalline polymer phase is formed by deprotonation of the polymer. Two crystal-solvate forms have been identified, as the moisture content increases up to about 10% (w/w), denoted form I and form II. Transitions between the different phases, as a function of temperature and time, were studied by X-ray diffraction using the high-intensity synchrotron source. The intensity of the crystalline reflections from the form I state decrease gradually with increasing temperature up to final melting at about 70°C. The orientation of the crystalline phase is maintained up to its melting. Recrystallization is observed upon quenching, showing the reversibility of this transition. The behaviour of the form II phase differs markedly. As the temperature is increased, a gradual crystal-crystal transition occurs in the temperature range of 250–300°C from the form II state to the crystalline polymer state. This transformation is irreversible. A novel recrystallization phenomenon is observed when the liquid-crystalline phase is heated to about 250°C. Crystalline reflections appear at spacings close to those of the crystalline polymer state. These reflections disappear upon cooling. These transformations are discussed in terms of the state of protonation of the polymer in its solution in polyphosphoric acid. Form I is considered a complex of the protonated polymer and the acid anions, which dissolves at moderate temperatures. Recrystallization at elevated temperature is suggested to result from deprotonation of the polymer. The state of protonation of the polymer in the form II state is still not understood.

(Keywords: phase transitions; rigid-rod polymers; solution; liquid crystals; crystallization; water absorption; X-ray diffraction)

## INTRODUCTION

Fibres and films exhibiting high modulus and strength are fabricated from solutions of rigid polymers by a spinning process. Typically, the polymer solution is in the liquid-crystalline state. In the dry-jet wet-spinning process the solution is extruded through a die into an air gap where it undergoes elongational flow resulting in a high degree of alignment of the polymer chains in the flow direction. The oriented solution is then introduced into a coagulation bath where solidification occurs by the action of a non-solvent. Post-treatments such as drying and heating under tension yield the final material. Because of their inherent rigidity, such polymers are soluble only in strongly interacting solvents, such as protonating acids. Water is commonly used as the coagulant. Solubility is thus a consequence of electrostatic repulsion between the protonated rod-like

molecules, and solidification during coagulation is due to deprotonation of the polymer by the coagulant leading to crystallization of the uncharged polymer.

A group of aromatic heterocyclic rigid polymers has been developed by the US Air Force Ordered Polymers Program. Among these are two polymers, poly(*p*-phenylene benzobisthiazole) (PBZT) and poly(*p*-phenylene benzobisoxazole) (PBO), from which high-performance fibres have been developed<sup>1–3</sup>. The polymerization of these polymers<sup>4</sup> is carried out in polyphosphoric acid (PPA), so that the processing of fibres and films usually proceeds from the PPA solutions of the polymers. The chemical formulae of these polymers are given in *Figure 1*.

The phase transition in the coagulation stage of the spinning process is from the oriented liquid crystal to the solid polymer crystal state. However, it has recently come to focus that other crystalline phases can occur in

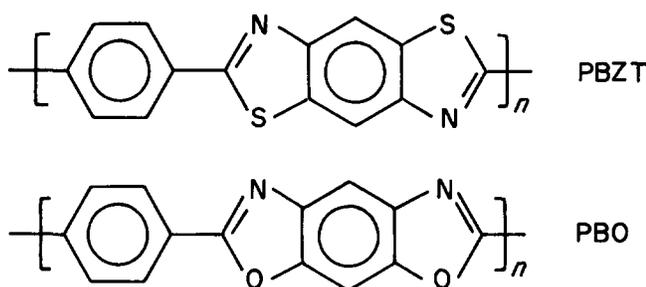


Figure 1 The chemical formulae of PBZT and PBO

solutions of rigid polymers. These are the so-called crystal-solvate phases, in which the rigid polymer co-crystallizes with its solvent<sup>5</sup>. Some crystal solvates can be considered as salts of the protonated polymer polycation and anions of the solvent acid. For example, poly(*p*-phenylene terephthalamide) (PPTA) forms a crystal solvate with sulphuric acid upon cooling<sup>5,6</sup>. Crystal solvates occur also in uncharged systems, such as poly(benzamide) solutions in *N,N*-dimethylacetamide/LiCl<sup>5,7</sup>.

Previous studies have demonstrated the existence of crystal-solvate phases in solutions of both PBZT<sup>8,9</sup> and PBO in PPA<sup>8,10</sup>. Furthermore, two distinctly different forms of the crystal-solvate phases have been identified, depending on the extent of exposure to the coagulant (moisture). Form I, which appears at low exposures to moisture, is characterized by several sharp equatorial reflections in the wide-angle X-ray diffraction pattern. In addition, sharp off-meridional (*hkl*) reflections indicate that unique three-dimensional order exists in this system, which is absent in the crystalline polymer state. The colour of PBZT/PPA solutions changes from dark to light green in this transition, whereas no colour change is observed in PBO/PPA solutions. Upon further exposure to moisture, a transition to form II occurs. The equatorial reflections become broad, as in the as-spun crystalline polymer state, but at different spacings. In the case of PBZT/PPA, the off-meridional reflections are not observed, and the colour changes from green to red. Again, no colour change is observed in PBO/PPA, and intense off-meridional peaks are still observed in the form II state<sup>8</sup>, but at different positions than in the case of the form I state<sup>8,10</sup>.

