Topology of the Ternary Phase System Poly(*p*-phenyleneterephthalamide)–Sulfuric Acid–Water

H. Rommel*

Max-Planck-Gesellschaft, AG Flüssigkristalline Systeme, Mühlpforte 1, 06108 Halle/S., FRG

G. Förster

Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, 06108 Halle/S., FRG

Received December 30, 1993; Revised Manuscript Received April 26, 1994[⊗]

ABSTRACT: In this article a ternary phase diagram for the system poly(*p*-phenyleneterephthalamide) (PPTA)–sulfuric acid–water is described. The concentration range between 3–23% polymer and 92–100% sulfuric acid were investigated. The phase system shows immiscibility of its components in the solid state, i.e. it exhibits compounds between the components and eutectic behavior. Experiments were carried out to detect the clearing temperatures of ternary PPTA–sulfuric acid–water solutions; the eutectic transition between solution, crystal solvate, and solid sulfuric acid; the transition temperatures from the solid phase into the liquid crystalline state; and the composition of the crystal solvate. Polarization microscopy, wide-angle X-ray scattering, and calorimetry were used to detect parts of the binary and ternary phase diagrams. Experiments were done to discover the influence of acid concentration on the degradation of the polymer in solution.

1. Introduction

Stiff-chain polymers are well known for forming liquid crystalline phases in good solvents.[1–4] Common substances for investigation of such lyotropic systems are aromatic polyamides. This article deals with poly(*p*-phenyleneterephthalamide) (PPTA) and its phase behavior with absolute sulfuric acid as its only known good solvent, and water as the coagulant. PPTA is spun into high-modulus fibers from a nematic solution,[4,5] and there is not only scientific interest in PPTA solutions but also technological. During the spinning process the nematic solution is coagulated into water or diluted sulfuric acid, but the mechanism of the coagulation process is not well understood. The ternary phase diagram PPTA–sulfuric acid–water is investigated in the present paper. It may clarify the equilibrium conditions for the coagulation process and give a new basis for fiber processing.

The binary phase diagram PPTA–sulfuric acid is partially known. Kulichichin et al.[6] described transitions in the anisotropic solutions, and Papkov et al.[7] proposed a partial binary phase diagram. It is based on immiscibility of polymer and acid. The difference between the melting temperatures of PPTA (500–600 °C)[2,4,8] and sulfuric acid (10 °C)[9] is unusually high. Therefore the eutectic point between polymer and sulfuric acid is shifted to low polymer concentrations and transitions like the melting of compounds between acid and polymer are hidden under the clearing curve. In the anisotropic region below the clearing curve the binary system shows two phases, which are separated by two-phase regions: the crystal solvate and the liquid crystalline phase. The former is a stoichiometric compound which was characterized by Arpin et al.[10] and Iovleva and Papkov[11] by means of X-ray diffraction. A homogenous liquid crystalline phase appears at a certain temperature above a monotectic three-phase reaction.[12,13] According to the occurrence of a nematic texture[10] this phase was classified as a lyotropic nematic phase. The nematic phase was also investigated by Gardener et al.,[14] who used a model system consisting of low molecular weight PPTA and sulfuric acid for their microscopic and calorimetric experiments.

PPTA shows degradation in sulfuric acid solution at higher temperature.[15,16] It is not useful to investigate the phase diagram at temperatures above 180 °C because of fast degradation. Picken[17] found the clearing temperatures to be dependent on the molecular weights of the used polymer. Furthermore transition temperatures depend on the acid concentration. It is difficult to prepare and to store absolute sulfuric acid. Most of the articles dealing with the system PPTA–sulfuric acid therefore describe experiments carried out not in the binary system but in the ternary system PPTA–sulfuric acid–water.[13] Experiments concerning the clearing temperature of the ternary system were carried out by Nakajima et al.[18] in the concentration range below 3% PPTA and 85–94% sulfuric acid.

2. Experimental Section

A commercial PPTA sample with an average molecular weight M_w = 31 000 g mol^{-1} was used. The molecular weight was determined by size-exclusion chromatography (SEC). Sulfuric acid (96%) was used as carrier solvent. The apparatus was calibrated with a standard polymer (M_w = 29 000 gmol^{-1}).

Solutions with different polymer content in 99.8% sulfuric acid were prepared in a 6-L Drais kneading machine. For the solution process frozen acid was used to avoid degradation. It was easy to prepare solutions with polymer contents up to 23% without heating. Concentrations given in this paper are in weight percent (wt %). To vary the acid concentration of a given solution water was added stepwise during kneading in an IKA laboratory kneader at room temperature. With this method it was possible to prepare samples down to acid concentrations of ca. 85% without coagulation of the polymer. The solutions were stored in vessels under P_2O_5-dried air. In absolute sulfuric acid the solutions with polymer contents below 8% PPTA were isotropic at room temperature, with decreasing acid concentration and at higher polymer concentration they became all anisotropic.

