Phase separation in blends of aromatic polyoxadiazole and polyamide-6

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The phase-separation phenomena in blends of poly(p-phenylene-1,3,4-oxadiazole) (p-PODZ) and polyamide-6 (PA-6) were studied and compared with results obtained for blends of poly(p-phenylene terephthalamide) and polyamide-6. It can be shown that p-PODZ exhibits no lyotropic liquid-crystalline phase in concentrated sulphuric acid solutions up to concentrations of 24%. The ternary solutions of p-PODZ/PA-6/sulphuric acid phase-separate into two isotropic phases. p-PODZ/PA-6 blend films could be coagulated from the ternary solutions under conditions that prevent large-scale phase separation. Transparent films of p-PODZ/PA-6 blends can be obtained from the ternary solutions if the p-PODZ content is higher than 30% of total polymer below and slightly above the critical concentration. The thermal properties of such 'forced' blends of p-PODZ and PA-6 were investigated. Interconnected two-phase structures, which are characteristic of spinodal decomposition, were found after thermally induced phase separation of the blends.

(Keywords: blends; phase separation; rigid-chain molecules; molecular composites; aromatic polymer)

INTRODUCTION

The synthesis of lyotropic and thermotropic liquid-crystalline polymers has induced significant scientific and practical interest and the hope for applications of such rigid-rod polymers as new materials[1,2]. Blends of liquid-crystalline and flexible polymers produced either by solution or by melt processing have attracted pronounced scientific interest.

The mechanical properties of these systems depend mainly on the state of dispersion of the rigid-rod component in the flexible-coil matrix. The ultimate aim is to disperse the rigid-rod polymers on a molecular level, leading to the so-called molecular composites[3]. In that case an optimal reinforcing effect of the rigid-rod macromolecules can be expected. This has been shown for blends of poly(p-phenylene benzobisthiazole) with poly(2,5(6)-benzimidazole) or poly(2,5(6)-benzothiazole) prepared by rapid coagulation in water from isotropic methanesulphonic acid solutions[4-7]. The mechanical properties of molecular composites can be approached by the Halpin–Tsai theory, treating the molecularly dispersed rigid-rod molecules as reinforcing elements.

However, mixing of rigid-rod and flexible molecules on a molecular scale is entropically unfavourable. As a result, self-alignment of the rigid chains occurs. Therefore, it is interesting to study the course of phase separation of such systems in detail.

Recently, we investigated the phase separation in poly(p-phenylene terephthalamide)/polyamide-6 (PPTA/PA-6) blends[8]. The phase diagram of ternary solutions of PPTA/PA-6/H_2SO_4, as well as the thermally induced spinodal decomposition of molecular composites

of PPTA and PA-6 have been reported. In the present study, we want to extend these investigations to blends of poly(p-phenylene-1,3,4-oxadiazole) (p-PODZ)/PA-6 and to compare the results for both systems.

p-PODZ can be synthesized either by polycondensation of dihydrazides and dichlorides followed by thermal cyclization of the intermediate polyhydrazide[9], or by direct polycondensation of terephthalic acid and hydrazine in fuming sulphuric acid[10], as shown in the following equation:
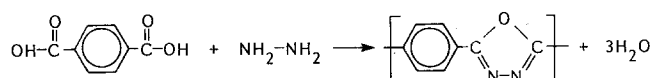
p-PODZ is expected to be a rigid molecule. p-PODZ fibres are high-modulus and high-strength polymer materials with a thermostability up to 500°C[10,11]. The crystallization behaviour and spherulite structure of p-PODZ have also been studied[12].