The transitions observed in the phase behaviour of the PBZT/PPA and PBO/PPA systems exposed to increasing amounts of moisture are therefore similar in nature. The state of the dry polymer solution depends on polymer concentration and temperature. It may be an isotropic solution, a liquid-crystalline solution or in the form I crystal-solvate state. At low moisture content the highly ordered form I crystal-solvate state is observed, and further absorption of moisture results in transition to the less ordered form II crystal-solvate state. Finally, large amounts of water results in transformation to the crystalline polymer state, which exists in the solid polymer fibres or films. However, there are distinct differences between the PBO/PPA and PBZT/PPA systems. In the form I state the sharpest off-meridional reflections are observed on a layer that has been associated with the repeat unit of phosphate groups. In the PBO/PPA system, the spacing of this layer line is 6.0 Å, half the length of the PBO monomer unit<sup>8,10</sup>,

whereas in PBZT/PPA it is 4.6 Å, three-eighths of the length of the PBZT monomer unit<sup>8,9</sup>. This indicates different conformations of the PPA oligomers forming a complex with the rigid polymer in the co-crystal. Concerning the form II state, the colour change to bright red and the disappearance of the strong off-meridional reflections in the PBZT/PPA system have been interpreted as due to deprotonation of the rigid polymer and loss of the ordered PPA conformation that existed in form I. The persistence of the strong off-meridional reflections in the form II state of PBO/PPA and its dark colour similar to that of form I have been interpreted as indicating that PBO is still protonated in this state and is complexed with PPA anions<sup>8,10</sup>.

The crystallization that occurs during the coagulation stage in the spinning process results in formation of the solid polymer microstructure that is responsible for its properties. This morphology was shown to be an interconnected network of oriented microfibrils, the width of which is less than 100 Å for PBZT fibres<sup>11</sup>. The motivation for this work stems from the hypothesis that there is a direct connection between the nature and kinetics of the phase transition during coagulation and the microstructure and properties of the final materials. In the common spinning processes, the nature of the phase transitions during coagulation is not well known and is not controlled. In general, very little is known about the transitions between the liquid-crystal, crystal-solvate and polymer crystal phases, and the role of protonation in these transitions. Visual observation of the colour changes in the spinning of PBZT/PPA solutions suggests that the form II state precedes the formation of the final crystalline polymer state, and that the form I state is not observed. The possible role of crystal-solvate phases in a controlled coagulation process is not clear. It is conceivable that the crystal-solvate phases may serve as intermediate stages in the solidification process, by which control may be exerted on the kinetics of crystallization and hence on the resulting morphology and properties.

Our objective in this study is to monitor transitions between the different crystalline phases in systems composed of rigid polymer (PBZT or PBO), solvent (PPA) and coagulant (water) by means of X-ray diffraction using the high-intensity X-ray synchrotron source. Uniaxially oriented samples obtained from polymer solutions usually used for the spinning of fibres are used in this study to mimic the situation encountered in a spinning process. We also report on preliminary experiments with solutions of low-molecular-weight PBZT in methanesulphonic acid (MSA). This is a model system with which higher polymer concentrations can be obtained, as compared to the PPA solutions of higher-molecular-weight polymers, and in which the transitions to the crystal-solvate phases occur at higher water content.

## EXPERIMENTAL

PBZT was obtained from Stanford Research Institute, and PBO from Dow Chemical Co. Both polymers were supplied as solutions containing 14% by weight polymer in PPA (82.6% P<sub>2</sub>O<sub>5</sub>). The intrinsic viscosity of both polymers in methanesulphonic acid was about 25 dl g<sup>-1</sup>, indicating a molecular weight of about 40 000<sup>12</sup>.

Samples were oriented in a glove-bag under dry

nitrogen by manual extension ( $4-6 \times$  draw ratio), to form thin fibre-like samples. PBZT could be oriented at room temperature, whereas the PBO solution was heated to about  $60^\circ\text{C}$ . For exposure to moisture, a sample of about 0.1 g was transferred to a vial and connected to a closed vessel of either 0.1 or 0.5 litre volume, containing ambient air. After several days of exposure the sample was cut into short fibres, which were sealed in short glass capillaries. An upper bound for the moisture content may be estimated by mass balance assuming that the hygroscopic PPA solution absorbed all the moisture in the volume with which it was in contact. The moisture content of the samples prepared in this manner is therefore estimated as 1% and 5% by weight, respectively, with the understanding that these are only very rough indications of the relative moisture exposure of the samples.