Microscopic samples were prepared in a glove bag under dry nitrogen atmosphere and sealed with a paraffin oil layer between the slides to protect the solutions from wet atmosphere. The samples were equilibrated over solid CO_2 for several hours. A Lomo Min 8 polarization microscope with a Linkam THMS 600 hot stage was used for texture observation. Transitions were investigated by stepwise heating with different annealing times between two steps. For the detection of the clearing curves heating rates between 3 °C/min and 15 °C/min were used.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

0024-9297/94/2227-4570$04.50/0

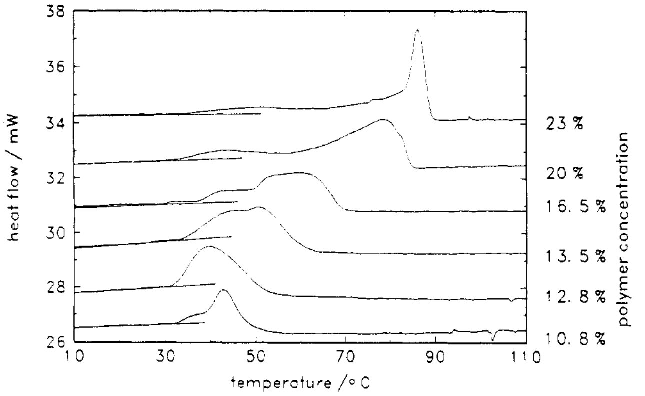


Figure 1. DSC heating scans with 3 °C/min. Baselines were calculated using a linear regression program. The beginning of the transitions signals the monotectic transition at 33 °C. The monotectic temperature should be constant for all polymer concentrations. Deviations from ideality may be caused by small differences between acid concentrations of the solutions. Measured monotectic temperatures lie between 31 and 35 °C.

Gold-coated cups were used for the calorimetric measurements. The samples were prepared in the glove bag, too. The experiments were carried out with a Perkin-Elmer DSC7 using a heating rate of 3 °C/min. Some of the samples with polymer contents lower than 12% were equilibrated over solid CO_2 before being measured.

WAXS experiments were carried out with a Huber-Guinier goniometer at room temperature. Samples were sealed in capillaries (diameter 1.5 mm).

Degradation was measured by means of SEC. The average molecular weights of the coagulated polymer were determined after being heated in solutions with different acid concentrations. All solutions were annealed at 85 °C for 2 h and coagulated. The polymer was washed in distilled water and dried at 40 °C in vacuum. All preparations were carried out in a dry box.

3. Results

3.1. The Binary System PPTA–Sulfuric Acid. The concentration range between 3–23% PPTA in 99.8% sulfuric acid was investigated. The eutectic crystallization of sulfuric acid and the monotectic transitions into the fluid state were investigated by DSC. The results of calorimetric measurements are shown in Figure 1. The onset of the melting process lies at 33 °C. It was found to be constant for all samples which exhibit a nematic phase at higher temperatures, independent of the polymer concentration. Small deviations from that ideal case may be caused by variations of the effective acid concentration of the investigated solutions. With rising polymer concentration the transition interval gets broader according to a greater temperature interval in which crystal solvate and nematic solution are coexisting. Simultaneously the shapes of the melting curves change. They get more asymmetric and more peaked according to a higher amount of crystal solvate due to the lever rule. For a 23% PPTA solution it looks much more like a single peak than like a broad transition. The upper limit of the transitions was found to be constant for solutions with polymer concentrations above 22%.

The melting behavior of a 14% PPTA solution in 99.8% acid was investigated by polarization microscopy. It is shown in plates 1 and 2 (Chart 1). The solution is composed of isotropic solution areas which are black under crossed polarizers, and crystal solvate areas showing characteristic textures at room temperature. At temperatures slightly above the monotectic point of 33 °C the isotropic solution becomes anisotropic if the sample is annealed long enough (several days or weeks). The temperature was increased to 40 °C after 20 h of annealing at 32 °C to accelerate this process. It is supposed that sulfuric acid diffuses from the isotropic solution into the crystal solvate. Some of the crystal solvate becomes nematic during this dissolving process. The isotropic black areas become anisotropic due to the decreasing acid concentration. The viscosity of the sample is very high, and differences between the textures of crystal solvate and nematic solution are hard to detect. At the upper end of the transition the whole sample was nematic and flowed under pressure. In plate 2 the areas of nematic textures are very small after 22 h of annealing, they are more pronounced in solutions with higher polymer concentration and after longer annealing times due to a lower viscosity of such solutions.[19]

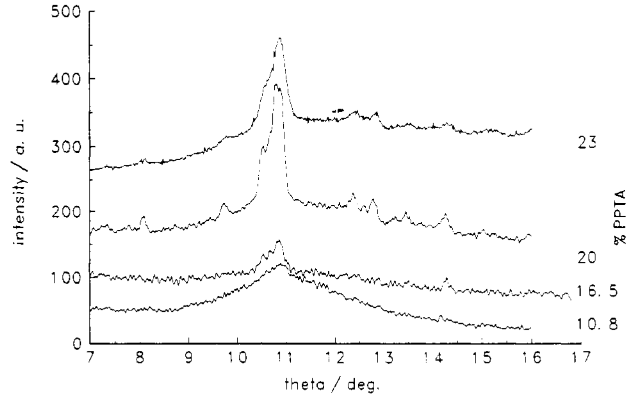


Figure 2. WAXS on PPTA–sulfuric acid solutions. Crystal reflections get weaker with decreasing polymer concentration.