EXPERIMENTAL

Two different p-PODZ samples were used in this study. p-PODZ 1 has an inherent viscosity of 2.04 and p-PODZ 2 has an inherent viscosity of 1.07 (determined at 30°C, 0.2 g/100 ml, concentrated H_2SO_4, $\eta = \ln(t/t_0)/c$). p-PODZ has been synthesized by direct polycondensation of terephthalic acid and hydrazine sulphate as described elsewhere[11]. The PA-6 used in this study has an inherent viscosity of 1.1 measured at 25°C in concentrated sulphuric acid. The polymers were dried at 80°C in a vacuum oven for 24 h before use.
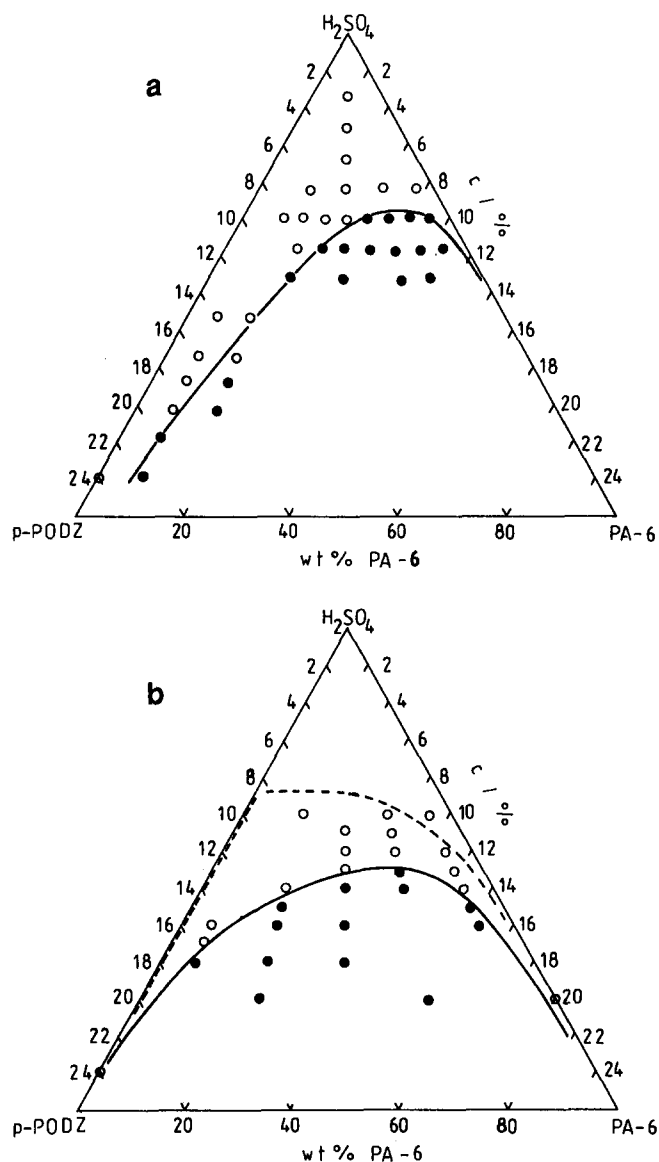
Figure 1 Ternary phase diagrams of p-PODZ/PA-6/conc. sulphuric acid: (a) p-PODZ 1, inherent viscosity 2.04; (b) p-PODZ 2, inherent viscosity 1.07. The broken curve in (b) shows the results for the system PPTA/PA-6/sulphuric acid from ref. 8; c is the total polymer concentration; the open and full circles represent one- and two-phase regions, respectively

To determine the ternary phase diagrams, suitable amounts of both polymers were dissolved in 1 ml H_2SO_4. This process takes 12–24 h depending on the composition and concentration of the polymers. The solutions were characterized by optical microscopy.

Thin films of p-PODZ/PA-6 blends were prepared by the following method. The p-PODZ/PA-6/H_2SO_4 solutions with total polymer concentrations slightly below the critical concentration and blend ratios of p-PODZ/PA-6 from 90/10 to 10/90 were spread over a glass slide, equipped with a Parafilm spacer of approximately 0.2 mm thickness, at room temperature and coagulated in distilled water.

The polymer films were washed in distilled water until the acid was completely removed. After that, the polymer films were placed on a glass slide and dried in a vacuum oven at 80°C for 48 h. The morphology of the polymer blend films was examined by optical microscopy. The blends obtained were used for the thermal investigations reported below.

D.s.c. experiments were carried out with a Mettler TA 3000 or a Perkin–Elmer DSC 4 at scanning rates of 10 K min^{-1}. A Mettler T6 instrument was used for thermogravimetric investigations. Here, the heating rate was 20 K min^{-1}. The thermally induced phase separation of the blends was examined by laser light scattering and optical microscopy. The films were inserted in a hot stage, which is adjusted in a laser light scattering apparatus. The scattering intensity was recorded as a function of temperature at a heating rate of 2 K min^{-1}.

All thermal investigations were carried out under nitrogen.

RESULTS AND DISCUSSION

Ternary phase diagrams of p-PODZ/PA-6/sulphuric acid

The ternary phase diagrams of p-PODZ/PA-6/H_2SO_4 are depicted in *Figure 1a* and *1b* for p-PODZ 1 and p-PODZ 2, respectively. p-PODZ does not show any lyotropic liquid-crystalline behaviour in concentrated sulphuric acid in the concentration range investigated. In that respect, the phase diagram for the p-PODZ/PA-6 solutions differs from that found[8] for the system PPTA/PA-6/H_2SO_4 and also from the theoretical description of rigid-rod/flexible-coil/solvent systems given by Flory[13]. For the system PPTA/PA-6/H_2SO_4 it could be shown that only a small amount of PA-6 in the solution leads to phase separation into an anisotropic PPTA-rich phase and an isotropic PA-6-rich phase. The p-PODZ/PA-6/H_2SO_4 solutions containing a small amount of PA-6, on the contrary, are homogeneous solutions up to very high polymer concentrations. For example, the solutions with 10% PA-6 are one-phase systems up to total polymer concentrations of 21 or 18% for p-PODZ 1 and p-PODZ 2, respectively. On the other hand, the solutions with high PA-6 content are two-phase at relatively small concentrations. It can be seen, for example, that the solutions containing 10% p-PODZ exhibit phase separation at total polymer concentrations of 10 or 15% for p-PODZ 1 and p-PODZ 2, respectively.

