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The phase diagram of the system PBZT/ polyphosphoric acid/water

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The phase diagram of the system PBZT/polyphosphoric acid/water has been investigated using differential scanning calorimetry, optical microscopy and ^{31}P nuclear magnetic resonance spectroscopy. A peritectic line at higher temperatures and a eutectic line at lower temperatures have been found independent from the polycondensation degree of the polyphosphoric acid (PPA). The phase transitions between the different regions in the phase diagram are strongly dependent on the condensation degree of the solvent. All phase transitions are completely reversible. The formation of crystal solvate phases is connected with the water content of the system and therefore with the polycondensation reaction of the PPA. The solvent molecules are strongly associated with the macromolecules. The nematic phase is formed by interaction of six solvent molecules per monomeric unit of the polymer and proton transfer from the solvent towards the polymer in the nematic phase.

1. Introduction

In the past interest in high-performance material has focused on improvement of mechanical properties, especially compressional strength. The transition from the dissolved state to the solid state is therefore of major interest in order to understand the final mechanical properties of the material obtained. During coagulation, a transition from a liquid to a solid phase occurs either by diffusion of a non-solvent or by decrease of temperature. The structure initially formed by this coagulation process is therefore the basis for the final fibre structure. A better understanding of equilibrium phases and their structures and of the possible transitions between them should permit better control of the final resulting fibre structure. The results presented here focus on the interest on the understanding of the phase behaviour of liquid crystalline solutions of PBZT and PBO in PPA (Fig. 1).

Previous investigations have shown that solutions show a more or less complex behaviour including the formation of different kinds of crystal solvates depending upon water content and temperature [1–6]. Orientation and relaxation of the dissolved macromolecules and the solvent molecules have been observed during shear experiments. There are some hints that there are two different kinds of solvent molecules present in the solution, molecules which are somehow adsorbed or bonded to the dissolved macromolecules and free solvent molecules in between them [7].

2. Experimental Procedure

The different mixtures investigated were prepared by dilution of a mother solution of 9% PBZT in orthophosphoric acid (OPA) by deuterated polyphosphoric acid (PPA) with a composition of 82% P_2O_5 in the system P_2O_5/D_2O. The deuterated PPA was obtained by dissolving anhydrous P_2O_5 in a solution of 85% D_3PO_4 in D_2O under dry conditions with stirring. Liquid crystalline behaviour was determined visually using a Linkam THM 600 hot stage mounted on a Zeiss Ultraphot optical microscope. A Sony videorecorder was used to record crystal solvate formation and phase transitions from the nematic to the isotropic phase or to the mixed phase. Thermal analysis was carried out using a Perkin Elmer DSC 7 with heating and cooling rates of 20 K min^{-1} to a temperature limit of 200 °C. Samples were prepared in stainless steel high-pressure pans from Perkin Elmer. The ^{31}P nuclear magnetic resonance (NMR) spectra were obtained using a Jeol Alpha 500 or a Jeol FX 90 Q.

3. Results and discussion

Optical microscopical studies with polarized light were used to examine the phase diagram of the System PBZT/PPA/H_2O. At room temperature between crossed polarizers, a 9% solution shows a fine grainy texture which is more or less unspecific with respect to a typical texture known for types of mesophases. By heating to 100 °C and annealing at this temperature for 48 h, the development of a large-scale *threaded* texture could be observed (see Fig. 2). This is the texture typical of nematic liquid crystals and is comparable with textures displayed by low molecular weight compounds [8].

With further heating, the formation of crystal solvates could be observed starting at 133 °C in solutions in OPA and at 270 °C in solutions in PPA. The

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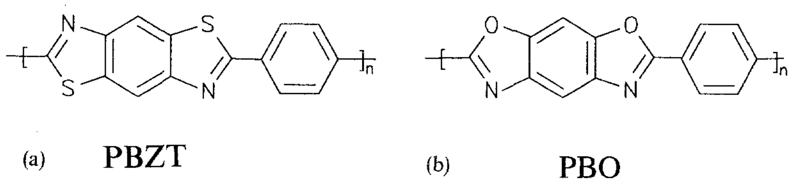

Figure 1 Chemical formulae of (a) PBZT and (b) PBO.