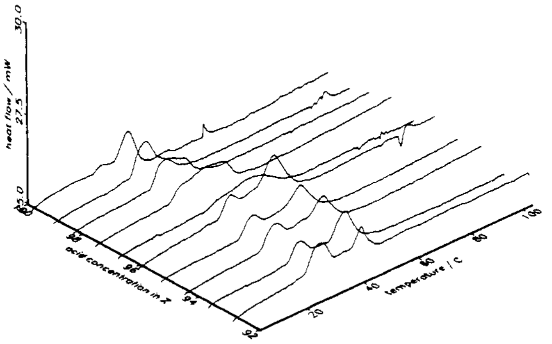


Figure 3. DSC on 11% PPTA solutions with different acid concentrations. See text for explanation. The small peaks in some of the curves at ca. 100 °C are an artifact caused by water or diluted sulfuric acid on the outside of the sample cups.

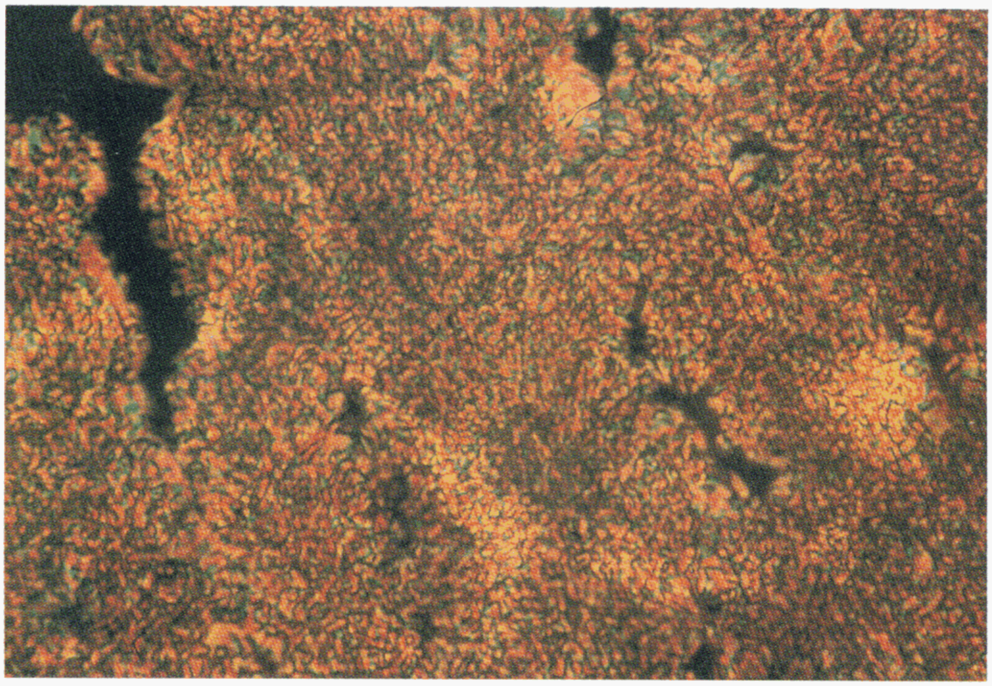
The clearing temperatures were also measured by polarization microscopy.

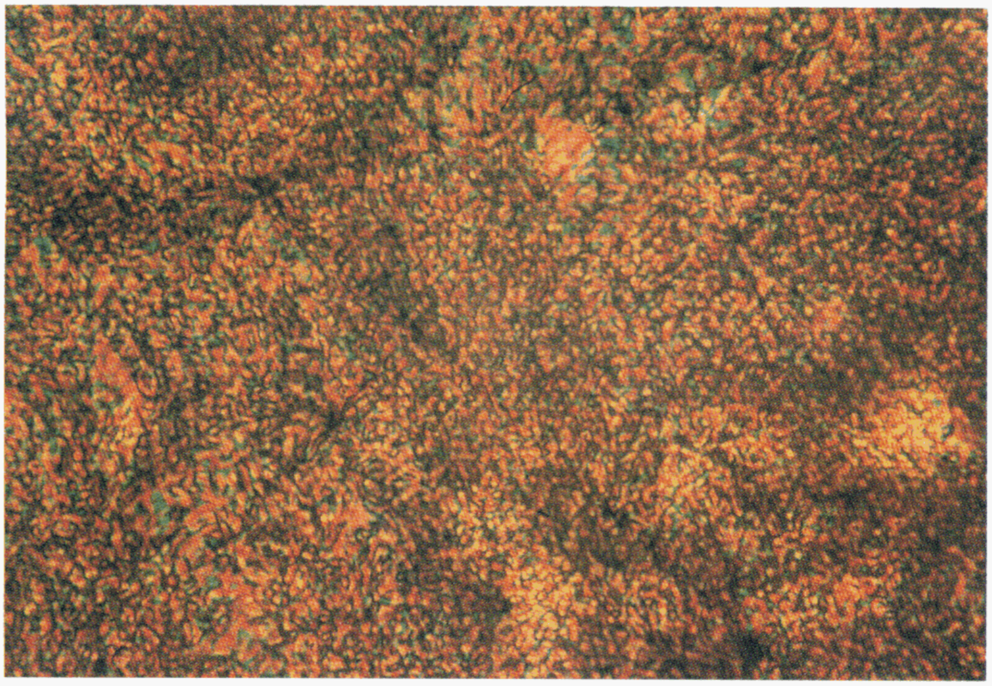
WAXS were carried out at room temperature on water-free solutions with polymer concentrations from 8% PPTA to 23% PPTA. The peaks of the 20% pattern in Figure 2 have the same positions as those published for crystal solvate.[10,20,21] There is no concentration dependence of the peak positions visible within the experimental limits. The height of the peaks lowers with decreasing polymer concentration. Simultaneously a halo becomes more pronounced due to the scattering of the isotropic phase. These observations correspond to a lower amount of crystal solvate in the solutions according to the lever rule.