A dependence of the critical concentration on the molecular weight of the p-PODZ used can be observed in solutions with high PA-6 content. Here, the critical concentration decreases with increasing molecular weight of p-PODZ. The molecular-weight dependence of the critical concentration is not clearly detectable in solutions with high p-PODZ content.

Some blend properties

Thin films of p-PODZ/PA-6 coagulated from solutions with polymer concentrations slightly below the critical concentration turned out to be nearly transparent if the PA-6 content was less than 70% by weight. Optical microscopic investigations do not show any phase-separation structures. The crystallization of PA-6 leads to cloudy films in blends with 70% PA-6 and more. These facts are demonstrated in *Figures 2a* and *2b* for blends with blend ratios of p-PODZ/PA-6 of 50/50 and 10/90, respectively.

Phase-separated structures observed in ternary solutions above the critical concentration are shown in *Figure 3* for a blend of p-PODZ/PA-6 70/30. The total polymer concentration increases from 16 to 20% by weight. The solution with a total polymer concentration of 14% is completely transparent and does not show any phase
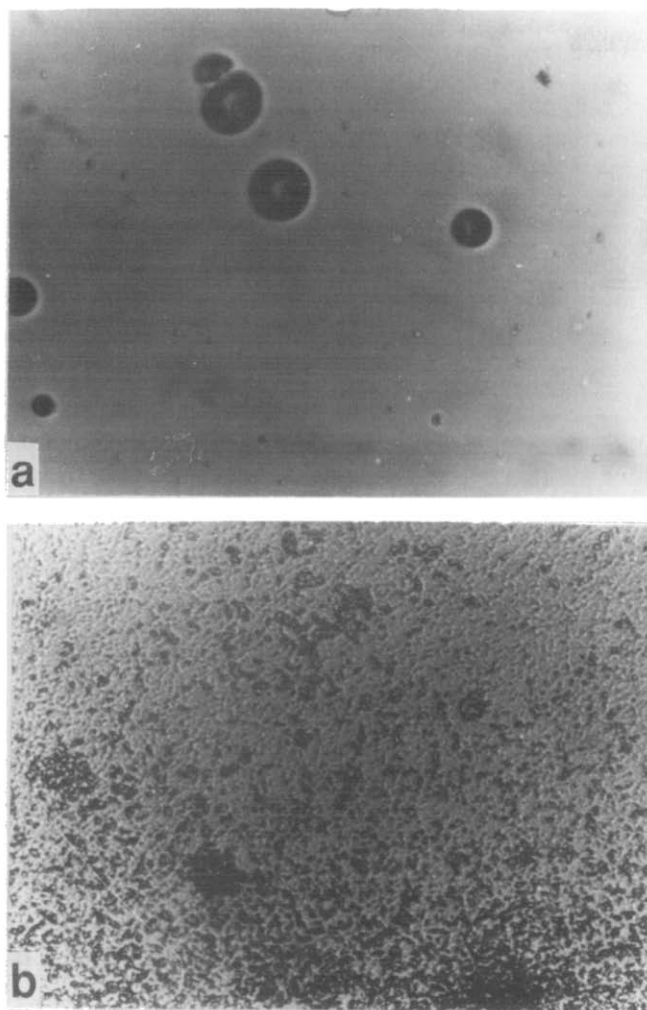
Figure 2 Optical micrographs of blend films of *p*-PODZ/PA-6 with blend ratio of (a) 50/50 and (b) 10/90 by weight

Thermal properties of p-*PODZ/PA-6 and PPTA/PA-6 blends*

Thermogravimetric investigations. Two examples of thermogravimetric curves for *p*-PODZ/PA-6 and PPTA/PA-6 blends are shown in *Figure 5*. The weight loss as a function of temperature as well as the first derivative are plotted. The peak temperatures of the first derivative are considered as degradation temperatures of the material. Two separated peaks were found for all blends. The first peak can be associated with PA-6 degradation and the second peak with that of *p*-PODZ and PPTA, respectively. The degradation temperature of pure PPTA is 589°C, that of *p*-PODZ is 533°C and that of pure PA-6 is 454°C. All values are measured in nitrogen.

