Crystal Solvates in the Poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)]/Poly(phosphoric acid)/Water System

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ABSTRACT: Two types of crystal solvates, formed by cocrystallization of the polymer and its solvent, were found in the poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)]/poly(phosphoric acid)/water (PBZT/PPA/water) system. These crystal solvates are formed during moderate coagulation of the liquid crystal phase of the PBZT/PPA system. Structural transitions between the nematic phase, the crystal solvates, and the PBZT crystal were studied by X-ray diffraction. The structural changes are associated with the absorption or removal of water. The different crystalline phases differ in their unit cell dimensions and in the extent of three-dimensional order in the packing of the parallel chains. The sequence of phases encountered upon increased water absorption is as follows: the liquid crystal phase; an ordered crystal solvate (form I); a less ordered crystal solvate (form II); and the poorly ordered crystalline PBZT phase. The well-developed crystalline order in the form I crystal solvate is considered to reflect unique associations between the protonated PBZT polycations and the oligomeric PPA anions. A schematic phase diagram is suggested for the ternary system composed of a rodlike polymer, a protonating solvent, and a deprotonating nonsolvent, which is in qualitative agreement with the observed phase transitions.

Introduction

Poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)] (PBZT) is a rigid rodlike polymer from which fibers and films exhibiting high tensile modulus and strength are fabricated.[1,2] In the processing of PBZT fibers and films, an oriented nematic solution of PBZT in a strong acid is coagulated by a nonsolvent. Most commonly, the solvent is poly(phosphoric acid) (PPA), which is the polymerization medium for PBZT,[3] and water is used as the coagulant. Studies of the morphology,[4,5] and mechanical properties,[6] which develop during coagulation of the PBZT/PPA solution in the process of fiber spinning have shown the formation of a network of microfibrils, the width of which is <100 Å. The microfibrillar network has the ability to sustain a tensile force that is comparable to that of the subsequently dried fiber. These studies indicate that the basic structural features responsible for the mechanical properties are set during coagulation and suggest that improved mechanical properties may be obtained by control of the coagulation process.

The structure of the crystalline PBZT phase, which is formed by coagulation in water, and subsequent improvements in crystalline order and orientation by postprocessing heat treatment under tension have been studied extensively.[7-11] However, details of the structural transitions during coagulation have not been studied. Such transitions may be revealed by coagulation under mild conditions. In solutions of PBZT in methanesulfonic acid (MSA), a crystal solvate phase can be formed by mild coagulation with moist air.[12,13] Crystal solvate phases, which result from cocrystallization of the polymer with its solvent, have been observed to form in solutions of several rigid polymers.[14,15] An understanding of the formation of crystal solvates in solutions of rigid polymer may be important in optimizing the coagulation process and the resultant mechanical properties.[16]

In a previous study on the coagulation of the PBZT/PPA system under mild conditions by 85% phosphoric acid, a crystal solvate phase has been observed.[17] However, we recently found that two forms of crystal solvates can be formed in the PBZT/PPA/coagulant system, the coagulant being either water or phosphoric acid. In this paper we report on the conditions of phase transitions among the various phases: the nematic phase, the crystal solvates, and the PZBT crystal. We also report on the structure of the crystal solvates.

Experimental Section

The starting material is a uniaxially oriented nematic solution of PBZT in PPA. The PBZT solution, obtained from the Stanford Research Institute, had the following characteristics: PBZT concentration, 13.7% (by weight); P_2O_5 content of PPA, 82.6%, PBZT intrinsic viscosity (in MSA), 25 dL/g, which indicates a molecular weight of approximately 40 000.[18] The PBZT/PPA solution was oriented by extrusion through a tubular die (2-mm gap, extrusion temperature 120 °C) at Foster Miller Inc. Subsequently, samples were handled under dry nitrogen. Coagulated samples were obtained from the oriented solution by immersion either in water or in commercial (85‰) phosphoric acid. Structural transitions due to absorption of a small amount of moisture were induced by exposing the oriented solution to atmospheric moisture for a few minutes.