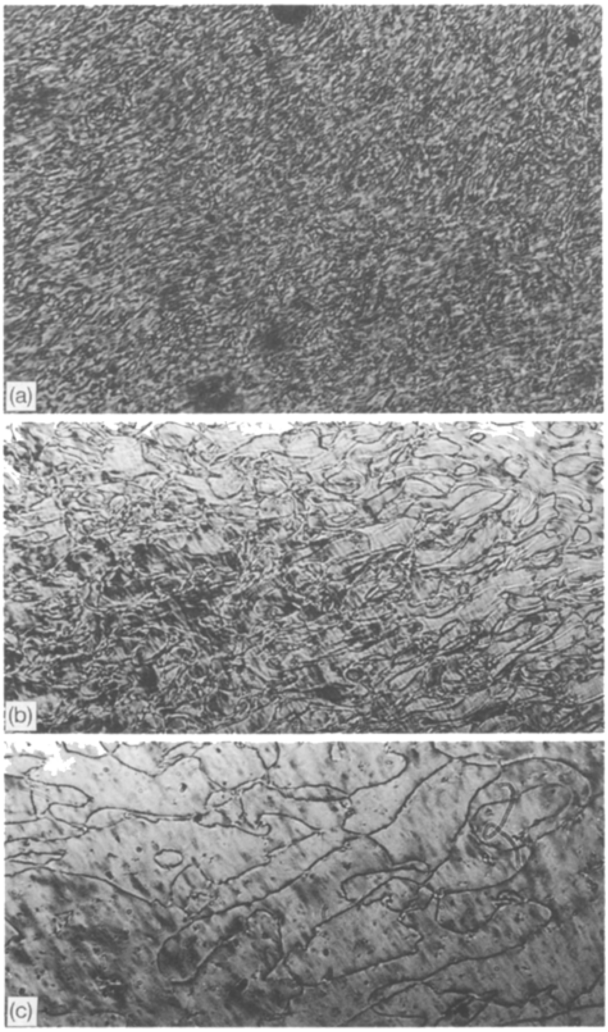

Figure 2 Development of a large-scale threaded texture out of (a) a grainy texture of a solution of PBZT (8%) in PPA after annealing at 100 °C for (b) 24 h and (c) 48 h, × 160

formation of the crystal solvates is associated with a change in colour of the solution from dark green to bright green and further to orange and dark red; also crystallization of a different structure could be detected under the polarizing microscope.

Fig. 3a and b show the development of a crystal solvate out of a large-scale texture nematic solution at 140 °C. Finally, an orange to dark red crystal solvate is formed, which exhibits much smaller crystal sizes and which irreversibly disturbs the large-scale monodomain structure at 150–180 °C (see Fig. 4). Those crystal solvates no longer show the properties of a solution: no flow under shear conditions can be observed. The crystal solvate behaves like a network of macroscopic crystals. Together with the crystal solvate, the presence of some isotropic liquid is observable.