The degradation temperature as a function of composition of the blends is depicted in *Figure 6* for the blends of *p*-PODZ and PPTA with PA-6. The upper and lower curves reflect the degradation temperatures of the respective stiff component and the degradation temperature of PA-6, respectively, in the actual blend. It can be seen that for *p*-PODZ/PA-6 blends the degradation temperature of PA-6 decreases with increasing *p*-PODZ content in the blend, whereas the degradation temperature of PA-6 is constant in blends of PPTA and PA-6. On the other hand, the degradation temperature of PPTA decreases slightly with increasing PA-6 content in the
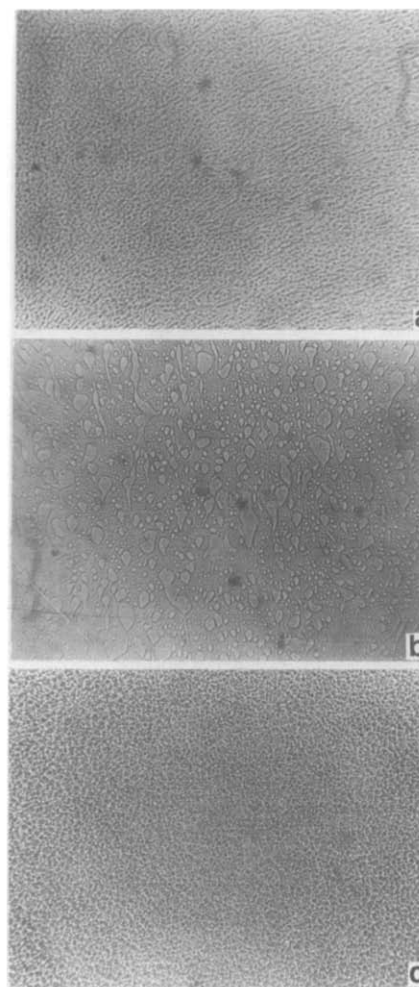
separation. Above 15% of total polymer, however, phase separation occurs in the ternary system. Now, we address the following question: Can shear-induced homogenization be observed in the solutions under discussion as has been reported[14] for solutions of flexible-type polymer mixtures? Indeed, it could be observed that, by stirring of the two-phase *p*-PODZ/PA-6 solutions, transparent, one-phase systems can be obtained. The two-phase structures recover after termination of the shear stress. Starting from these observations, we tried to obtain transparent films of our blends from solutions with total polymer concentrations above the critical concentration. For that purpose the two-phase solutions were sheared on the glass slide with the help of a second glass slide and coagulated immediately after shearing. Care has been taken that the solutions did not have enough time to recover. The morphologies of blend films obtained from the solutions shown in *Figure 3* are presented in *Figure 4*.

Shear homogenization could be achieved for the 16% polymer-containing solution. At higher concentrations the applied shear stress was not sufficient to get one-phase systems. Highly elongated two-phase morphologies can be observed (cf. *Figures 4b* and *4c*). One may establish that also for blends of *p*-PODZ and PA-6 the critical concentration can be shifted to higher values under shear conditions. Therefore, it is possible to prepare transparent films also from solutions with concentrations above the critical concentration of the quiescent system.

Figure 3 Optical micrographs of solutions of *p*-PODZ/PA-6 30/70 blend in sulphuric acid with total polymer concentrations of (a) 16%, (b) 18% and (c) 20%
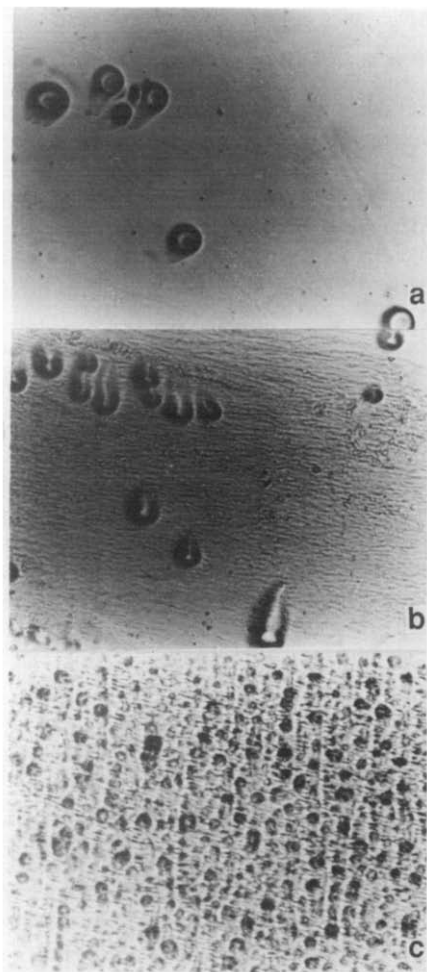
Figure 4 Optical micrographs of *p*-PODZ/PA-6 30/70 blends coagulated from solutions with different concentrations *c* and subjected to shear: (a) *c* = 16%, (b) *c* = 18%, (c) *c* = 20%
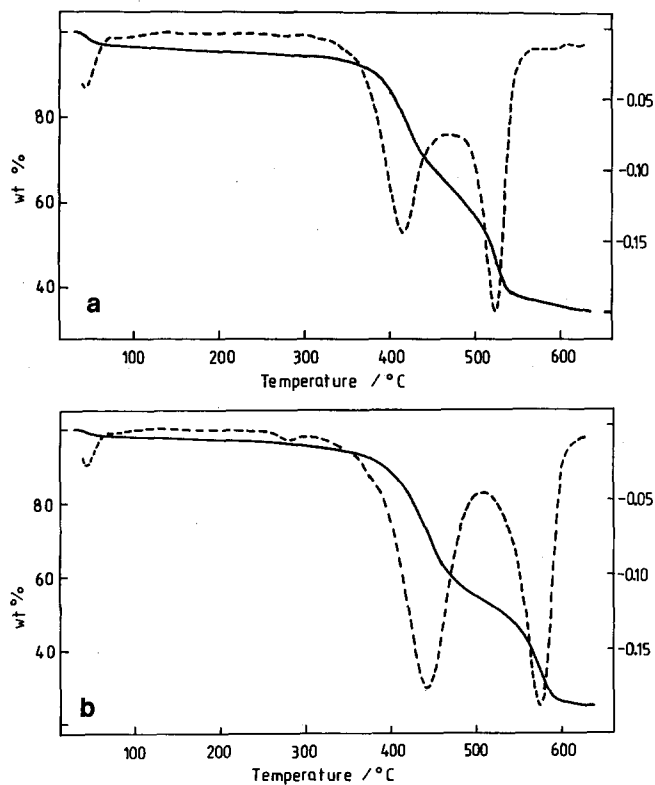