Low-molecular-weight PBZT (intrinsic viscosity  $2.5 \text{ dl g}^{-1}$ ) was also obtained from SRI. MSA (Aldrich Chemicals) was distilled under vacuum before use. Dilute solutions were prepared by dissolution in a sealed vial, which was subsequently allowed to absorb moisture until a phase transition could be observed by a change in colour. The water content was monitored gravimetrically.

Wide-angle X-ray diffraction experiments were conducted on the Polymer Physics beamline of HASYLAB at the DESY synchrotron facility, Hamburg, using a double-focusing camera<sup>13</sup>. Both linear and two-dimensional Gabriel position-sensitive wire detectors were used, as well as a vidicon camera. The linear detector was aligned perpendicular to the fibre axis of the oriented sample, so that the equatorial reflections are observed. The capillaries were placed in copper holders in a vacuum heater. Further details of the experimental design are described by Elsner *et al.*<sup>14</sup>. A heating rate of  $5^\circ\text{C min}^{-1}$  was used, and a diffraction pattern was collected every 30 s, unless stated otherwise. Diffraction patterns were calibrated using silicon powder, and scattering angles are expressed as equivalent to the use of  $\text{Cu K}_\alpha$  radiation.

## RESULTS AND DISCUSSION

The PBO/PPA solution used in this study already exhibits the form I crystal-solvate state at room temperature<sup>8,10</sup>, even when kept scrupulously dry. The equatorial reflections from the dry oriented solution, as a function of temperature, are shown in Figure 2. At the lower temperatures, shown in Figure 2, sharp and intense equatorial reflections are observed, which are superimposed on an amorphous halo of lower intensity. This is evidence for the biphasic nature of the solution at these temperatures, in which the form I crystal-solvate phase coexists with the liquid solution. As the temperature is elevated, a gradual decrease in the intensity of the crystalline reflections and increase in the intensity of the amorphous halo is observed, up to a final melting into the liquid state at about  $72^\circ\text{C}$ . The change with temperature of the integrated intensity (over  $2\theta$ ) of the lower-angle reflection ( $9.2 \text{ \AA}$  spacing) is plotted in Figure 3.

The gradual decrease in the intensity of the equatorial crystalline peaks can be due either to disorientation of the crystallites or to their gradual dissolution. To check the orientation of the crystalline phase as the temperature is increased, the diffraction pattern was measured at different temperatures using a two-dimensional wire

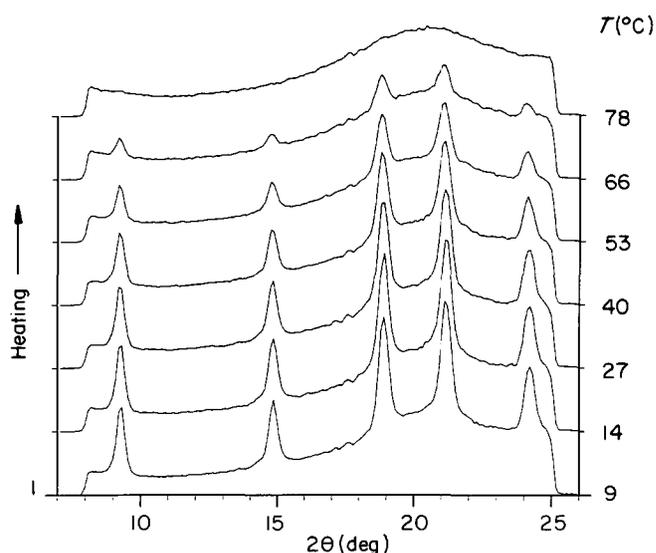


Figure 2 The equatorial reflections of the PBO/PPA form I crystal solvate as a function of temperature

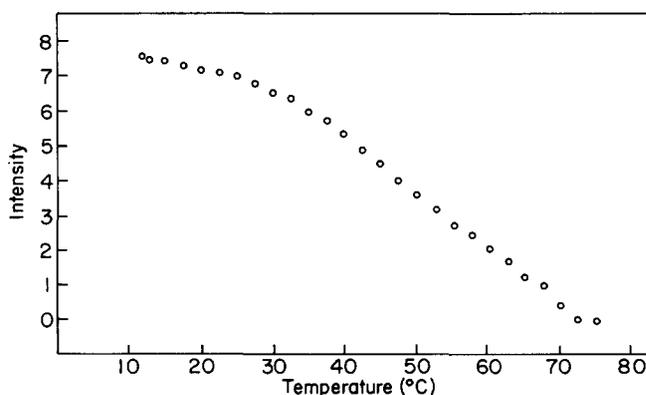


Figure 3 The integrated intensity of the  $9.2 \text{ \AA}$  reflection of the form I PBO/PPA crystal solvate as a function of temperature