The structure of the samples was investigated by X-ray diffraction using monochromatized Cu Kα radiation with a Statton camera or a cylindrical camera. To avoid structural changes during the X-ray diffraction experiment, the samples were sealed

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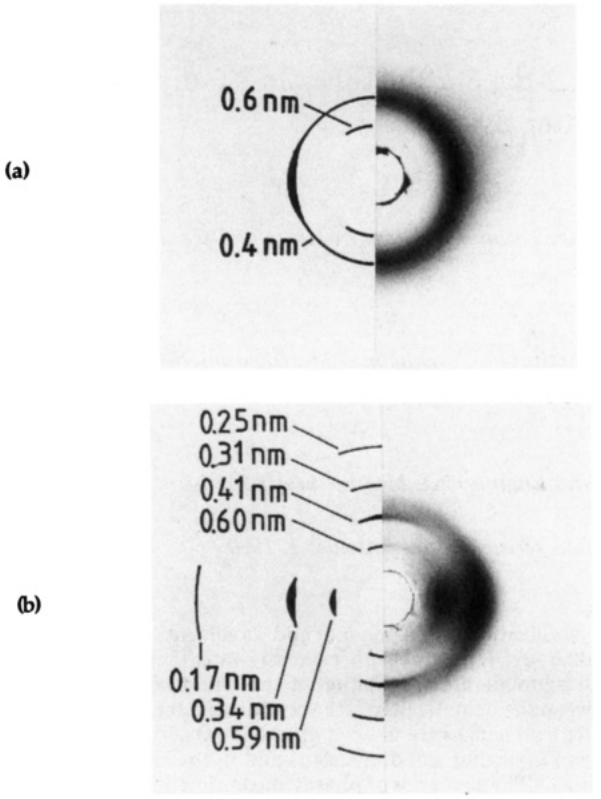

Figure 1. X-ray diffraction patterns from (a) the oriented nematic PBZT/PPA solution and (b) the solution after immersion in a water bath (orientation direction vertical, cylindrical camera).

in glass capillaries. The samples were oriented in the camera with the chain direction perpendicular to the incident X-ray beam and parallel to the camera axis when in the cylindrical camera. Densitometer scans were made along the equatorial reflections using a Joyce Loebel Scandig system.

Structural Transitions

In the processing of fibers and films, the PBZT/PPA nematic phase is coagulated in a water bath where it changes into the solid PBZT crystal phase. Typical X-ray patterns of a PBZT film before and after coagulation in the water bath are shown in Figure 1. Figure 1a exhibits a diffuse amorphous ring, with somewhat enhanced scattering on the equator and a weak streak around the meridian. It is a characteristic pattern of the oriented nematic state. Since the polymer content in the sample was much lower than the solvent content, the amorphous ring from the disordered solvent is much stronger than the scattering from the more oriented polymer molecules. Figure 1b shows only the crystalline PBZT reflections, which agree with the data from previous structural studies of as-coagulated PBZT.[7,8] The chain orientation in the as-coagulated PBZT film is approximately the same as that of the precursor nematic film.

When the structural changes were induced under moderate conditions, two types of ordered structures were observed. The following section details the observed structural changes and their interrelationships.

The Form II Crystal Solvate. During slow coagulation in 85% phosphoric acid, the color of the sample turns from dark green to red. Sample thickness was about 0.5 mm, and more than 5 h was required to complete the change (as judged by the time for complete color change through the thickness of the sample). The diffraction pattern of this red sample is shown in Figure 2a. The equatorial reflections of this phase are sharper that those

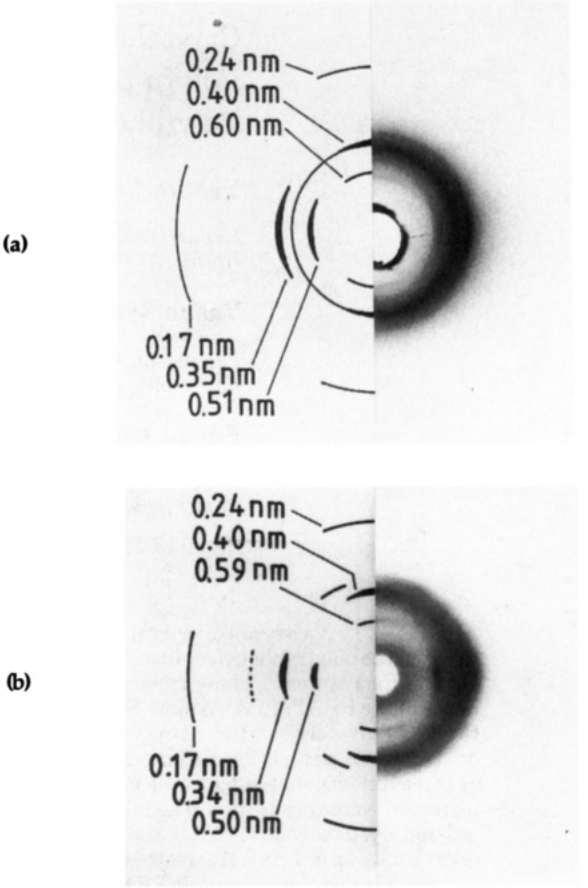

Figure 2. Diffraction patterns from the form II crystal solvate: (a) obtained by coagulation in 85% phosphoric acid; (b) obtained by absorption of atmospheric moisture (orientation direction vertical, cylindrical camera).