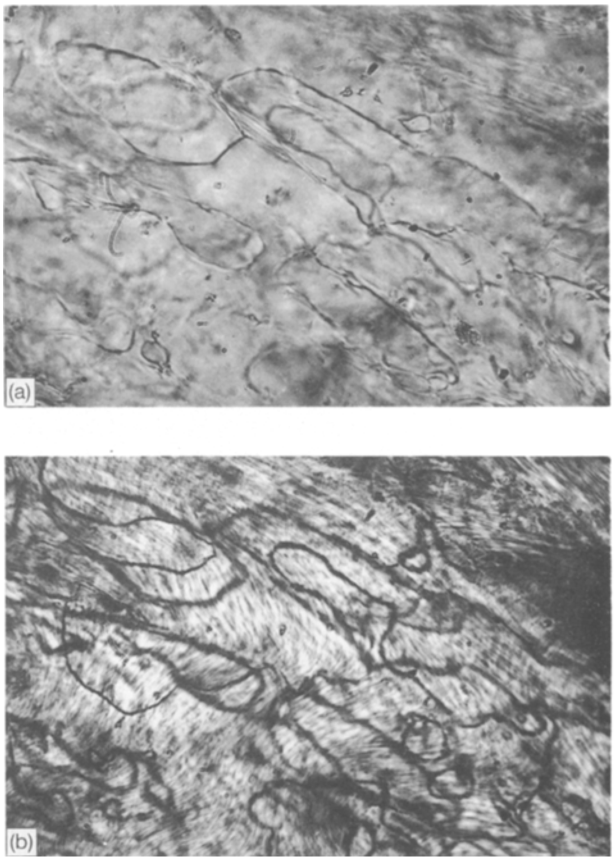

Figure 3 Development of a crystal solvate (b) out of a large-scale threaded texture (a) at 140 °C; × 320.

Figure 4 Growth of the red crystal solvate out of a nematic homogeneous solution of PBZT (8%) in PPA at 160 °C; × 320.

With a change in temperature, there is a change in the degree of polymerization with splitting off of water into the gas phase. Water is acting in the polymer solution as a non-solvent. At elevated temperatures above 100 °C, the amount of water which is split off could be large enough to attract the nematic solution and therefore to force the formation of crystal solvates or a precipitation of the polymer.

The formation of the crystal solvates is reversible. By cooling to 25 °C for solutions in OPA and to 60 °C for solutions in PPA, a biphasic solution of crystals (bright green) and the nematic solution is present. The crystals remelt in the 9% solution at approximately 60 °C. The texture again exhibits very small monodomains and is grainy. The reformation of the nematic phase is associated with a change in colour back to dark green.

For the more diluted solutions (3%–5%) phase transitions in the heating mode from a homogeneous nematic into a biphasic nematic/isotropic and finally into a homogeneous isotropic solution have been detected (see Fig. 5).

Cooling to − 30 °C forces the rapid formation of crystals (see Fig. 6a). Additionally, an increase of birefringence of the isotropic parts of the biphasic region of the 4.62% solution with the growth of the crystals could be observed. The crystals are well defined and more similar to crystals of a low molecular weight compound, than to the crystals of a polymer.

Those crystals are again stable upon subsequent heating to a temperature of ~ 30 °C, beyond which they melt into the nematic solution (see Fig. 6b). We assume that the crystals are formed by crystallization of OPA, which has a reported melting point of 42.3 °C, but in a mixture with other polyphosphoric acids a melting point of 34.6 °C. A similar behaviour is observed for solutions in PPA. Here the formation of crystals starts at 60 °C. The phase transition is reversible and we believe is due to the formation of DPA crystals, which melt at 61 °C, (64 °C for deuterated DPA).

Similar behaviour could be observed by DSC (see Fig. 7). The graph obtained from the PBZT solution shows two phase transitions and a recrystallization at the heating curve. The first phase transition at 31 °C would correspond to a melting temperature of the crystals as observed optically into a nematic solution, and the second-phase transition to the formation of the crystal solvate at high temperatures. A recrystallization of the crystal solvate takes place afterwards. On cooling, the transition from the red crystal solvate to the nematic solution is supercoolable by 45 K. Similar results have been obtained by Cohen *et al.* [6].

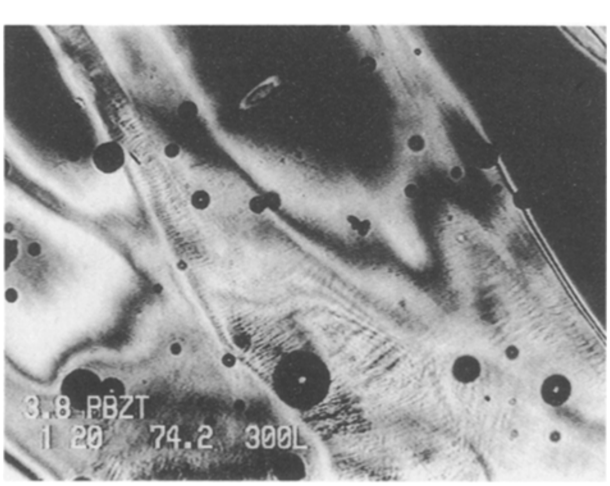

Figure 5 Transition of the nematic to the isotropic phase (biphasic region) of a 3.8% solution of PBZT in OPA at 74.2 °C.