detector. Temperature steps of about  $10^\circ\text{C}$  were used, and data collection for 1 min followed an equilibration time of about 5 min. To check on the orientation of the crystalline phase, the azimuthal spread of the lower-angle equatorial reflection ( $9.2 \text{ \AA}$  spacing) is evaluated as a function of temperature. This reflection is chosen as it is the farthest from the amorphous halo in the observed pattern. The intensity, integrated over the scattering angle  $2\theta$ , is plotted in Figure 4 as a function of the azimuthal angle  $\phi$ , at different temperatures. The azimuthal spread of the reflection, measured as its full width at half the maximum intensity, remains constant at about  $10^\circ$  up to the final dissolution above  $70^\circ\text{C}$ . The decrease in intensity with increased temperature thus indicates a gradual decrease in the crystalline fraction. This is in accord with the expected behaviour of a system composed of two components (PBO, PPA) with two phases (form I crystal solvate and liquid crystal), and reflects the dissolution of the crystal solvate to the liquid crystal.

The PBZT/PPA solutions used in this study are in the liquid-crystalline state at room temperature, and only a broad amorphous halo is observed on the equator of their diffraction pattern<sup>8,9</sup>. When the PBZT/PPA solution is exposed to a small amount of moisture,

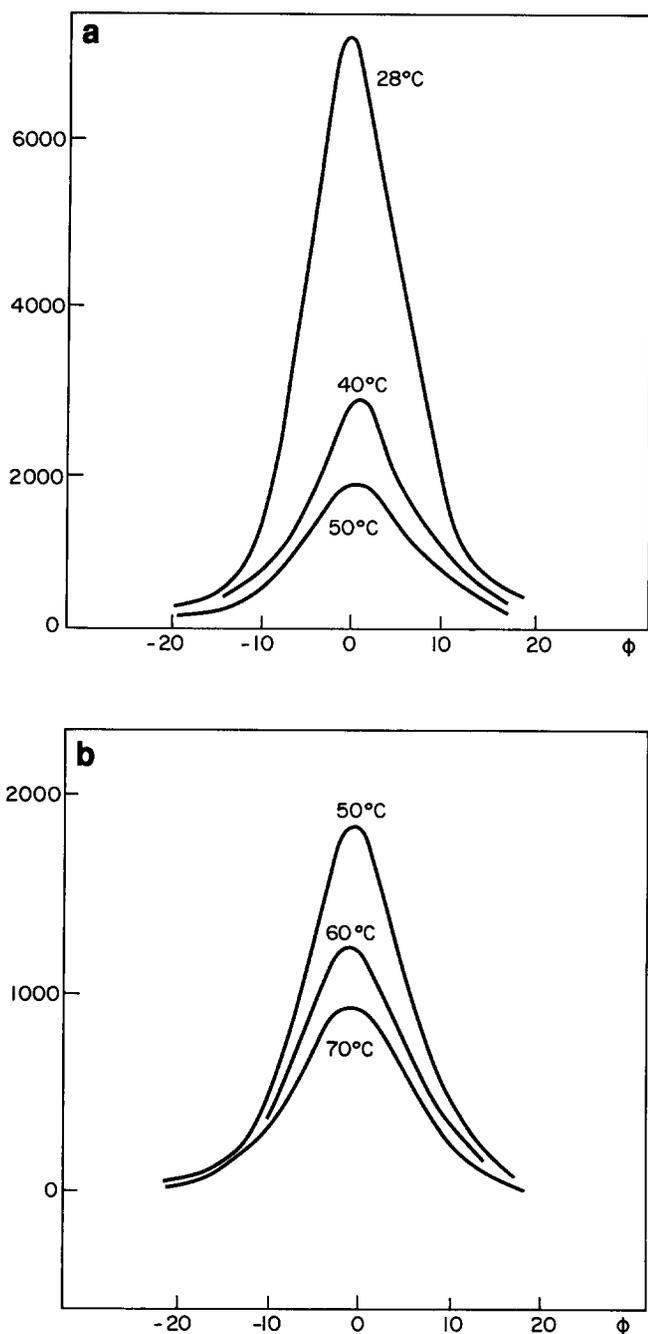


Figure 4 The intensity of the 9.2 Å reflection of the form I PBO/PPA crystal solvate, integrated over  $2\theta$ , as a function of azimuthal angle  $\phi$  (deg) at different temperatures

estimated as 1% by weight, sharp crystalline reflections appear on the equator, as shown in Figure 5, indicating formation of the form I crystal-solvate phase. Similar to the behaviour of the PBO/PPA system, a gradual transition to the liquid-crystal phase is observed at increasing temperatures, as shown in Figure 5. Dissolution is complete by about 70°C.