The eutectic point between sulfuric acid and crystal solvate was determined by DSC and polarization microscopy. It lies at 4 °C and 6.5% polymer.

3.2. The Ternary System PPTA–Sulfuric Acid–Water. The melting curves for a solution series containing 11% PPTA measured by DSC are plotted against the acid concentration in Figure 3. The transition interval shifts toward higher temperatures with decreasing acid concentration. The single transition which was visible in the binary system divides into two transitions.

Chart 1. Plate 1 (top, 14% PPTA in 99.8% Sulfuric Acid, 24 °C) and Plate 2 (bottom, as Plate 1, after 22 h, 40 °C)





The clearing surface of the ternary phase diagram was investigated by polarization microscopy in the concentration range 9–16% polymer and 100–92% sulfuric acid. It is shown in Figure 4. With decreasing acid concentration the clearing temperature decreases, reaches a minimum, and increases again. The nematic phase is separated from the isotropic phase by a two-phase region. It exists below the right part of the surface (i.e. at acid concentrations above 96%). The minimum of the clearing temperatures is broader for lower polymer concentrations.

After passing the minimum the clearing temperature rises again with decreasing acid concentration. Below that part of the clearing surface a two-phase region exists containing isotropic solution and anisotropic areas which look like little spots between crossed polarizers. At lower temperatures another transition is visible under the microscope. An anisotropic solid phase appears which shows a transition in DSC, too. The texture of the phase is not very similar to that of the crystal solvate, it looks more disturbed and less homogenous.

In Figure 5 diffraction patterns of a 20% PPTA solution in dependence on the acid concentration are shown. The positions of the peaks are independent of the acid concentration, but their intensity decreases with decreasing acid concentration. This behavior is similar to that shown in Figure 2 with a fixed acid concentration and decreasing polymer concentration.

The results of the degradation experiments are shown in Figure 7. The molecular weight of the coagulated polymer increases with increasing acid concentration of the solutions and has a maximum for 100% sulfuric acid. It depends also on the polymer concentration. Solutions with lower polymer content lead to lower molecular weights after degradation experiments. That means that lower

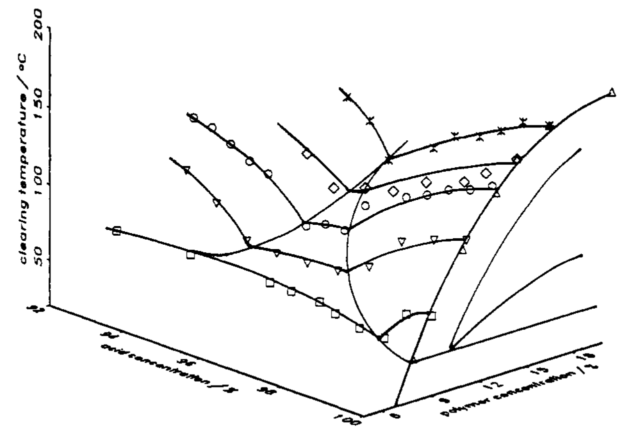


Figure 4. Clearing surface of the ternary system PPTA–sulfuric acid–water in the concentration range 9–20% PPTA and 100–92% sulfuric acid. The binary phase diagram is shown, too. The eutectic trough divides the surface into two parts. The nematic phase exists under the right part of the surface.

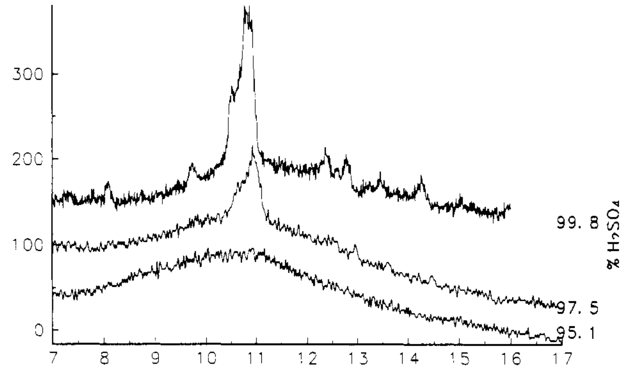


Figure 5. WAXS on 20% PPTA solutions with different acid concentrations. Crystal reflections get weaker for decreasing acid concentration. See text for explanation.