Figure 6 (a) Formation (19.1 °C) and (b) melting (25.1 °C) of the crystalline phase at low temperatures in a 4.62% solution of PBZT in OPA.

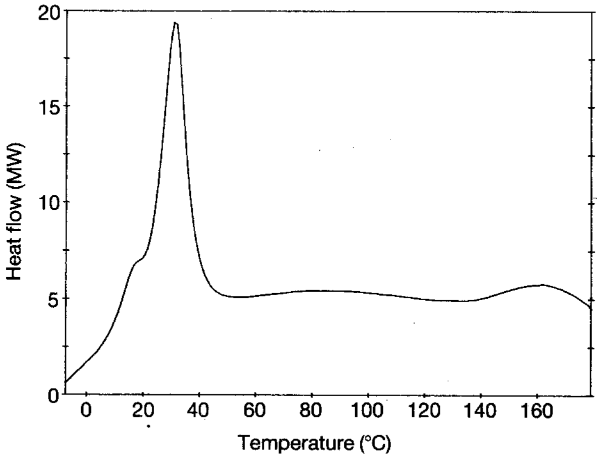

Figure 7 DSC heating trace of an 8.5% solution of PBZT in OPA.

The DSC traces of the pure solvent, polyphosphoric acid have shown a broad endothermic peak at 250 °C which is obviously due to structural and chemical changes of the solvent. This was sufficient reason to look closer at the nature of the solvent. In the literature of the nematic solutions of rigid-rod polymers, polyphosphoric acid (PPA) is only described as a mixture of P_2O_5 and H_2O with a P_2O_5 content of about 82%–84%. A characterization with respect to the molecular weight or polymerization degree and the molecular weight distribution of the phosphoric acids is only described in general terms in GMELIN [9, 10]. This is possible by chromatography, by infrared spectroscopy or by ^{31}P NMR spectroscopy of the aqueous solutions of neutral salts of the polyphosphoric acid. Difficulties arise due to the fact that, on neutralization of the free acids, the degree of condensation can change. The concentration of 84% would correspond to a polymerization degree of 4 (tetraphosphoric acid). In the present method of synthesis a formation of cyclic polyphosphoric acids (metaphosphoric acids) can be excluded. However, the PPA is not one single compound but rather a mixture of polyphosphoric acids with polymerization degrees ranging from 1 to more than 9 (see Fig. 8). "Free" water, connected with orthophosphoric acid is also present.

The composition of the crystal solvate (orange to dark red phase) could be calculated by separation of the isotropic liquid phase from the solid crystal solvate and comparing the weight of the dry crystal solvate thus obtained with the calculated amount of PBZT in the solution used. The crystal solvate was found to consist of approximately four phosphoric acid units per monomeric unit of PBZT and hence will be described as crystal solvate 4 (CS 4).

One of the best methods for the investigation of the structure of the different liquid and solid phases in the system PBZT/PPA/H_2O should be ^{31}P NMR spectroscopy, where the investigation should be possible in solution without changing the character or the chemical structure and the condensation degree of the solvent. Surprisingly sharp lines have been obtained from pure isotropic and nematic solutions, even from solutions with a comparatively high viscosity (see Fig. 9). All spectra show, beside the line at ~ 0 p.p.m. (OPA), one line at approximately -14 p.p.m. (DPA, end groups of PPA). In no spectra were lines at 29 p.p.m. (middle groups of PPA) or at 44 p.p.m. (cross-linked PO_4-groups) observed [11]. This means that the solvent is only a mixture with a rather high content of OPA and a low content of DPA; polymeric phosphoric acid and cross-linked phosphoric acid are not present. Unfortunately most of the spectra show no significant splitting of the lines due to different degrees of protonation of the different phosphorus nuclei. Only one sample, a solution with a concentration of 6.4% and a condensation degree of the polyphosphoric acid of about 2 showed a splitting of the OPA line due to different species of the acid present in the solution; (Fig. 9b). Therefore, we believe that the interacting molecules are mostly OPA molecules, and from the shift towards lower field, it is quite clear that the interaction, at least in the nematic solution, involves a proton transfer from the OPA to the polymer. The number of OPA molecules which are involved in the formation of the nematic phase could be estimated from the NMR spectra and is about six. An investigation of the differences between the interaction of the solvent with the polymer in the nematic solution and the two crystal solvate phases was not possible.