Figure 5 Thermogravimetric plots for (a) *p*-PODZ/PA-6 70/30 blend and (b) PPTA/PA-6 60/40 blend

blend and it remains constant for *p*-PODZ. So far, no explanation for these dependences can be given.

D.s.c. measurements. The results of d.s.c. examinations are shown in *Figure 7* for blends of PPTA/PA-6 as a
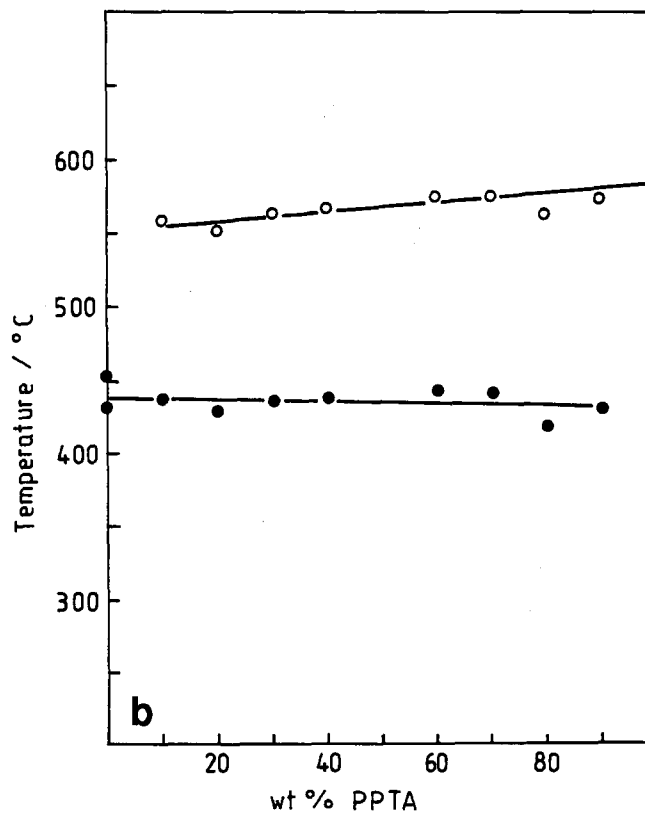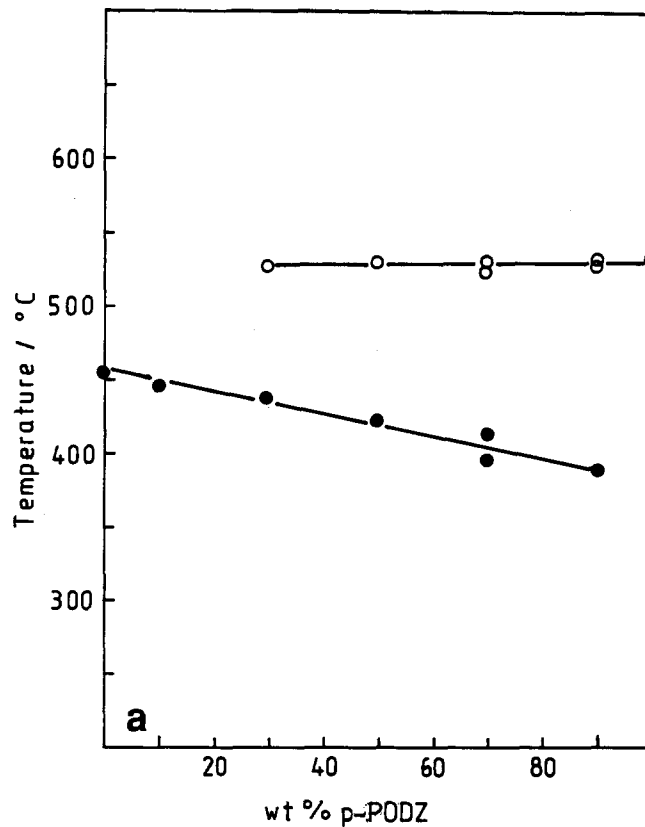

