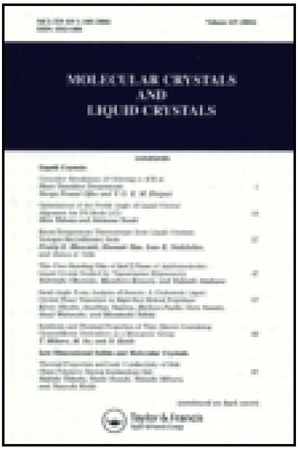

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Formation of Solid Phases by Coagulation Of A Monodomain Nematic Solution of Poly(P-Phenylene Benzobisthiazole)

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FORMATION OF SOLID PHASES BY COAGULATION OF A MONODOMAIN NEMATIC SOLUTION OF POLY(P-PHENYLENE BENZOBISTHIAZOLE)

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Abstract The effect of the coagulation environment on the nature of the solid phase formed from solutions of poly(p-phenylene benzobisthiazole) in polyphosphoric acid is studied. Coagulation in water results in formation of the crystalline polymer phase. A novel crystal-solvate phase, a co-crystal of the protonated polymer and the acid anion, is formed by coagulation in a mixture of phosphoric acid and water. The key to formation of the crystal-solvate phase is controlled deprotonation of the acid solvent without deprotonation of the polymer.

INTRODUCTION

High Performance fibers and films can be formed from lyotropic solutions of rigid polymers by a spinning process. In the coagulation state of this process, a monodomain nematic solution undergoes a transition to the solid state, which is induced by the action of a non-solvent. Usually it is the crystalline polymer phase which is formed by this transition. Recently, attention has been focused on formation of a crystal-solvate phase in solution of rigid polymers.[1] This is a solid phase which is formed by co-crystallization of polymer and solvent. Formation of crystal-solvates has been observed in several solutions of rigid polymers. Co-crystallization has been induced in solutions of poly(p-phenylene terephthalamide) in sulfuric acid by a decrease in temperature,[1,2] poly(benzamide) in dimethyl acetamide/LiCl by solvent evaporation under a magnetic field[3] and poly(p-phenylene benzobisthiazole) (PBT) in methane-sulfonic acid by absorption of atmospheric moisture.[4,5]

Due to their molecular rigidity, such polymers are soluble only in strongly interacting solvents. The propensity for co-crystallization of polymer and solvent is thus understandable. In particular, crystal-solvates obtained from solutions in protonating acids can be viewed as a salt of the protonated polymer and the acid anion. In such cases the nature of the solid phase which is formed, whether crystalline polymer or crystal-solvate, is determined by a delicate balance of proton-transfer equilibria between the polymer, solvent and coagulant. In most cases the coagulant, typically water, is a stronger base than the polymer. Deprotonation of the polymer results in formation of the crystalline polymer phase.

Poly(p-phenylene benzobisthiazole)-(PBT) is a rigid polymer developed by the U.S. Air Force Ordered Polymers Program. In this study we investigate the effect of the coagulation environment on the nature of the solid phase which is formed from a monodomain nematic solution of PBT in polyphosphoric acid (PPA). Since PBT is polymerized in PPA,[6] such solutions are often used for the spinning of fibers and films. The coagulants chosen for this experiment were water, which is commonly used in spinning processes, and commercial phosphoric acid (85% phosphoric acid 15% water). The coagulating solution is thus maintained within the P_2O_5/H_2O system, for which the chemical transitions and their kinetics are known.[7]

EXPERIMENTAL METHODS

A 13.7% (w/w) solution of PBT in PPA, its polymerization medium,[6] was obtained from J. Wolfe of SRI. The intrinsic viscosity of the polymer in methane sulfonic acid was 25 dl/g, from which a molecular weight of 41,000 can be estimated.[8] The solution was extruded through a tubular die and extended in air at a ratio of 20:1, at Foster Miller Inc. The oriented nematic solution was subsequently coagulated either in water or in a mixture of 85% phosphoric acid with water.

X-ray diffraction patterns were recorded on flat film in a Statton camera. A Siemens D-500 diffractometer was used to scan the equatorial reflections. Ni filtered CuK_α radiation was used. The diffraction pattern from the water-coagulated sample was obtained after drying. Due to their sensitivity to moisture, the acid-coagulated sample, as well as the oriented solution, were sealed between polyimide films.