of the as-coagulated PBZT phase, which indicates a longer range and/or a higher degree of order in the crystalline packing within this phase. The spacings of the two strongest reflections are 0.507 and 0.347 nm, which differ considerably from those of crystalline PBZT. The positions of the meridional reflections are identical with those of the crystalline PBZT in which the chain is extended. This phase will be referred to as form II. The amorphous ring, centered at about 0.4 nm in Figure 2a, shows the existence of a slightly oriented liquid phase in this sample, which is effectively excess solvent.

The form II structure can also be obtained by exposing the nematic phase to atmospheric moisture. The necessary exposure time depends on the relative humidity but is typically much less than required for the transformation by coagulation in 85% phosphoric acid. The X-ray pattern of form II made by exposure to atmospheric moisture for about 4 min is shown in Figure 2b. All reflections of Figure 2a are present, and there are additional off-meridional reflections which indicate improvement in the three-dimensional order. The chain orientation is also better than in the form II made by immersion in 85% phosphoric acid, as indicated by the wider angular spread of the equatorial arcs in Figure 2a compared to those in Figure 2b. In Figure 2b, the relative intensity of the amorphous ring to the crystalline reflections is weaker than in Figure 2a. Some solvent is removed by exposing the sample to moisture, since the sample thickness has shrunk by about 25% while some yellow liquid droplets, resembling phosphoric acid, appeared on the surface of the sample.

The Form I Crystal Solvate. Form II can be converted to another ordered structure by exposure to

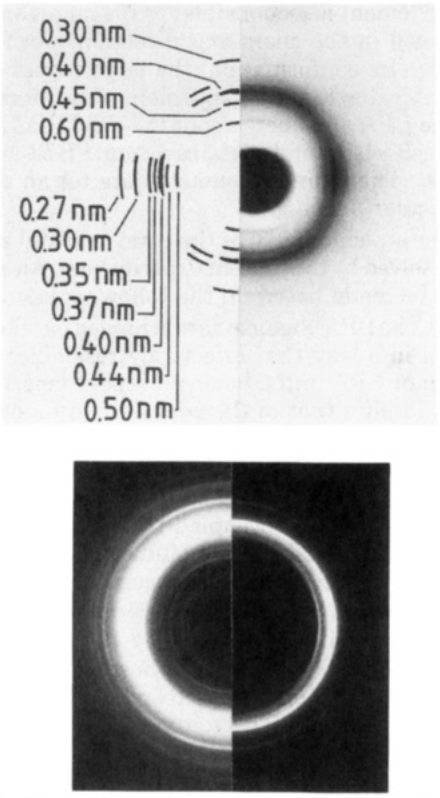

Figure 3. Diffraction patterns from the form I crystal solvate (a) obtained from form II by exposure to vacuum (cylindrical camera); (b) obtained from the oriented nematic solution by slow absorption of a minute amount of moisture, showing loss of orientation (flat-film camera).

vacuum for several hours. The color of the sample changes from red to light green. The X-ray pattern is shown in Figure 3a. This pattern is quite different from those of both the PBZT crystal and the form II structure. It is similar to the diffraction pattern reported previously for the PBZT/PPA crystal solvate obtained by coagulation in 85% phosphoric acid,[17] which had been converted to this form by the vacuum in the X-ray camera. We call this phase form I. Existence of off-meridional reflections shows that form I has three-dimensional order. Form I could be obtained from form II independent of the route to the form II state. It should be noted that the reflections of form I are very sharp in comparison with those of the PBZT crystals and form II.

Several additional features concerning forms I and II should be noted: Exposing form II to vacuum sometimes resulted in a reversal to the original dark green nematic phase instead of the form I. Form I quickly turns to form II when exposed to further atmospheric moisture. The color of the sample surface begins to change to red in a few minutes.