Figure 6 Degradation temperatures as a function of composition for (a) *p*-PODZ/PA-6 and (b) PPTA/PA-6 blends (○). The full circles represent the degradation temperature of PA-6
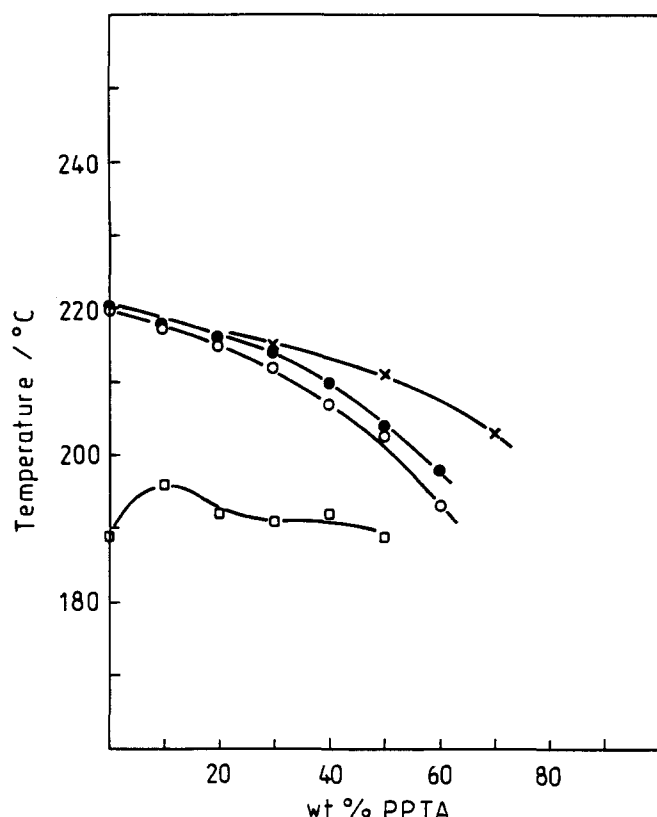
Figure 7 Melting and crystallization temperatures of PA-6 in PPTA/PA-6 blends: (●) melting temperature, first scan; (○) melting temperature, second scan; (□) crystallization temperature; and in p-PODZ/PA-6 blends: (×) melting temperature, first scan

function of composition. A melting peak of PA-6 in the blends could be observed up to a PA-6 content of 40% in the blend. This is in agreement with results published by Kyu[15], who did not find any melting or crystallization peak in blends with an excess of PPTA. We also observed that the melting temperature of PA-6 decreases with increasing PPTA content. This trend is also detectable in the second scan. Since the blend components are thermodynamically incompatible, morphological effects like size and perfection of the PA-6 crystals that are damaged by the PPTA molecules are responsible for the melting-point depression. But at least the presence of a PA-6 melting peak shows that we did not achieve a dispersion of the components on a molecular level as the result of the coagulation process. The prepared blends consist of a crystalline PA-6 phase, an amorphous phase (which may be a mixture of PA-6 and PPTA) and a crystalline PPTA phase. The crystallinity of PA-6 in the blends decreases with increasing PPTA content continuously. The pure PA-6 has a crystallinity of 32% but the PA-6 in the PPTA/PA-6 50/50 blend has a crystallinity of only 2% as revealed by d.s.c. The crystallization temperature as a function of the PPTA content stays essentially constant up to 50% of PPTA. There is some indication that small amounts of PPTA act as heterogeneous nuclei, which promote the crystallization of PA-6.