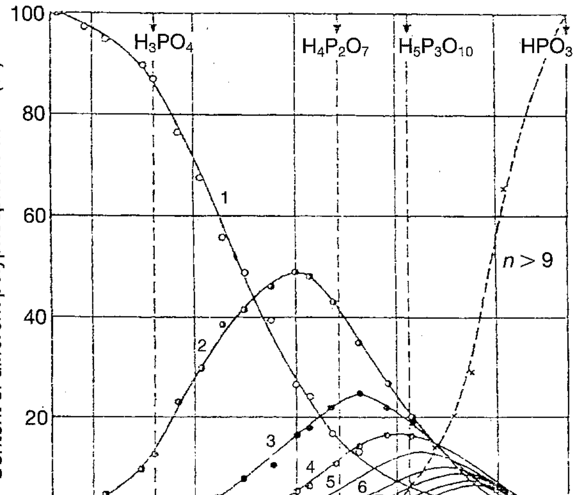

Figure 8 Distribution of the molecular weight of polyphosphoric acids in the system P_2O_5/H_2O in a concentration range between 68% and 89% P_2O_5.

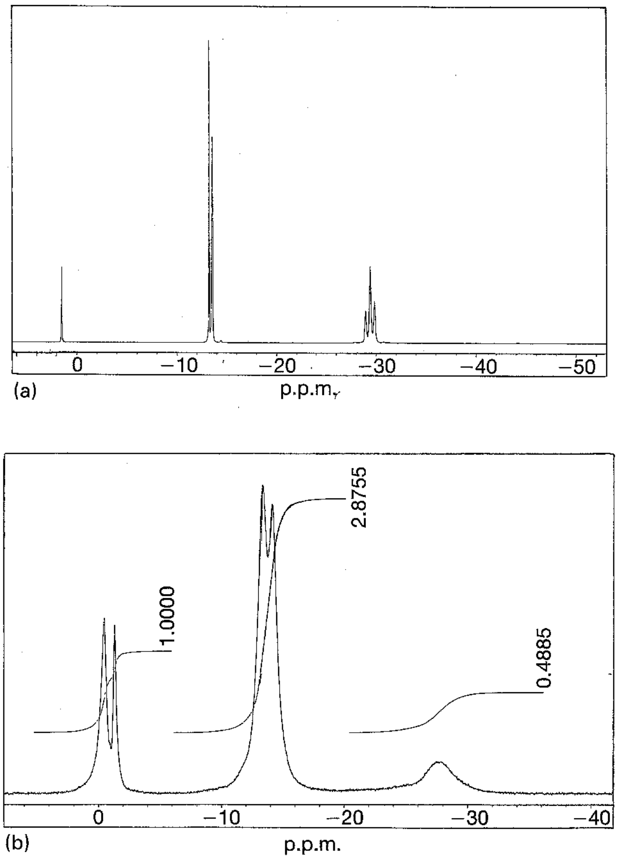

Figure 9 ^{31}P NMR spectra of (a) deuterated PPA, 500 MHz; and (b) 6.4% solution of PBZT in deuterated DPA, 500 MHz.

Spectra at room temperature from solutions with higher concentrations of PBZT (9%) show a line-broadening effect and a solid-state like spectrum of the DPA part. This is due to the solidification process during the formation of the crystalline DPA. It is clear that at concentrations > 8% at temperatures in the range 25–30 °C there are solid particles present in the solutions, even when there is no visible sign of them, because they are too small (see Fig. 10a and b). After application of vacuum to the different solutions at 150 °C, a significant increase of the condensation degree of the polyphosphoric acid could be detected.