The transition from the form I crystal solvate to the liquid crystal is reversible, and when the temperature is lowered, the crystalline reflections reappear, although at much lower intensities. This is due to the loss of uniaxial orientation in the samples heated above the temperature of the transition to the liquid-crystal state. Recrystallization of the PBO/PPA form I crystal-solvate phase is shown in Figure 6, where the intensity of the 9.2 Å

reflection, integrated along the equator, is plotted as a function of time following a quench from the liquid-crystal state. In this case the PBO solution in the form I crystal-solvate state was heated to 75°C, into the liquid-crystal state, and quenched immediately to 19°C. The time that the sample is maintained in the liquid state plays an important role in the recrystallization process. During this time the disorientation of the rigid polymer occurs by rotational diffusion, and extended annealing in the liquid-crystal state may eliminate residual small crystallites, which act as nuclei for recrystallization. Neither effect has been studied extensively. Preliminary observations suggest that recrystallization following annealing for 25 min at 90°C is slower than in the case shown in Figure 6. This is subject to further studies. The

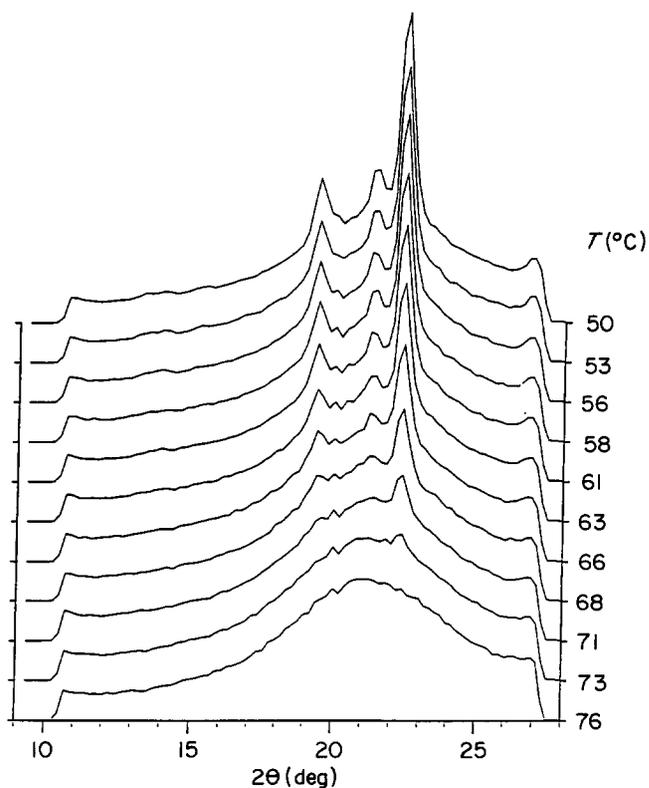


Figure 5 The equatorial reflections of the PBZT/PPA form I crystal solvate as a function of temperature

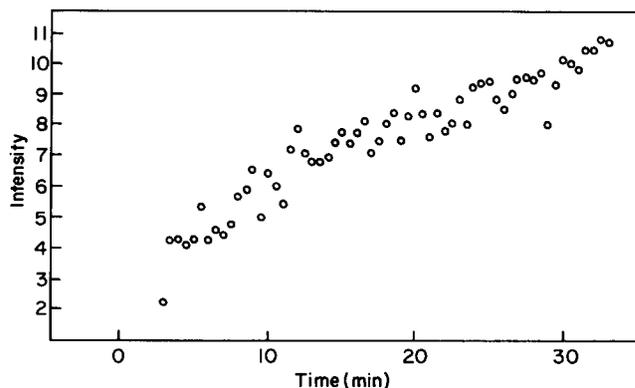
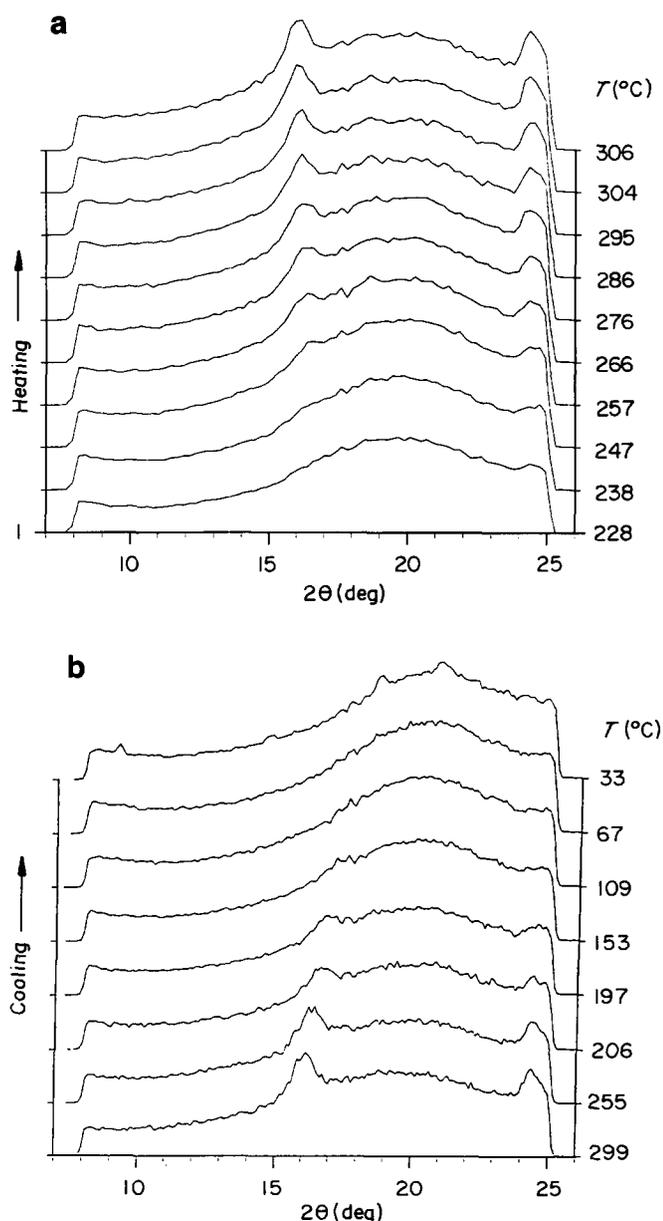