The results of d.s.c. experiments for p-PODZ/PA-6 blends show the same trends as discussed for the PPTA/PA-6 blends. The melting temperature in the first scan as well as in the second scan decreases with increasing p-PODZ content in the blend. But it can be

seen in *Figure 7* that the melting temperature of the PA-6 in the p-PODZ/PA-6 blends is higher than that in comparable PPTA/PA-6 blends. Also the crystallinity of PA-6 is higher in the blends with p-PODZ. For example, the PA-6 in the p-PODZ/PA-6 50/50 blend has a crystallinity of 5%. A melting and crystallization temperature of PA-6 was detectable down to a PA-6 content of 30% in the p-PODZ/PA-6 blends. All these facts illustrate that p-PODZ does not disturb the crystallization of PA-6 as much as PPTA.

Thermally induced phase separation. The thermally induced phase separation of the p-PODZ/PA-6 blends was studied by laser light scattering analogously to the investigations of the PPTA/PA-6 blends published elsewhere[8]. The scattering intensity of the laser light was measured as a function of temperature. The temperature at which the intensity increases is defined as the onset of the phase separation. The phase-separation temperatures as a function of composition of the p-PODZ/PA-6 blends are shown in *Figure 8*. The results published in ref. 8 for the system PPTA/PA-6 are indicated by a broken curve. The phase-separation temperatures of the p-PODZ/PA-6 blends are nearly constant up to a p-PODZ content of 60% in the blend. A dramatic increase of the phase-separation temperature can be observed for blends with 70 and 80% p-PODZ. No phase separation can be seen in the blend with a p-PODZ content of 90% up to 300°C.

The onset process for liquid–liquid phase separation in blends with an excess of PA-6 is superimposed on the melting of the PA-6 crystallites. No significant distinction can be seen between blends of p-PODZ and PPTA, respectively, with PA-6 in that range of composition. Surprisingly, although the melting temperature decreases with increasing p-PODZ content, the onset temperature of the liquid–liquid phase separation stays constant. On
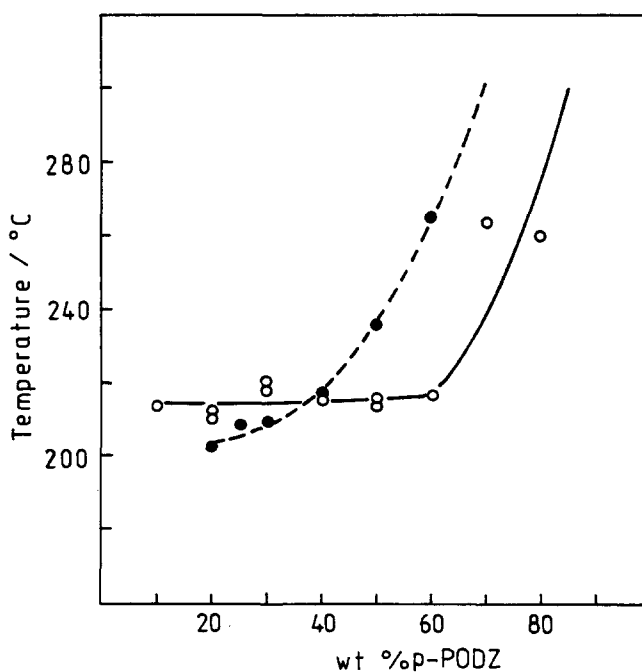