Form I could also be obtained by exposing the nematic phase to a very small amount of moisture. For example, an originally nematic sample enclosed in a sealed vial transformed after several days to form I. This structural change must have been induced by the small amount of moisture in the sealed vial. When the transformation, observed as a change in color from dark to light green, has been very slow, it was accompanied by an almost complete loss of the preferred chain axis orientation. The diffraction pattern from the form I phase obtained in this way is shown in Figure 3b. Very sharp reflections are observed as almost fully circular arcs, at spacings similar to those of the oriented form I phase described above. Apparently, during the slow crystallization process, crystallites of the form I phase having a lower axial ratio are formed within the liquid phase. These crystallites may disorient before the solidification has been completed. Relaxation of molecular orientation in the nematic phase may be discounted, since a similar sample of the oriented nematic solution, kept scrupulously dry at otherwise identical conditions, was transformed to the highly oriented crystalline PBZT phase when coagulated in water. Formation of an isotropic phase due to molecular aggregation in a menatic solution of PBZT in MSA was previously described by Se and Berry.[19]

Table I
Equatorial Reflections from the Form I Crystal Solvate

obsd spacings, nm	calcd spacings, nm	index
1.221	1.221	020
0.815	0.814	030
	0.812	100
0.752	0.757	110
0.612	0.610	040
0.487	0.488	050
0.465	0.473	140
0.439	0.431	$\bar{1}50$
0.401	0.407	060
	0.407	150
	0.406	200
	0.405	$\bar{2}10$
	0.396	210
	0.393	$\bar{2}20$
0.373	0.378	220
	0.374	$\bar{1}60$
	0.373	$\bar{2}30$
0.356	0.354	160
	0.354	230
0.352	0.349	$\bar{2}40$
	0.349	070
0.305	0.305	080
	0.302	250
0.287	0.292	$\bar{1}80$
0.271	0.271	300
	0.271	090
	0.271	$\bar{3}10$
	0.268	$\bar{3}20$

Structure of the Crystal Solvates

The X-ray pattern from the form I crystal solvate exhibits several unique features: several closely spaced reflections appear on the equator, which are much sharper than the equatorial reflections of both the form II solvate and the as-coagulated PBZT crystal. Off-meridional (*hkl*) reflections are apparent; in particular, relatively intense reflections are observed on a layer line at a meridional spacing of 0.465 nm, which is incommensurate with the layer line spacings due to the PBZT monomer repeat length of 1.24 nm. Since the number of observed reflections is not sufficient for a three-dimensional analysis, we consider the two-dimensional order in a plane perpendicular to the chain axis.

Fourteen reflections were observed on the equator of the diffraction pattern and are listed in Table I. The pattern was recorded on flat film in a vacuum camera, using a graphite monochromator, and the spacings were calibrated by use of silicon powder. A densitometer trace of the equatorial reflections is given in Figure 4. The following two-dimensional lattice is determined from the spacings listed in Table I: $a = 0.815$ nm, $b = 2.449$ nm, $\gamma = 94.5°$. The calculated spacings and their indices are also given in Table I. Many reflections are clustered about a spacing of 0.4 nm, as indicated by the breadth of the intense reflection centered at that spacing in Figure 4.

We next evaluate the dimension of the unit cell along the chain direction by considering the layer lines observed

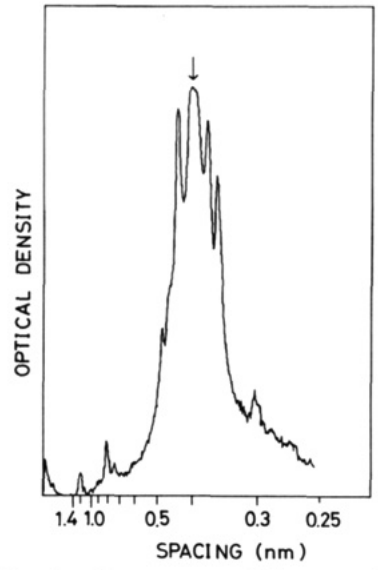

Figure 4. Microdensitometer scan of the equatorial reflections of the form I crystal solvate.