Figure 6 The PBO/PPA solution heated to 75°C and quenched immediately to 19°C: the intensity of the 9.2 Å reflection, integrated along the equator ( $2\theta$ ) as a function of time following the temperature quench

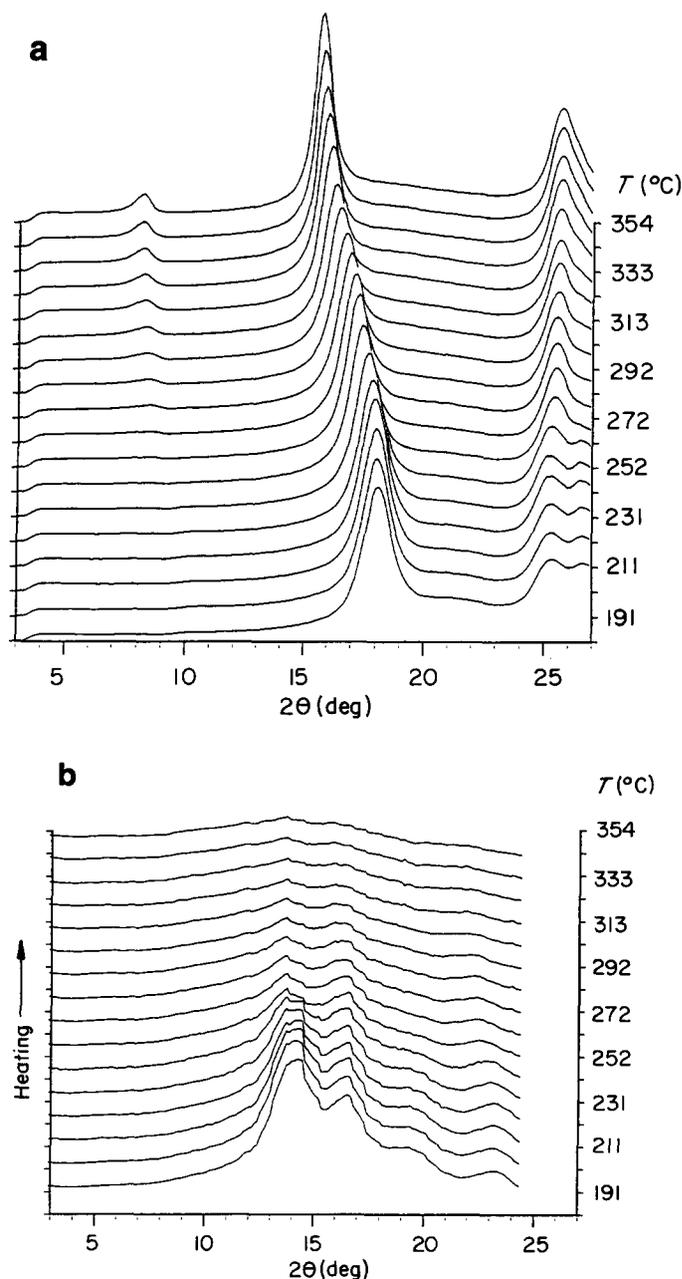
rate of disorientation in liquid-crystalline solutions was studied by Fejoo *et al.*<sup>15</sup> for PBZT/PPA and by Pickens *et al.*<sup>16</sup> for PPTA/sulphuric acid.