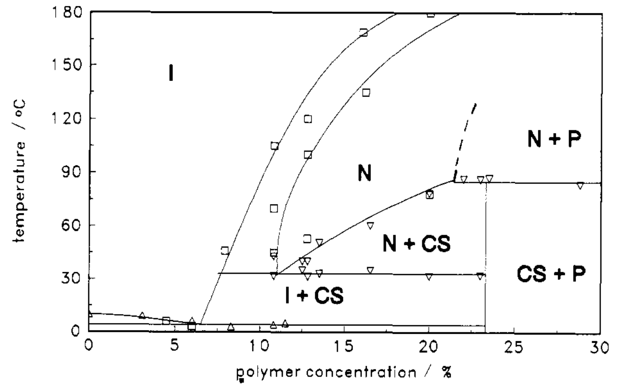


Figure 6. Binary phase diagram PPTA–sulfuric acid. The points designated by boxes were measured with polarization microscopy, those designated by triangles with DSC. The following phase regions are indicated: I, isotropic; N, nematic; CS, crystal solvate; P, polymer.

polymer and acid concentration lead to higher degradation rates.

All microscopic and calorimetric experiments were carried out at acid concentrations greater 90% in times short enought that the influence of degradation on the transition temperatures was not significant.

4. Discussion

4.1. The Binary System. The binary phase diagram is shown in Figure 6. Clearing curves were detected by polarization microscopy at low heating rates. The clearing point was defined as that temperature at which the last

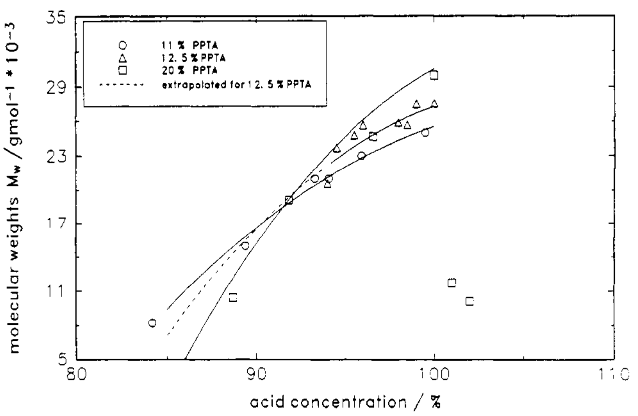


Figure 7. Degradation of PPTA solutions. The molecular weights of polymer samples after degradation experiments in solutions with different acid concentrations are plotted against the acid concentration of the solutions. The molecular weights are lower (i.e. the degradation is higher) for solutions with lower acid concentration and lower polymer concentration.

nematic solution disappeared, i.e. the high-temperature end of the biphasic region between nematic and isotropic solution. The beginning of the transition was determined by observation of the first isotropic droplets in the nematic sample. This procedure allows it to determine the width of the biphasic region. Found clearing temperatures are slightly higher than those published by Picken, who took that temperature at which 50% of the sample became black under crossed polarizers.[17]

The onset temperature of the transitions measured by DSC are nearly constant for all investigated concentrations (see Figure 1) and are interpreted as the monotectic temperature. Below that monotectic temperature of 33 °C two phases are stable (isotropic solution and crystal solvate). The nematic phase is formed by a three-phase reaction at this temperature.

We assume that the crystal solvate is incongruently melting into a nematic phase and crystalline polymer, because the upper limit of the transitions measured by DSC is constant for solutions with polymer concentrations above 22% and a homogenous nematic phase without any solid particles was not observed under the microscope in such solutions. From the calorimetric measurements it follows that the crystal solvate is composed of more than 22% polymer. From this value the molecular ratio between

$$\frac{n_{\mathrm{acid}}}{n_{\mathrm{polymer}}} = \frac{M_{\mathrm{w,monomer}} \times \text{acid concentration}}{M_{\mathrm{w,acid}} \times \text{polymer concentration}}$$

monomer units and acid molecules was calculated using the molecular weights of 238 g mol^{-1} for the PPTA and 98 g mol^{-1} for sulfuric acid. Using the equation leads to an acid molecules/monomer ratio of 8.6. The crystal solvate is a stoichiometric compound between acid and polymer, because it exhibits crystalline reflexions[10,11] (see Figure 2). Therefore the ratio between monomer units and acid molecules should be integer and the crystal solvate should at least be composed of 8 acid molecules per monomer unit. A model structure for the crystal solvate is proposed as follows: two of the eight acid molecules connect via hydrogen bonds neighboring polymer chains in the plane of the peptide bonds and produce polymer sheets. The other six acid molecules form a layer between them. The correctness of this model can be verified with the help of molecular modeling. This method has been applicated by Rutledge et al.[22] to test simulated structures of PPTA fibers with respect to experimental data. The proposed