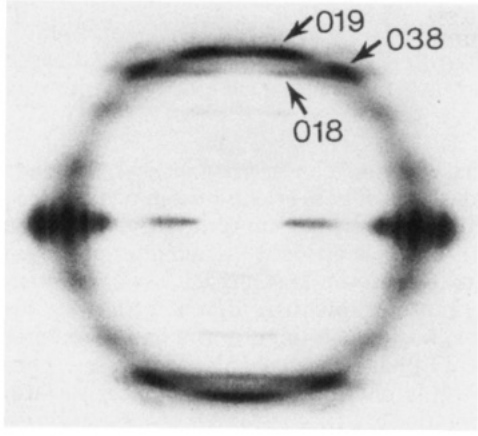

Figure 5. Diffraction pattern from the form I crystal solvate. The fiber axis has been tilted about the equator by 15°. (*hk*8) reflections are labeled according to the proposed unit cell.

in the fiber diffraction pattern of the form I crystal solvate. Several orders of the layer line spacing given by the PBZT repeat unit of 1.24 nm are observed. Furthermore, we observe strong reflections on a layer line at a meridional spacing of 0.465 nm, which does not coincide with any of the PBZT layer lines. The shortest dimension compatible with the observed layer line spacings is 3.72 nm, i.e., 3 times the PBZT repeat length and 8 times the spacing of the layer line at 0.465 nm. The off-meridional reflections on this layer line are highlighted as (*hk*8) reflections in Figure 5, where the fiber axis has been tilted about the equator by approximately 15° to bring this layer line region onto the Ewald sphere. The most intense off-meridional reflection, observed on this layer line at a spacing of 0.39 nm, is indexed as (038).

The origin of the 0.465-nm layer line can be postulated with reference to the conformation of PPA anions in polyphosphate salts.[20] In particular, the 2/1-helical conformations of PPA in its salts with lithium and rubidium, having two phosphate groups in a repeat lenth of 0.42 and 0.52 nm, respectively, suggest the possibility of a similar extended conformation of PPA in the PBZT/PPA form I crystal solvate. With the likely assumption that the extended PPA molecule is parallel to the PBZT chain, a repeat length of 0.465 nm, containing two phosphate groups, is indicated. It is still not clear what molecular arrangement is responsible for the large dimension of the unit cell in the chain-axis direction. As PBZT can not change its conformation, the large repeat length is presumably due to the arrangement of the phosphate groups of the PPA oligomers about the rigid PBZT chains. The unit cell is large and contains several PBZT and PPA repeat units. There are not enough data for an analysis of the molecular packing.

The stoichiometry of the form I crystal solvate cannot be resolved by the present experiments. An approximation may be made based on the following assumptions:

(a) The PPA oligomers are arranged parallel to the PBZT chain in a way that effectively resembles a continuous chain of PPA units, having a repeat length of 0.465 nm. This implies that in the *c*-axis direction of the unit cell, the length of which is 3.72 nm, there are three PBZT monomer units and eight PPA repeat units (sixteen phosphate groups).

(b) The volume occupied by the PBZT repeat unit in the solvate is similar to its volume in the pure PBZT crystal (0.268 nm^3).[7] The volume occupied by a PBZT chain in the solvate unit cell is thus 0.804 nm^3.

(c) The volume occupied by the PPA repeat unit is similar to its volume in a polyphosphate salt. An estimated volume of 0.099 nm^3 is based on the structure of rubidium polyphosphate.[21] The volume occupied by a PPA chain in the solvate unit cell is thus 0.792 nm^3.

The volumes occupied by the PBZT and PPA chains are nearly equal, so there are nine chains in the unit cell, the volume of which is 7.402 nm^3. Charge neutrality requires that since each PBZT repeat unit is doubly protonated there should be six deprotonated phosphate groups per PBZT chain in the unit cell. A plausible arrangement may have four protonated PBZT chains complexed with three PPA chains, on which every other phosphate group (i.e., every repeat unit) is deprotonated. In addition, there are two more PPA chains in the unit cell, which are not deprotonated. The unit cell in this model contains 33% (by weight) PBZT, and its density is 2.15 g/cm^3. Incorporation of both attached (i.e., deprotonated) and unattached solvent molecules in the unit cell of the crystal solvate follows a suggested structure for the crystal solvate of poly(*p*-phenyleneterephthalamide) (PPTA) with sulfuric acid,[22] in which unattached acid molecules separate sheets of hydrogen-bonded PPTA and sulfuric acid molecules.

In the diffraction pattern of the form II crystal solvate, only four reflections were observed on the equator. Two intense reflections appear at spacings of 0.507 and 0.347 nm. The second order of these two reflections was also observed. The 0.347-nm reflection is close to 0.354 nm, the spacing of the strongest reflection of the PBZT crystal.[7-9] In the PBZT crystal the 0.354-nm spacing corresponds to the intermolecular distance between the neighboring molecules along the *b* axis (approximately perpendicular to the wide surface of the ribbonlike shape of the PBZT molecule). On the other hand, the 0.507-nm spacing is much smaller than 0.583 nm, the distance between the (100) planes in the PBZT crystal. It is probable that a first-order reflection having a larger spacing than 0.507 nm is absent due to a symmetry condition.