A novel recrystallization phenomenon is observed in the liquid state. It appears in the original PBZT/PPA solution as well as in the liquid state obtained by melting of the form I phase of PBO/PPA. When heated above 250°C, crystalline reflections appear in the diffraction pattern of the heated solution. An example of this effect is shown in *Figure 7* for the PBO/PPA system. The spacings of these reflections are close to those of the crystalline polymer state. This phenomenon is reversible, as the crystalline reflections disappear upon cooling, although at a lower temperature. We suggest that this phenomenon may be associated with deprotonation of the polymer at the elevated temperature, which results in crystallization of the uncharged polymer.

Upon absorption of a larger amount of moisture, estimated at about 5% by weight, the form I



**Figure 7** The diffraction pattern from the PBO/PPA solution at elevated temperatures showing reversible crystallization upon heating: (a) heating; (b) cooling



**Figure 8** The diffraction pattern from the form II crystal solvate of PBO/PPA as a function of temperature: (a) the equatorial reflections; (b) the off-meridional reflections on the second layer line (6.0 Å meridional spacing)

crystal-solvate phase transforms to form II. The phase behaviour of form II, as a function of temperature, differs markedly from that of form I. The diffraction pattern of the form II crystal solvate in the PBO/PPA system was monitored as a function of temperature using the vidicon camera, so as to evaluate changes in the equatorial reflections as well as the off-meridional reflections on the second layer line. Contrary to the melting of the form I phase, at about 70°C, no melting of the form II phase is observed. As temperature increases, the diffraction pattern does not change appreciably up to about 200°C. In the temperature range of 250–300°C a gradual crystal-crystal transformation takes place. *Figure 8* shows the changes in the equatorial reflections and the reflections on the second layer line of the form II PBO/PPA phase as a function of temperature. Three

gradual changes mark the transition: On the equator, the first reflection at a spacing of 4.8 Å shifts to smaller angles above 250°C, reaching a spacing of 5.6 Å at about 300°C, and does not change much further at higher temperatures. In the same temperature range, 250–300°C, a smaller-angle reflection appears at a spacing of 10.7 Å. On the second layer line (6.0 Å meridional spacing), the four distinct off-axis reflections of the form II phase gradually decrease in intensity and finally disappear in the same temperature range, 250–300°C, as shown in *Figure 8b*.

The positions of the equatorial reflections of the crystalline phase that develops at elevated temperatures are in general agreement with the non-primitive unit cell assigned to the crystal structure in PBO fibres<sup>17</sup>. Minor differences are due to the breadth of the reflections and the high temperature at which the measurement was made. It should be noted that in the diffraction pattern from PBO fibres the low-angle reflection is not observed<sup>17</sup>. There may be some differences in the symmetry of chain packing in the non-primitive unit cell of the crystalline PBO phase in the two cases.

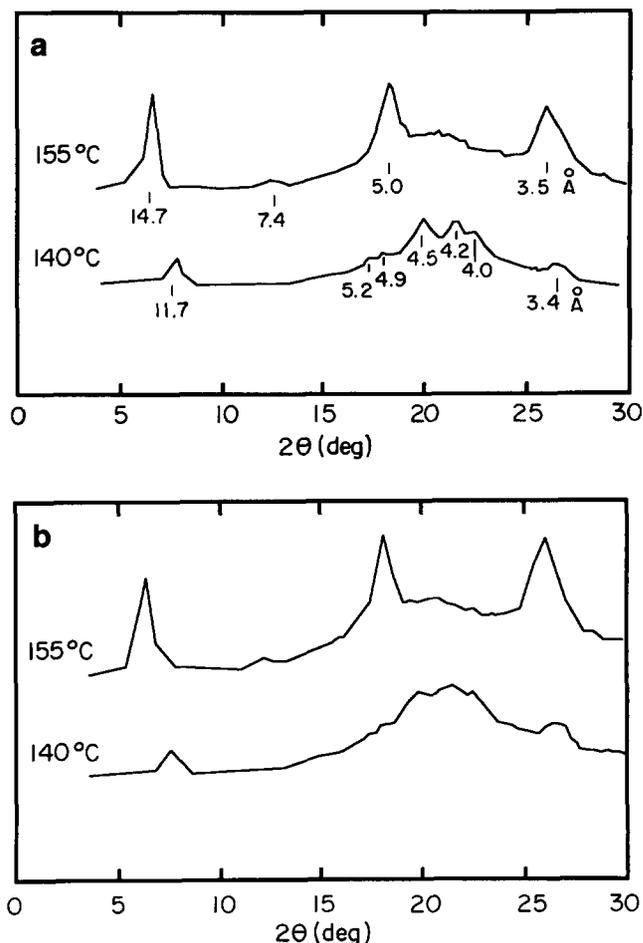
The off-meridional reflections on the second layer line of the form II phase have been interpreted as arising from the ordered PPA conformation in the co-crystal of PBO and PPA<sup>8,10</sup>. The disappearance of these reflections in the same temperature range in which the changes in the equatorial reflections are observed supports the interpretation that PPA is removed from the crystalline phase in this transition. We therefore suggest that heating transforms the form II crystal-solvate phase of PBO/PPA to a crystalline PBO phase by removal of PPA from the crystalline phase, possibly due to deprotonation of the polymer. This transformation is irreversible. If the sample is cooled during the transformation, the spacings of the equatorial reflections remain close to the value reached during heating, and off-meridional reflections are not observed.