Thermal analysis was performed using a Perkin Elmer DSC-2 apparatus. Samples were sealed in gold pans designed for volatile materials.

RESULTS

The phase transitions during coagulation of the oriented solution of PBT in PPA under the different coagulation conditions can be followed visually by the color changes of the coagulating solutions. The initially green solution develops an orange yellow color instantaneously when coagulated in water. When the solution is immersed in phosphoric acid, a bright red color can be observed after about one hour. In both cases a solid phase is formed.

The transition to the crystalline phases is demonstrated by the diffraction patterns shown in Figure 1. Figure 1a is the diffraction pattern from the PBT/PPA solution prior to coagulation. In addition to the diffuse rings due to the unoriented PPA, it exhibits a broad equatorial reflection at a spacing of about 15.5 Å, and diffuse layer lines at the characteristic spacings due to the PBT repeat unit (12.4 Å).[9,10] This pattern is typical of the oriented nematic state, and thus characterizes the initial state of the solution as such.

The diffraction pattern obtained from the water-coagulated solution after drying is shown in Figure 1b. It is similar to the PBT fiber diffraction pattern characteristic of the crystalline PBT phase,[9,10] although the breadth of the equatorial reflections indicates formation of small and imperfect crystallites. It should be noted that heat-treatment enhances both the orientation and the perfection of the lateral packing between PBT chains, but not their axial registry.[11]

The diffraction pattern from the film coagulated in phosphoric acid (the "red" phase) shown in Figure 1c represents a new structure which has not been previously observed. Its significant features are several sharp equatorial reflections at spacings which are not common to solid PBT, off-meridional reflections indicating a degree of three-dimensional order which is absent in PBT, and a layer line at a meridional spacing of 4.6 Å which is incommensurate with the layer line spacings of the normal PBT fiber diffraction pattern.

The difference between the diffraction patterns obtained from the samples which were coagulated in water and in phosphoric acid is evident in the equatorial scans shown in Figure 2. The two maxima at scattering angles of 15° (5.9 Å) and 25° (3.5 Å), which appear in the diffraction pattern from the water coagulated sample shown in Figure 2a, are the (100)