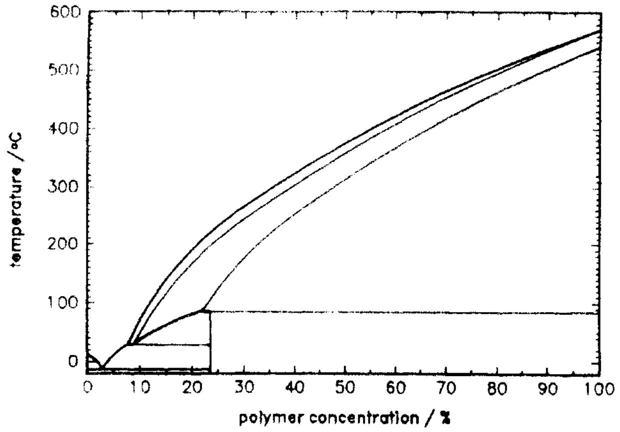


Figure 8. Possible binary phase diagram PPTA–sulfuric acid: the pure polymer shows thermotropic liquid crystalline behavior.

model should describe the real structure of crystal solvate satisfactorily if a calculated diffraction pattern of it is similar to that shown in Figure 2. The simulations necessary to verify the structure for the crystal solvate model have not yet been carried out.

The eutectic point between polymer and sulfuric acid lies at 4 °C; thus the melting point depression of the sulfuric acid by the polymer is very low.

From a topological point of view and under consideration of Gibbs' phase rule there are two possibilities to extrapolate the binary phase diagram (Figure 6) above the limits which are set for the experiments by chemical reasons (T = 180 °C, c = 25%). (1) With the assumption that the nematic phase exists over the whole concentration range above 9% PPTA the phase diagram has the form shown in Figure 8. In this case the pure PPTA polymer has a thermotropic liquid crystalline phase. Such thermotropic behavior of PPTA was not described in literature until now, and is hard to detect it because the decomposition temperature of the polymer is near to its melting point.[4] (2) Otherwise the nematic phase can exist only as an intermediate phase. Those intermediate phases are well known from alloy phase diagrams[23] and organic systems in which the molecules are able to form hydrogen bonds.[24,25] Possible localizations of intermediate phases between the isotropic phase and a compound were deduced from phase diagrams of real alloys (for instance Al–Ni, C–Cr, Ag–In, Cu–Sn, and Cu–Zn) and are shown schematically in Figure 9. In the case of PPTA–sulfuric acid, the nematic phase exists at concentrations lower than that of the crystal solvate and at temperatures higher than its melting point. The crystal solvate is incongruent melting. That is why the intermediate phase can exist only outside of the compound. The phase diagram with an intermediate nematic phase which is in accordance to all observations is shown in Figure 10. It is not possible to prove which of the phase diagrams is the correct one, because the demixing experiments which would be necessary to do so take a rather long time. Fast polymer degradation prevents conclusions from such long-time experiments at the required temperatures.

4.2. The Ternary System. All clearing curves of the PPTA–sulfuric acid solutions with different acid concentrations can be drawn into a three-dimensional clearing surface (Figure 4). The minimum of the clearing temperature belongs to an eutectic trough at 96.5% sulfuric acid and 105 °C which opens into a surface at lower polymer concentrations. The clearing temperature lowers and the surface transforms into the eutectic trough starting in the binary system sulfuric acid–PPTA at 4 °C. The drop of the clearing curve can be interpreted as a melting point depression of the solution caused by water. Below a certain acid concentration the first step of the coagulation process starts and the nematic phase precipitates. The clearing temperature rises. It was always possible to get the samples isotropic by heating them. This is evidence that the polymer was not coagulated into the pure PPTA because crystalline coagulated PPTA cannot be dissolved in 96% sulfuric acid by increasing the temperature for short times.

In a ternary systems three phases can be stable at the same temperature according to Gibbs' phase rule. This complicates the investigation of the phase diagram, because it is not easy to detect experimentally how many phases exist in a special temperature range and what they are composed of.

From topological reasons there should exist a three-phase region above the two-phase region isotropic–crystal solvate. Inside this region isotropic solution, crystal solvate, and nematic solution coexist. At higher temperatures the monotectic reaction takes place: above the three-phase region there exist the two-phase region nematic–isotropic at lower and nematic–crystal solvate at higher polymer concentration, between them the nematic phase lies. The dimension of the transition from the three-phase region to the two-phase region is two (surface); the dimension is one (line) for the transition from isotropic phase–nematic phase–crystal solvate into nematic phase.[26] The temperature vs concentration surface of the monotectic transitions above which the nematic phase exists either in a one- or in a two-phase region is shown in Figure 11. The network in Figure 11 is formed by the melting curves detected by DSC, which run parallel to the axis of acid concentration and by conodes which connect the crystal solvate with the equilibrium point on the clearing surface at a constant temperature.

From the given data measured by calorimetry and microscopy a partial phase diagram for the system PPTA–sulfuric acid–water can be proposed. The homogenous nematic phase exists above a monotectic transition and is separated from the clearing surface by a two-phase region. The clearing surface shifts to higher temperatures with increasing polymer concentration and increasing acid concentration. The temperature at which the nematic phase appears in the binary system is 33 °C. The temperature at which the nematic phase is the only stable one rises with decreasing acid concentration. Below the monotectic surface which marks the lowest temperature at which a homogenous nematic phase may exist at a certain concentration three phases are stable: the nematic one, crystal solvate, and isotropic solution.