The crystal-crystal transition of the form II PBO/PPA phase should be compared to the transformation of the PBZT/PPA form II phase as a function of temperature. In this case no off-meridional reflections are observed, and the transformation is monitored following changes in the equatorial reflections, as reported previously<sup>8,9</sup>. Similar to the PBO/PPA system reported above, the first equatorial reflection, at a spacing of 5.1 Å, shifts to smaller angles at elevated temperatures, reaching a spacing of 5.6 Å at 300°C. It should be noted that the spacing of this reflection even at 300°C is far from that of the crystalline PBZT phase (5.9 Å). In addition, a smaller-angle reflection appears at 10.7 Å above 300°C. These observations were confirmed in this study. Thus, contrary to the PBO/PPA system, it is possible that the form II PBZT/PPA phase is a metastable non-stoichiometric state containing PBZT and PPA in varying composition. Its transformation at elevated temperatures can be viewed as an annealing process involving gradual removal of the acid.

The phase transitions as a function of temperature are the most important distinctions between the two crystal-solvate forms in both the PBZT and PBO systems studied. The small amount of moisture, which results in a transformation of the form I crystal-solvate phase to form II, changes drastically the nature of the phase. The questions that have been raised concerning the form II crystal-solvate phase are not fully resolved. The state of

protonation of the polymer in the form II state is still an open issue. It is not clear whether this state constitutes a true equilibrium phase. The role and amount of PPA in this phase, and whether it forms a stoichiometric complex with the rigid polymer, are not determined.

Finally, we report a preliminary experiment on solutions of low-molecular-weight PBZT in MSA. The objective was to compare the crystal-solvate phase obtained by absorption of moisture into a dilute solution with that obtained by soaking dry PBZT with a relatively small amount of MSA. The high intensity of the synchrotron X-ray source allows diffraction experiments with samples containing a significant amount of MSA. The temperature dependence of the diffraction patterns from the following two samples were compared. The first sample was prepared from a 2% (w/w) PBZT/MSA solution, which absorbed moisture over a period of one week to a total of 20% by weight. The light-green solid phase that precipitated was centrifuged and the sample for X-ray measurement was collected from the solid mass at the bottom of the centrifuge tube. The second sample for this experiment was prepared by soaking dry PBZT flakes with dry (distilled) MSA to form a light-green solid mass containing 40% PBZT. The surprising result was that the X-ray diffraction patterns from these two samples were identical, as shown in *Figure 9*. As the



**Figure 9** The diffraction pattern from crystal-solvate phases of low-molecular-weight PBZT with methanesulphonic acid at 140 and 155°C. The samples were obtained by: (a) absorption of moisture into a dilute isotropic solution; (b) soaking dry PBZT flakes with dry MSA. Notice that the patterns in (a) and (b) are essentially identical

temperature was raised, a crystal-crystal transition was observed in both samples between 140 and 155°C. The nature of this transition is not yet understood. However, it is evident that the same phase obtained by direct complexation of PBZT and MSA is formed by absorption of moisture into a dilute PBZT/MSA solution. In view of its light-green colour, this crystalline phase is identified as the form I PBZT/MSA phase. It transforms to a bright red phase, identified as form II, upon further absorption of moisture. This result supports the notion that the form I crystal-solvate phase is a co-crystal composed of protonated polymer cations and solvent anions. Furthermore, the form II (red) state was not observed in PBZT/MSA mixtures at any ratio in the absence of water.

## CONCLUSIONS

Several phase transitions are observed in solutions of the rigid polymers in their acid solvent as a function of moisture content and temperature. The phases involved are the liquid-crystalline solution, form I and form II crystal-solvate phases and the crystalline polymer phase. The main conclusion is the distinction between the crystal-solvate forms based on their behaviour as a function of temperature. At low moisture content, two reversible transitions are observed. Dissolution of the form I crystal solvate at about 70°C supports the idea that it is a salt of the protonated polymer and the solvent anions. At elevated temperatures above 250°C the crystallization of the rigid polymer from its solution is observed, possibly due to its deprotonation. Form II is a crystalline state obtained at higher moisture content. It undergoes an irreversible crystal-crystal transformation at an elevated temperature. The role of solvent in this phase is not clear yet, and may be different with PBZT and PPA.

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