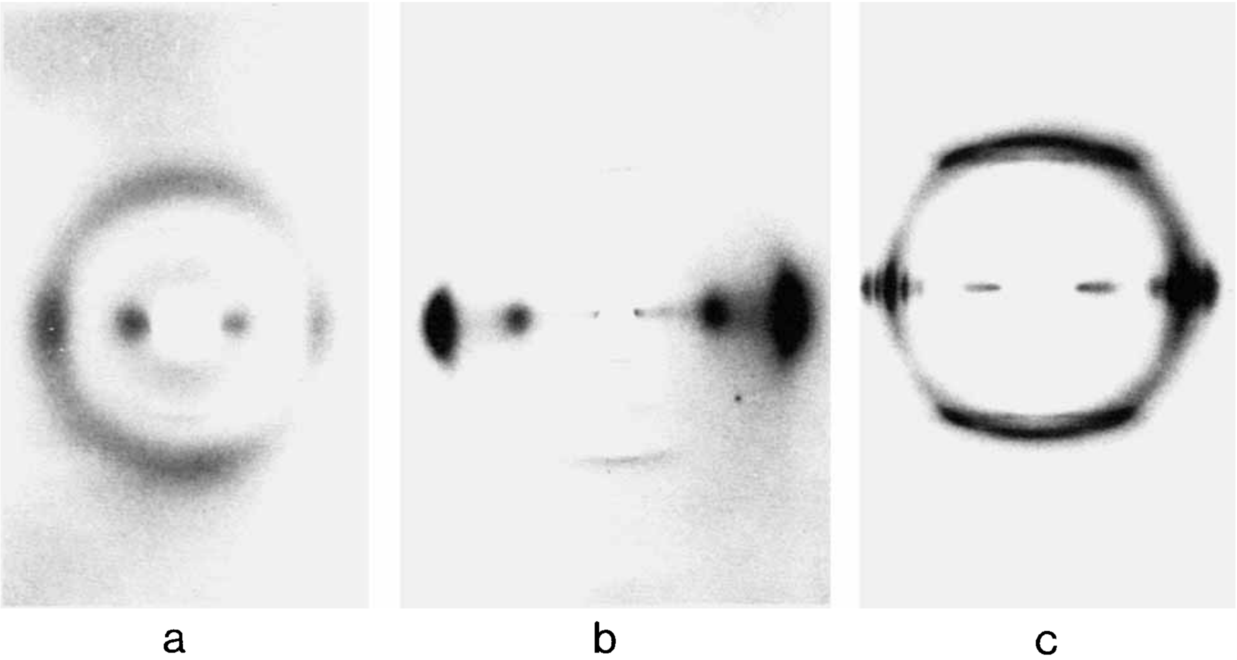

FIGURE 1. X-ray diffraction patterns from the oriented solution of PBT in PPA (a); and from the solution after coagulation in water (b), and 85% phosphoric acid (c).

and (010) reflections of the crystalline PBT phase.[9,10] Again, the breadth of these maxima indicates that the crystallites are small and imperfect. The diffractometer scan of the equatorial reflections of the sample coagulated in phosphoric acid, shown in Figure 2b, differs distinctly from that of the crystalline PBT phase shown in Figure 2a. It exhibits several sharp reflections which are not in agreement with the crystalline PBT Lattice. In particular the reflections at spacings of

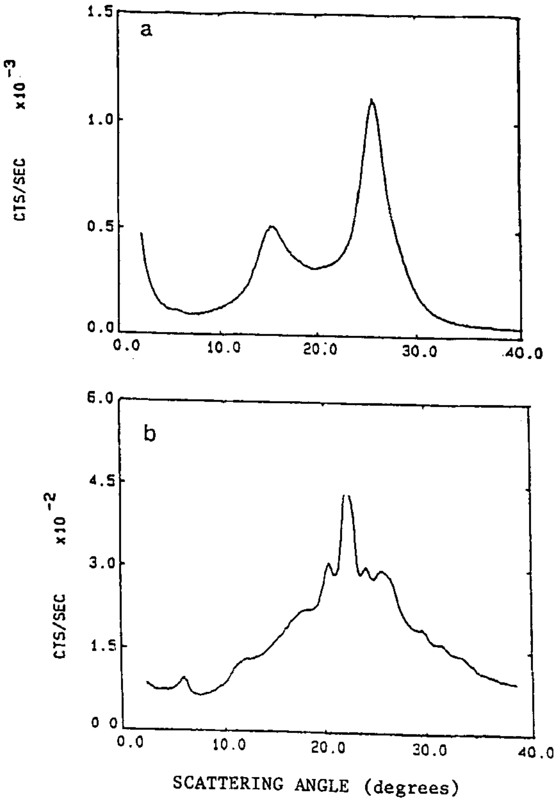

FIGURE 2. Diffractometer scans of the equatorial reflections of the crystalline phases obtained by coagulation in: (a) water, and (b) 85% phosphoric acid.

15.9 Å and 7.9 Å indicate a larger unit cell for this phase. It should be noted that the large amorphous halo in Figure 2b is due to the presence of the coagulant in the sample. Neither the quantity of phosphoric acid present, nor the nature of its dispersement within the sample are known at this point.

The thermal analyses of the systems under study are shown in Figure 3. The DSC trace of the PBT/PPA solution coagulated in phosphoric acid is given as trace (a) in Figure 3. It exhibits a slight endotherm at about 200°C and a very sharp transition at about 250°C. This transition, although reproducible in several samples, is not reversible as it appears only in the first heating. Water-coagulated PBT does not exhibit thermal transitions up to its decompostion temperature which is higher than 600°C.[11] For comparison, trace (b) in