^{31}P NMR spectra were also recorded at high temperatures. Fig. 11 shows the spectrum of an 8% solution of PBZT in OPA at 40 °C in the nematic phase and a spectrum of the same sample at 200 °C in the mixed phase crystal solvate 4/isotropic solution. The spectrum at the higher temperature shows not only broader lines than the spectrum of the nematic solution, but also changed intensities of the lines. The calculated content of diphosphoric acid has increased from 5% in the nematic solution to 9.6% in the mixed phase. This increase is due to the condensation of the OPA at elevated temperature. Diphosphoric acid forms, water splits off at the condensation temperature which induces the formation of the mixed phase and the precipitation of the crystal solvate 4. These results are contrary to the assumptions by Cohen and Thomas [2]; it is quite clear that at elevated temperatures there is no indication for hydrolysis of PPA.

Finally, it is possible to construct phase diagrams for different condensation degrees of the polyphosphoric acid (see Figs 12 and 13). The different regions are marked in the phase diagrams. This type of phase diagram is well known for systems of stiff polymers in solution and has been theoretically predicted by Flory [12].

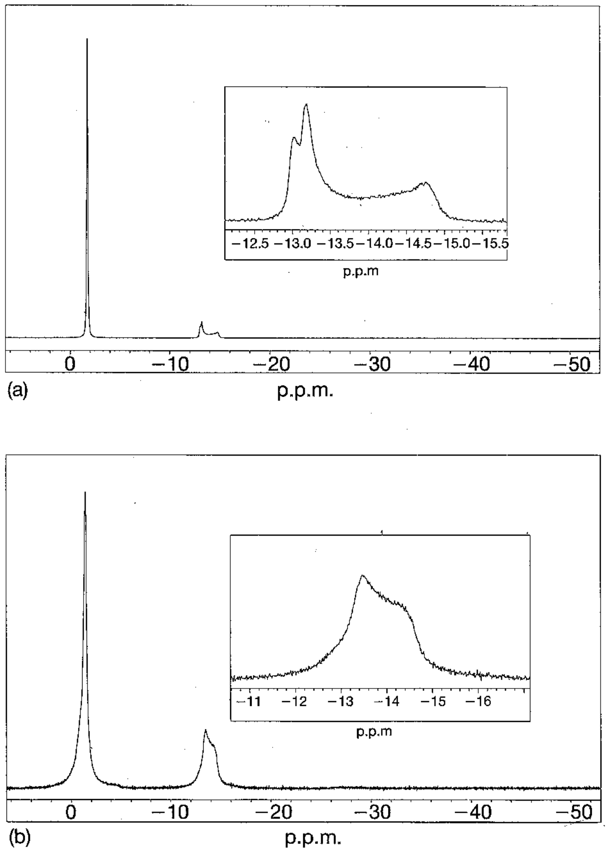

Figure 10 ^{31}P NMR spectra of (a) 8.5% and (b) 9% solutions of PBZT in deuterated OPA, 500 MHz.

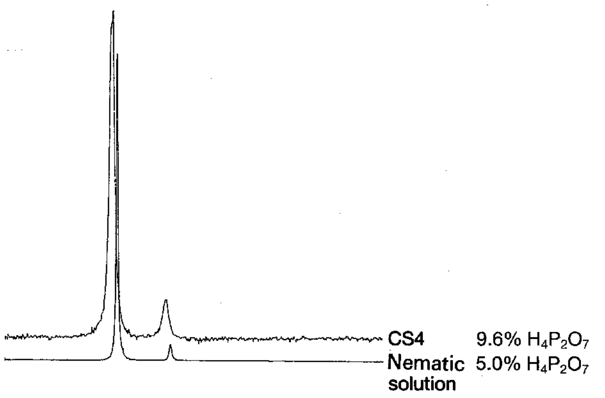

Figure 11 ^{31}P NMR spectra of 8% PBZT in deuterated OPA; spectra obtained from the nematic solution at 40 ° C, and from the crystal solvate 4 at 200 °C, 90 MHz.