It is not clear which phases exist inside the region which lie below the part of the clearing surface toward lower acid concentrations. There should be something other than the crystal solvate described in the binary system, because the crystal reflexions of the crystal solvate disappear with decreasing acid concentration (see Figure 5). On the other hand, no reflections from coagulated PPTA were detectable by X-ray diffraction. If crystalline PPTA exists in this region, the ordered regions should be very small or distorted because crystal reflections were not found. In this case the PPTA should form the spots in polarisation microscopy and shows an enormous melting point depression (from ca. 600 °C to below 100 °C). The other possible explanation of the experimental data is the assumption of another, ternary compound. This compound does not show crystalline reflexions, either because the high content of sulphuric acid and water suppresses the existence of large ordered areas or because it exists in some kind of gel

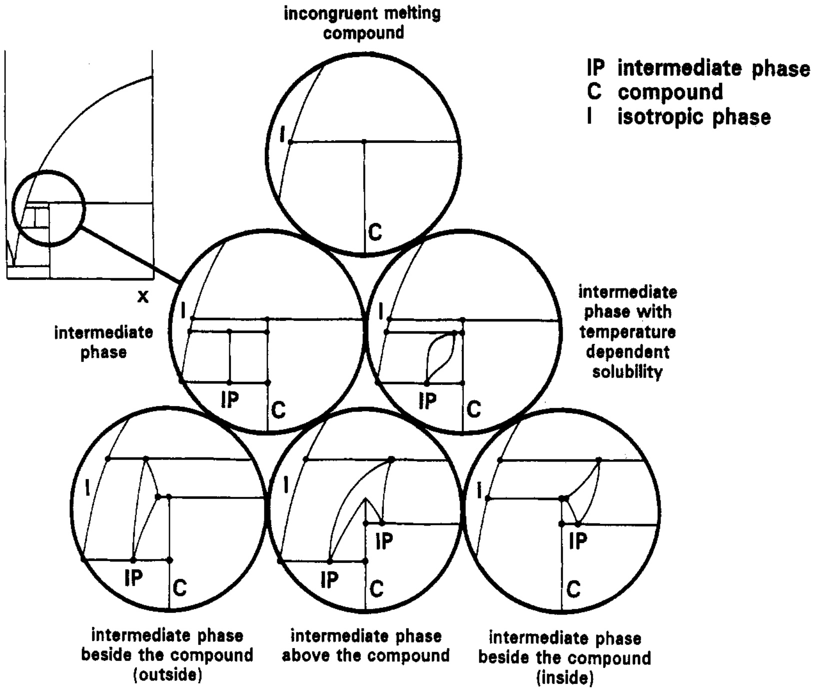


Figure 9. Possible localizations of intermediate phases in a binary phase diagram with a compound.

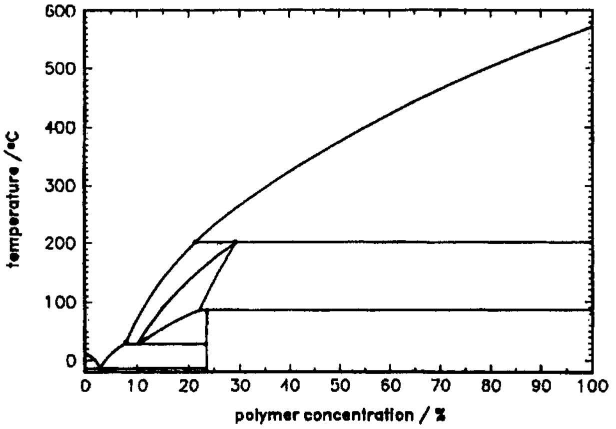


Figure 10. Possible phase diagram PPTA–sulfuric acid: nematic solution exists as an intermediate phase.

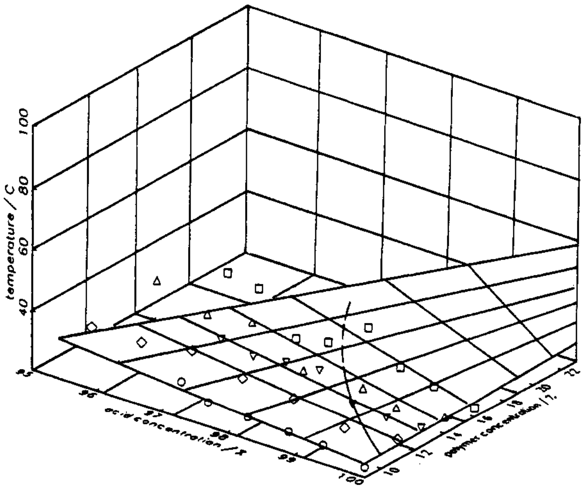


Figure 11. Monotectic transition surface in the concentration range 10–20% PPTA and 95–100% sulfuric acid. See text for explanation.

state. The experimental results cannot answer that question yet. From a topological point of view there should be a miscibility gap between the components of the ternary system in the solid state.[12]

5. Conclusions

The equilibrium structure of the ternary phase diagram PPTA–sulfuric acid–water is based on immiscibility of the components in the solid state. In the binary system an incongruent melting stoichiometric compound (crystal solvate) composed of 23% PPTA in 99.8% sulfuric acid exists. The nematic phase exists at polymer concentrations above 9% and acid concentrations above 96%. No other liquid crystalline phases were found in the ternary system. The crystalline polymer is not formed directly from the nematic phase during the coagulation process. An anisotropic gel-like phase may exist inside of the ternary phase diagram. The ternary phase diagram PPTA–sulfuric acid–water in the given concentration range is described in this paper for the first time.