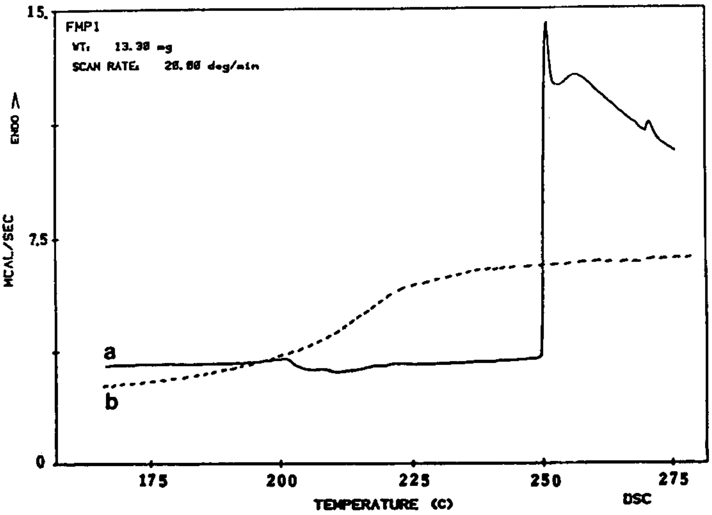

FIGURE 3. Differential scanning calorimetry of: (a) the PBT/PPA solution coagulated in 85% phosphoric acid, (b) a mixture of PPA, phosphoric acid and water.

Figure 3 is due to a mixture of 50% PPA, 42.5% H_3PO_4 and 7.5% water, which is taken to represent the components of the system in the absence of PBT. (The trace is plotted on the same ordinate scale by assuming the mixture to represent 75% of the weight of the coagulated PBT solution). Clearly the relative amounts given above are arbitrary, as the composition of the coagulated film is not known. Nevertheless it demonstrates that the sharp transition at 250°C is due to the presence of PBT in system. It also demonstrates the gradual hydrolysis of PPA which occurs even at low temperatures, but is accelerated above 200°C.[7]

DISCUSSION

Two different crystalline phases have been formed by coagulation of the monodomain nematic PBT/PPA solution under different conditions. Coagulation with water results in formation of the well-known crystalline PBT phase,[9,10] as is the usual case in the spinning of PBT fibers and films. The solid phase which yields the diffraction patterns shown in Figures 1c and 2b is interpreted as a crystal-solvate phase which is formed by co-crystallization of PBT and PPA. Details of the crystal structure of this phase, in particular its stoichiometry and the conformation of the PPA anion, are still under study. Tentatively, the reflections index on an orthorhombic unit cell of dimensions[12] : a = 15.9 Å b = 20.6 Å c = 36.9 Å.

The layer line at 4.6 Å meridional spacing, on which the intense off-meridional peaks are found, can be postulated to arise from the periodicity of extended chain PPA oligomers. This is in accord with the repeat lengths of extended chain PPA anions in certain polyphosphate salts. An extended 2/1 helical conformation having two phosphate groups in a repeat unit, the length of which varies from 4.2 Å (Rb^+) to 5.2 (Li^+), has been reported.[13]

It is therefore postulated that the PBT chains and the polyphosphate oligomers co-crystallize parallel to each other in an overall uniaxial orientation. Crystallizable polyelectrolyte complexes of the polyphosphate anion with flexible polybases have been reported.[14,15] This is believed to be the first report of such a complex with a rod-like polymer, obtained from the monodomain nematic state.

The formation of a crystal-solvate phase is supported by the thermal analysis shown in Figure 3. The sharp endotherm at 250°C is attributed to the melting of the crystal solvate. The PPA oligomers which have been "locked" in the co-crystal with PBT are then released into the acid environment at the elevated temperature. This results in rapid hydrolysis, that would have otherwise occurred more gradually at lower temperatures. Once PPA is hydrolyzed, the phosphoric acid which is formed is not acidic enough to dissolve PBT, and hence the transition is not reversible.

The sequence of events leading to formation of the crystal-solvate is envisaged as follows: since the 15% water in the coagulant is protonated, coagulation is induced by the phosphate anion. As it diffuses into the PBT/PPA solution it deprotonates the PPA oligomers, the strongest acid in the system, which then complex and co-crystallize with the protonated PBT cations. It is possible that the deprotonation and complexation/crystallization are cooperative, in the sense that the PPA oligomers, which are already associated with PBT due to previous proton-exchange, will be deprotonated in preference of other molecules. Such cooperativity has been reported in the complexation of the PPA anion with basic oligomers.[16]

CONCLUSION

The nature of the crystalline phase formed by coagulation of a PBT/PPA solution can be controlled by the coagulation environment. A strongly deprotonating coagulant such as water results in formation of the crystalline PBT phase. Controlled deprotonation of PPA, which is achieved by coagulation with 85% phosphoric acid, results in formation of a crystal-solvate phase. Protonated PBT chains and the polyphosphate anions co-crystallize parallel to each other.

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