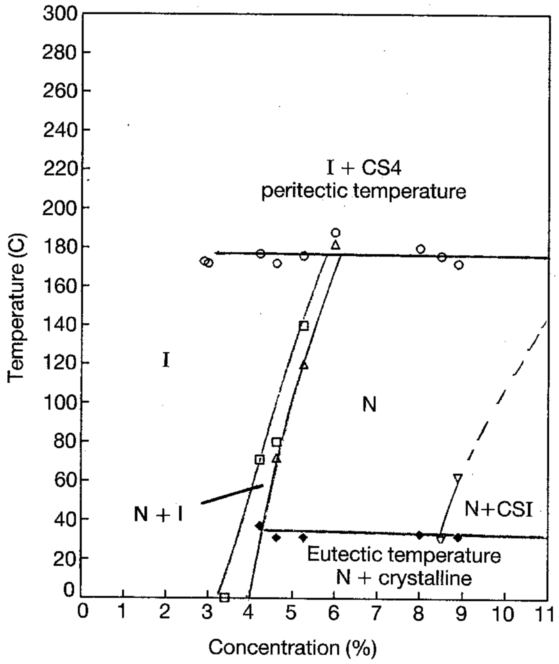

Figure 12 Phase diagram of the system PBZT/OPA.

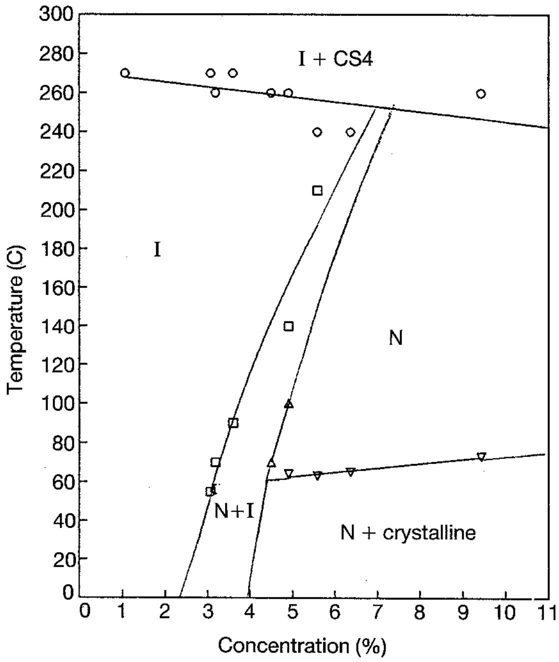

Figure 13 Phase diagram of the system PBZT/DPA.

A quite general change was detected by changing the polycondensation degree of the PPA from OPA with ~ 5% DPA to a PPA with a condensation degree of 2. At first a large shift of the phase transition line [nematic]–biphasic region [isotropic/crystal solvate 4] towards higher temperatures (270 °C) takes place. This is in good agreement with the results obtained for PPA (83% P_2O_5 in the system P_2O_5/H_2O) [6]. The temperature shift is basically due to the higher condensation degree of the PPA, and therefore due to higher temperatures required to split off a sufficient amount of water for the formation of the crystal solvate 4. This is in agreement with the results obtained by thermal condensation of OPA [13–15]. Secondly the width of the chimney became much broader than in the system PBZT–OPA. This is visible by a shift of the transition line between the biphasic region [nematic]/[isotropic] towards the homogeneous nematic region. Also a significant shift of the eutectic line/formation of crystalline phases at lower temperatures took place. This is basically due to the change in the composition of the PPA and the resulting amounts of the different species of polyphosphoric acids and changing their melting temperatures. The melting temperature of DPA is 61 °C, whereas the melting temperature of OPA in a mixture of different species of PPA is only 34.6 °C. These melting temperatures of the major components have a strong influence on the solidification temperature of the crystalline phase at lower temperatures as is usual in eutectic systems.

4. Conclusions

The system PBZT/PPA/H_2O shows a quite complex phase behaviour. The phase transitions between the different regions in the phase diagram are strongly dependent on the condensation degree of the solvent. At high temperatures, a precipitation of a crystal solvate phase is forced due to an increase in the condensation degree of the solvent and the elimination of water as a non-solvent. The nematic phase is formed by interaction of six solvent molecules per monomeric unit of the polymer and proton transfer from the solvent towards the polymer.

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