Figure 8 Phase-separation temperatures as a function of composition for p-PODZ/PA-6 blends; the broken curve shows the results for the system PPTA/PA-6 from ref. 8
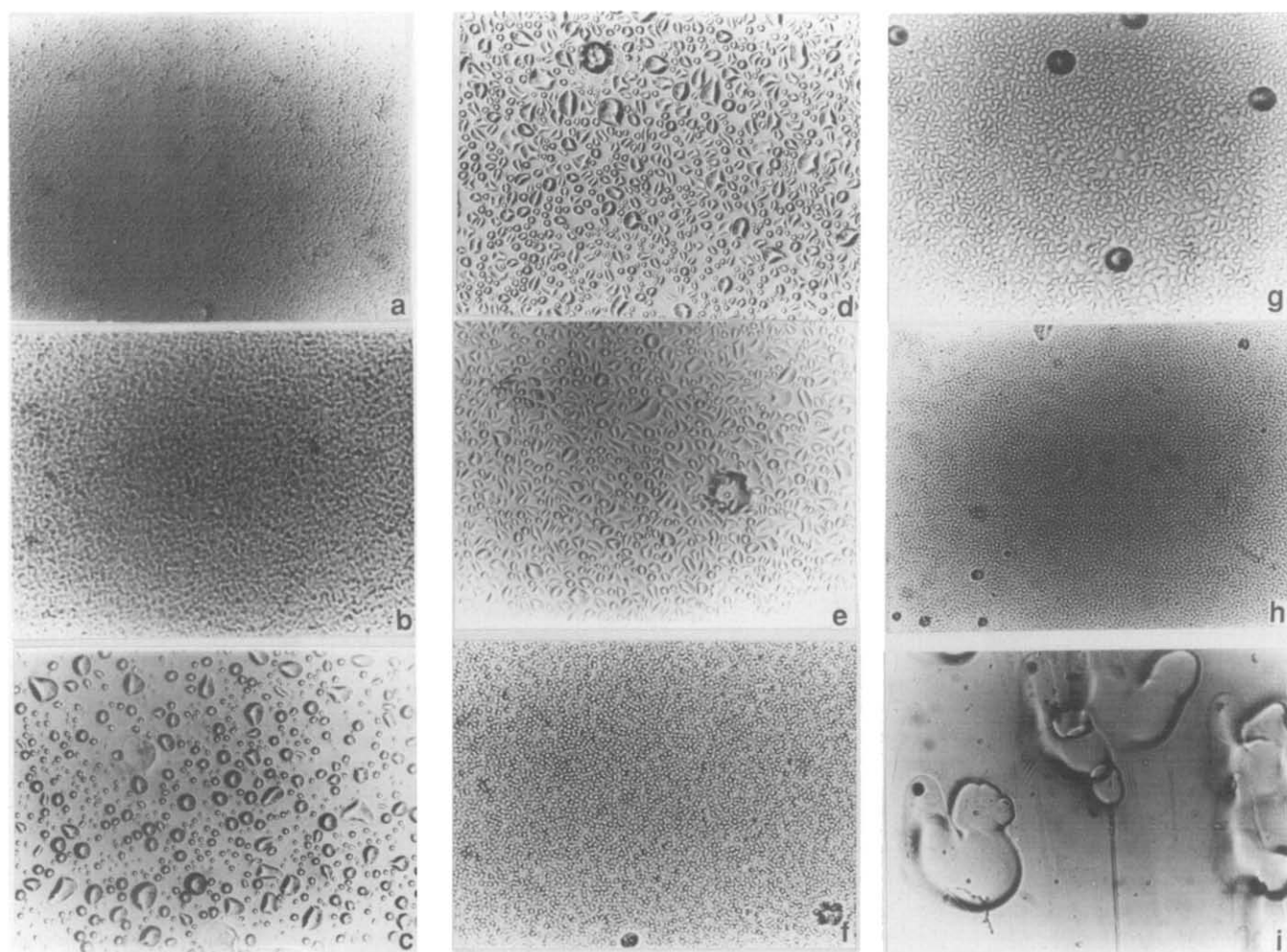
Figure 9 Phase-separation structures of *p*-PODZ/PA-6 blends: (a) *p*-PODZ/PA-6 10/90, (b) 20/80, (c) 30/70, (d) 40/60, (e) 50/50, (f) 60/40, (g) 70/30, (h) 80/20, (i) 90/10

the other hand, the phase-separation temperature of blends with an excess of *p*-PODZ or PPTA is clearly influenced by the rigid component. In comparison with *p*-PODZ/PA-6 blends, the phase-separation temperatures are shifted to higher values for the PPTA/PA-6 blends. For example, no phase separation can be observed for the PPTA/PA-6 70/30 blend, whereas the *p*-PODZ/PA-6 70/30 blend undergoes phase separation at 264°C. This seems to be an indication that the *p*-PODZ/PA-6 system is more flexible than the PPTA/PA-6 blends.

The phase-separation structures of *p*-PODZ/PA-6 blends that appear after thermally induced phase separation are shown in *Figure 9*. These morphologies result when liquid–liquid phase separation proceeds for approximately 1 min. One should stress the point that the phase separation does not progress further, obviously, for a long period of time. As can be seen, interconnected morphologies develop in blends with high *p*-PODZ or high PA-6 content. Such morphologies are indicative of phase separation via spinodal decomposition. A droplet/matrix morphology can be seen for blends in the medium range of composition. Here spinodal decomposition with rapid coarse graining takes place, leading to more irregular two-phase morphologies. No phase separation could be found in the *p*-PODZ/PA-6 90/10 blend.

CONCLUSIONS

The phase-separation behaviour of *p*-PODZ/PA-6 blends has been studied and compared with earlier investigations of blends of PPTA/PA-6. *p*-PODZ does not show lyotropic liquid-crystalline behaviour. The ternary solutions of *p*-PODZ and PA-6 in sulphuric acid phase-separate into two isotropic phases. This behaviour can be influenced by shear stress. The thermally induced phase separation of the *p*-PODZ/PA-6 blends with an excess of PA-6 in the blend is characterized by an overlapping of melting of PA-6 crystallites and phase separation. In that range of composition, *p*-PODZ and PPTA blends with PA-6 show nearly the same behaviour. But the phase separation of PPTA/PA-6 blends with high PPTA content is much more hindered than that of similar *p*-PODZ blends. From that, it may be concluded that PPTA is more rigid than *p*-PODZ.

ACKNOWLEDGEMENT

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