Acknowledgment. All SEC experiments, most of the preparations of the polymer solutions, and some of the DSCs were carried out at Akzo Research Laboratories Arnhem. The work of H.R. was supported by Akzo. The Guinier goniometer for the WAXS measurements is a gift of the Volkswagenstiftung. The work of G.F. is part of the projekt B1 within the Sonderforschungsbereich 197 "Lipidorganisation and Lipid-Protein-Wechselwirkung in Bio- und Modellmembranen", which is supported by the Deutsche Forschungsgemeinschaft.

References and Notes

(1) Ballauff, M. *Angew. Chem.* **1989**, *101*, 261–276.

(2) Jaffe, M.; Jones, R. S. *High technology fibers*; Dekker: New York 1985; 349 ff.

(3) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R. *Encyclopedia of polymer science and engineering*, 2nd ed.; Wiley-Interscience: New York, 1988; Vol. 9, p 1.

(4) Northolt, M. G.; Sikkema, D. J. *Adv. Polym. Sci.* **1990**, *98*, 115–177.

(5) Prevorsek, D. C. *Polymer Liquid Crystals*; Academic Press: New York, 1982; 346 ff.

(6) Kulichichin, V. G.; Platonov, V. A.; Kogan, Y. G.; Millkova, L. P.; Andreyeva, I. N.; Lukasheva, N. V.; Volochina, A. V.; Papkov, S. P. *Polym. Sci. USSR* **1979**, *20*, 2500–2509.

(7) Papkov, S. P.; Kalashnik, A. T. *Polym. Sci. USSR* **1984**, *26*, 2505–2517.

(8) Hindeleh, A. M.; Abdo, Sh. M. *Polymer* **1989**, *30*, 218–224.

(9) Gmelin. *Handbuch der anorganischen Chemie* (*Handbook of inorganic chemistry*); Springer: Heidelberg, 1960; Vol. 9, Part 2, p 615.

(10) Arpin, M.; Strazielle, C.; Skoulios, A. *J. Phys.* **1977**, *38*, 307.

(11) Iovleva, M. M.; Papkov, S. P. *Polym. Sci. USSR* **1982**, *24*, 236–257.

(12) Predel, P. *Heterogenous Equilibria*; Steinkopf: Darmstadt, 1982; 58 ff.

(13) Förster, G.; Reussner, J.; Jankowski, A.; Kuschel, F.; Wagner, R. *Cryst. Res. Technol.* **1989**, *24*, 201–206.

(14) Gardener, K. H.; Matheson, R. R.; Aviakan, P.; Chia, Y. T.; Gierke, T. G. In *Polymers for fibers and elastomers*; ACS Symposium Series 260; American Chemical Society: Washington, DC, 1984; pp 91–102.

(15) Sokolova, T. S.; Efimova, S. G.; Volochina, A. V.; Papkov, S. P. *Chim. Volokna* **1976**, *1*, 29–30.

(16) Jingsheng, B.; Anji, Y.; Shengquing, Z.; Shufan, Z.; Chang, H. *J. Appl. Polym. Sci.* **1981**, *26*, 1211–1220.

(17) Picken, S. J. *Macromolecules* **1989**, *22*, 1766–1771.

(18) Nakajima, A.; Hirai, T.; Hayashi, T. *Polym. Bull.* **1978**, *1*, 143–147.

(19) Kulichichin, V. G. *Liquid-crystalline Polymers*; Chimia: Moscow, 1988; pp 331–371.

(20) Xu, D.; Okuyama, K.; Kumamaru, F.; Takayanagi, M. *Polym. J.* **1984**, *16*, 31–40.

(21) Iovleva, M. M.; Papkov, S. P.; Banduryan, S. I. *Vysokomol. Soed. B* **1979**, *21*, 351.

(22) Rutledge, G. C.; Suter, U. W.; Papaspyrides, C. D. *Macromolecules* **1991**, *24*, 1934.

(23) Hansen, M. *The building of two component alloys*; Springer: Heidelberg, 1936.

(24) Kresse, H.; Dorscheid, C.; Emmerling, U.; Frank, R.; Paschke, R.; Szulzewski, I. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1345–1349.

(25) Moenke-Wedler, T.; Förster, G.; Brezesinski, G.; Steitz, R.; Peterson, I. R. *Langmuir* **1993**, *9*, 2133–2140.

(26) Greiner, W. *Theoretical Physics*; Deutsch: Frankfurt, 1987; Vol. 9, p 67.