This claim is supported by the changes in the diffraction pattern at elevated temperature. The diffractometer scans of the equatorial reflections of the form II crystal solvate at elevated temperatures are given in Figure 6, and the spacings of these reflections are given in Table II. The position of the 0.347-nm reflection does not change appreciably. However, the position of the 0.507-nm

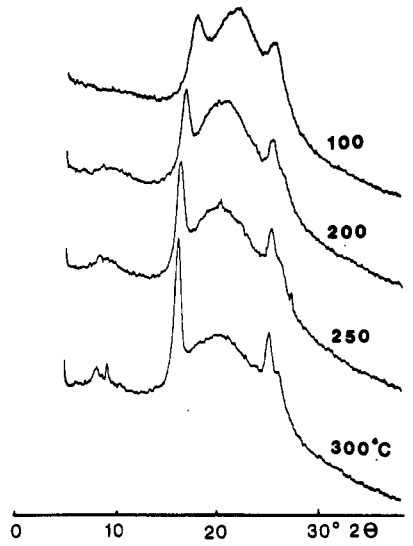

Figure 6. Equatorial reflections of the form II crystal solvate as a function of temperature.

Table II
Spacings of the Equatorial Reflections of the Form II Crystal Solvate at Different Temperatures

temp, °C	spacings, nm			
100		0.508	0.351	
200		0.539	0.353	
250		0.552	0.356	0.339
300	1.12	0.559	0.355	0.339

reflection changes to larger values as the temperature increases. Furthermore, a lower angle reflection at a spacing of about 1.12 nm appears at 300 °C. This reflection has been observed in as-spun PBZT fibers before heat treatment.[8] The changes of the diffraction pattern with temperature may be interpreted by an expansion of the solvated crystal predominantly along one direction, until a structural transition occurs above 250 °C, in which the symmetry condition forbidding the appearance of the larger spacing reflection is relieved. A phase transition of the PBZT/PPA crystal solvate at about 250 °C has been observed by differential scanning calorimetry.[17]

The following characteristics may be summarized for the form II phase: a change in color from green to red upon formation of the form II phase, which suggests deprotonation of PBZT, the loss of three-dimensional order relative to form I, and the diffuseness of its equatorial reflection, indicating small disordered crystallites. The form II crystal solvate may be viewed as a less ordered phase, compared with form I, which contains PBZT, PPA, and possibly water.

Discussion

We have shown that an increase in the nonsolvent content induces structural transitions in an initially liquid crystalline solution of PBZT in PPA. When water is the nonsolvent used, absorption of a minute amount results in a transition from the nematic solution to the solid form I crystal solvate. Further moisture absorption yields the form II crystal solvate, and when the sample is finally immersed in a water bath, the solid crystalline PBZT phase is formed. When the nematic solution is immersed in 85% phosphoric acid (15% water), the form II crystal solvate phase is formed. Irrespective of the way in which it has been formed, the form II crystal solvate can be converted to form I by removal of water under vacuum. Transformation of the form I phase to the nematic state by removal of water under vacuum has also been observed in some cases, but the conditions for this transition are not yet clear.

The sharp reflections in the diffraction pattern of form I suggest that the intermolecular forces responsible for the crystalline order are stronger in form I than in form II and the PBZT crystal. As the PBZT molecule is known to form a polycation in strong acids,[18,23] we consider the electrostatic forces between the PBZT polycations and the PPA anions to be resposible for the good crystalline order in the form I crystal solvate. The form I crystal solvate may thus be viewed as a "salt" of the PBZT polycations and the PPA anions, having a distinct composition.

On the other hand, the poorer order of the form II crystal solvate suggests that the electrostatic forces are not as strong as in form I. The change in color to red, associated with the transition to the form II crystal solvate, is reminiscent of the color changes observed in solutions of PBZT in methanesulfonic acid upon absorption of moisture.[13,19,24] This color change has been interpreted as indicating deprotonation of the PBZT chain.[19,24] Incorporation of water molecules (as H_3O^+) within the structure may screen the interactions between the PBZT and PPA chains and may render the distinct stoichiometric relationship between the PBZT and PPA molecules as unnecessary. The form II crystal solvate phase is thus viewed as an intermolecular compound containing PBZT, PPA, and water, possibly having a range of allowable compositions.

The transitions between the various phases described above can now be considered in terms of the phase equilibria in the ternary rigid polymer/solvent/nonsolvent system. In particular, we seek to answer the question of why absorption of a minute amount of water into the liquid crystalline phase results in formation of the ordered form I crystal solvate phase. Cloud point measurements in the system containing poly(γ-benzyl L-glutamate) (PBLG), dimethylformamide (DMF), and water have shown that 1–2% water could force the system into a wide biphasic region separating a very dilute isotropic phase from a concentrated liquid crystalline phase.[25] This effect was confirmed by Russo and Miller,[26] who explained it by extending the lattice theory of Flory[27] to the ternary polymer/solvent/nonsolvent system.

In the case of PBZT solutions in strong acids, the effect of water is expected to be even more pronounced, due to equilibria with respect to the protonation of PBZT and PPA (eqs 1 and 2). Furthermore, liquid–solid phase equilibria need to be considered, in particular the solubility limit of the form I crystal solvate (eq 3). By the law of

$$\mathrm{PBZT}_{\mathrm{monomer}}(\mathrm{crystal}) + 2\mathrm{H}^+ \overset{K_p}{\leftrightarrow} \mathrm{H_2PBZT}^{2+}{}_{\mathrm{monomer}} \quad (1)$$

$$\mathrm{PPA}_{\mathrm{monomer}} \overset{K_a}{\leftrightarrow} \mathrm{PPA}^-{}_{\mathrm{monomer}} + \mathrm{H}^+ \quad (2)$$

$$\mathrm{H_2PBZT}^{2+} + 2\mathrm{PPA}^- \overset{K_{xs}}{\leftrightarrow} [\mathrm{H_2PBZT}^{2+}(\mathrm{PPA}^-)_2] \quad \text{(form I crystal solvate)} \quad (3)$$

mass action, the crystal solvate phase will form when the product of the concentrations of the PPA anions and PBZT cations exceeds the solubility limit. In terms of the PBZT and PPA monomer units, the solubility limit is given by

$$[\mathrm{PBZT}^{2+}][\mathrm{PPA}^-]^2 \le K_{xs} \quad (4)$$

The effect of water on the equilibria described by eqs 1–4 requires knowledge of the equilibrium constants, which

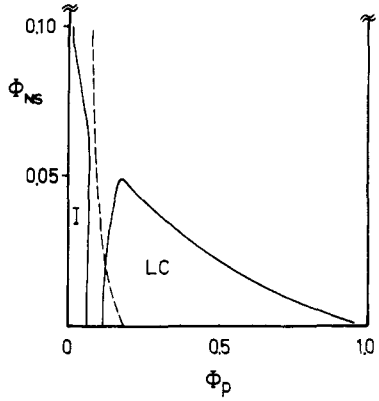

Figure 7. Ternary phase diagram for a system comprising a rigid polymer (P, axial ratio 100), solvent (S), and nonsolvent (NS). Solid lines: phase boundaries from Russo and Miller[26] with the binary interaction parameters $\chi_{S-P} = \chi_{S-NS} = 0$ and $\chi_{NS-P} = 1$. Dashed line: the solubility limit with regards to precipitation of the crystal solvate, given by eq 7. Φ = volume fraction; I = isotropic solution; LC = liquid crystal.

is not available. However, considering the absorption of a small amount of water, we may make the approximation that the water molecules serve only to deprotonate PPA, creating more PPA anions. If the initial polymer concentration, given as moles of monomer repeat units per liter solution, is denoted P_0, the concentration of absorbed water at which the crystal solvate first appears, denoted δw, can be given by

$$P_0(2P_0 + \delta w)^2 = K_{xs} \tag{5}$$

which for small values of absorbed water may be written as

$$\delta w = K_{xs}/(4P_0^2) - P_0 \tag{6}$$

The value of K_{xs} is likely to depend on the molecular weight of both PBZT and PPA. An approximate value may be obtained from an estimate of the solubility limit of binary PBZT/PPA solutions. As shown in this work, at 14% by weight of PBZT no noticeable crystallinity is observed. However, a solution of a similar rigid polymer, poly[*p*-phenylene(benzobisoxazole-2,6-diyl)] (PBO), of comparable molecular weight, concentration, and P_2O_5 content of PPA exhibits already significant formation of an ordered crystalline phase.[28] We can thus estimate the solubility limit to be roughly <20%. Taking the densities of PBZT, PPA, and their solutions to be equal to 2.0 g/cm^3, we obtain an approximate value of 10 (moles of monomer/liter)^3 for K_{xs}.

A schematic phase diagram may be constructed for the PBZT/PPA/H_2O system based on the principles mentioned above. First, liquid–liquid phase separation is considered. The boundaries of the isotropic and liquid crystalline phases are shown as continuous lines in Figure 7. They were calculated following Russo and Miller[26] for a polymer axial ratio of 100 and the following interaction parameters: solvent–polymer and solvent–nonsolvent $\chi_{S-P} = \chi_{S-NS} = 0$; nonsolvent–polymer $\chi_{NS-P} = 1$. Superimposed on the liquid–liquid equilibrium, suitable for the uncharged polymer/solvent system, is the solubility limit with regards to formation of the form I crystal solvate. This is given as the dashed line in Figure 7, which was calculated from eq 6 with the estimated equilibrium constant and the given initial polymer concentration. Polymer and water concentrations were converted to volume fractions using the approximate densities given above, yielding

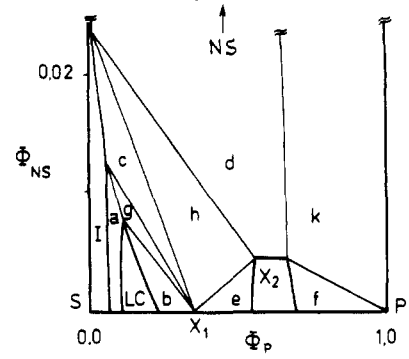

Figure 8. Schematic phase diagram for the ternary system that consists of a protonated rigid polymer, a protonating solvent, and a deprotonating coagulant (nonsolvent). Phase identification as in Figure 7. X_1 and X_2 = form I and form II crystal solvates. Biphasic regions: (a) I + LC; (b) LC + X_1; (c) I + X_1; (d) I + X_2; (e) X_1 + X_2; (f) X_2 + P. Triphasic regions: (g) I + LC + X_1; (h) I + X_1 + X_2; (k) X_2 + P + NS. Note: all discontinued lines meet at the nonsolvent apex of the ternary diagram.

$$\delta w = 4 \times 10^{-4}/P_0^2 - 7 \times 10^{-2}P_0 \tag{7}$$

Figure 7 clearly demonstrates the effect of water on the stability of the nematic phase relative to formation of the crystal solvate. If 1–2% of water results in liquid–liquid phase separation in an uncharged system, <0.5% will result in formation of crystal solvates in an acid solution. A schematic representation of the full ternary phase diagram is given in Figure 8. The form I crystal solvate is shown as a distinct composition of 33% PBZT, as discussed in the previous section. The form II crystal solvate is shown with a range of allowable compositions, containing PBZT, PPA, and water (the limits of which were set arbitrarily). The phase transitions that occur during absorptions of moisture can be understood following a trajectory on this phase diagram, as shown in Figure 8.

Conclusion

Two crystal solvate forms were found in the PBZT/PPA/water system. The two forms differ markedly in the degree of order exhibited in their diffraction patterns and hence in the nature of the packing of the PBZT and PPA chains in these crystals. The ordered crystal form I is interpreted as an ionic polymer complex of the protonated PBZT and the PPA anions, analogous to stoichiometric complexes identified previously in some other rigid polymer/solvent systems. Form II resembles the as-spun crystalline PBZT phase in its apparent lack of three-dimensional crystallinity but differs in the spacings of its equatorial reflections.

Conditions for the structural transitions between the nematic phase, the crystal solvates, and crystalline PBZT were investigated. It was found that water content in the material is primarily responsible for determining the structure. As the water content increases, the structure changes from a nematic solution to form I and then form II crystal solvates and finally to the solid-state crystalline PBZT phase.

The two-dimensional lattice perpendicular to the chain axis was determined for form I. Electrostatic interactions between the PBZT cations and PPA anions in the form I crystal solvate are proposed as an explanation for its highly ordered structure. The unique association between the rigid polycation and the flexible PPA polyanion is reflected in the X-ray diffraction pattern from this phase, which exhibits strong refelections on a layer line having

a meridional spacing of 0.465 nm. This spacing, which is incommensurate with the PBZT monomer repeat length, represents the repeat length of the PPA anion in an extended conformation dictated by its association with the PBZT polycation.

It is not clear if the form I crystal solvate can be obtained under the conditions of the spinning process of PBZT fibers. However, we believe that form II may be particularly relevant to structure formation during fiber spinning, as it is the state that directly precedes, in terms of its moisture content, formation of the pure polymer crystals.

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