Phase behaviour of rigid-rod/coil/solvent ternary systems with rod–coil interaction

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This paper reports the phase diagrams of PBZT/nylon/MSA, PBZT/NaAMPS polymer/MSA, PBZT/HAMPS monomer/MSA and PBZT/PPTA-PS/MSA, with PBZT = poly(*p*-phenylene benzobisthiazole), MSA = methanesulphonic acid, NaAMPS = sodium 2-acrylamido-2-methylpropanesulphonate, HAMPS = 2-acrylamido-2-methylpropanesulphonic acid and PPTA-TS = poly(*p*-phenyleneterephthalamido)propanesulphonate). The ternary phase diagram of rigid-rod polymer PBZT and amorphous nylon in MSA solvent was found to follow Flory's prediction of a rod/coil/solvent ternary system very well. Flory's theory assumes no interaction between the rod and the coil, and the PBZT/nylon system fits this model nicely. When sulphonated polymers, such as NaAMPS polymer and PPTA-PS, were used instead of nylon in a ternary solution, it was found that the phase behaviour deviated from Flory's theory. This deviation could be due to the possible coil–rod intermolecular interaction in the ternary solution. Flory's formalism was used to analyse these data. It was found that for the PBZT/nylon/MSA system, the X_3 value was consistent with the contour length of the coil molecules as predicted by Flory's theory. However, both PBZT/HAMPS monomer/MSA and PBZT/NaAMPS polymer/MSA systems showed an X_3 value of unity. The ternary phase diagram of the PPTA-PS system showed an X_3 value between 1 and 5. This suggests that the degree of intermolecular interaction between rod and coil plays an important role in determining the phase behaviour of a rod/coil/solvent ternary system.

(Keywords: ternary systems; rod/coil/solvent; poly(*p*-phenylene benzobisthiazole); nylon; poly(sodium 2-acrylamido-2-methylpropanesulphonate); 2-acrylamido-2-methylpropanesulphonic acid; poly((*p*-phenyleneterephthalamido)propanesulphonate); phase diagram)

INTRODUCTION

Flory analysed the ternary phase diagram of a rod/coil/solvent system and predicted the critical concentrations of the isotropic–nematic phase transition[1]. This theory assumes that the ternary solution is an athermal system and there is no interaction between the coil and the rod. This theory has been confirmed by the phase diagram of the ternary system of poly(*p*-phenylene benzobisthiazole) (PBZT) and poly(2,5(6)-benzimidazole) (ABPBI) in methanesulphonc acid (MSA)[2]. An accurate description of the phase behaviour is very important in understanding the processing condition–property relationship in molecular composites[2] and in developing advanced composite systems with desirable properties. However, phase separation between non-interacting rod and coil molecules is thermodynamically favourable and is difficult to avoid during processing. A strong coil–rod intermolecular interaction may be desirable in two respects: it can enhance the coil–rod compatibility and it can influence the electronic structure of the rod molecules. The former may be important for physical and mechanical properties of the resultant molecular composite and the latter can influence the electronic properties of the system.

Tan *et al.*[3] reported the use of poly(sodium 2-acrylamido-2-methylpropanesulphonate) (NaAMPS polymer), a high-molecular-weight alkyl polymer with sulphonated side chains, in forming a molecular composite film with PBZT. They prepared a transparent film of 50/50 PBZT/NaAMPS polymer composition and reported that the detectable rod aggregation was less than 500 Å in size. This system represents a new class of rigid-rod molecular composite that is different from the other rigid-rod molecular composites. Owing to the presence of the sulphonated side groups of NaAMPS polymer, it serves as an ideal model compound for studying the effect of coil–rod interaction on the ternary phase behaviour. All the previously studied ternary solution systems[4–8] did not contain specific intermolecular interaction between the coil and rigid rod and their phase diagrams appeared to follow Flory's theory reasonably well.

In this study, the phase behaviours of several ternary systems were studied by determining the critical

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concentration values at various compositions. The rod and the solvent component were PBZT and MSA, respectively, as in the previous studies. The coil components used in this study included amorphous nylon, 2-acrylamido-2-methylpropanesulphonic acid (HAMPS monomer), NaAMPS polymer and poly(*p*-phenyleneterephthalamido)propanesulphonate) (PPTA-PS). The nylon used is an amorphous nylon and its ternary system represents a model system that satisfies Flory's athermal condition. NaAMPS polymer is a fully sulphonated linear chain and PPTA-PS is a partially sulphonated polymer. These sulphonated systems can have intermolecular coil–rod interactions and are expected to violate Flory's athermal assumption. HAMPS monomer is low-molecular-weight and its ternary system would serve as a good comparison with the polymer system. Flory's formalism and the influence of the coil–rod interaction on the ternary phase behaviour are interpreted in terms of the three geometrical parameters defined in Flory's theory.

EXPERIMENTAL

Materials

PBZT, a rod-like polymer, has a *para*-catenated backbone leading to a rod-like structure[9]; its chemical structure is sketched in *Figure 1a*. The PBZT dope was obtained from SRI International as a solution in polyphosphoric acid. The dope was coagulated in distilled water and neutralized with ammonium hydroxide. The coagulated PBZT was pulverized and dried to yield PBZT flakes. The details of the flake preparation procedure were described elsewhere[10]. The intrinsic viscosity of this batch of PBZT was 16 dl g^{-1} in MSA solution, corresponding to an average molecular weight of 27 000. The solvent used in this study was MSA from Aldrich Chemical Inc.. Since 'as-received' MSA usually contains a small amount of residual water, either distilled MSA or a mixture of 97% MSA and 3% chlorosulphonic acid (CSA) was used.

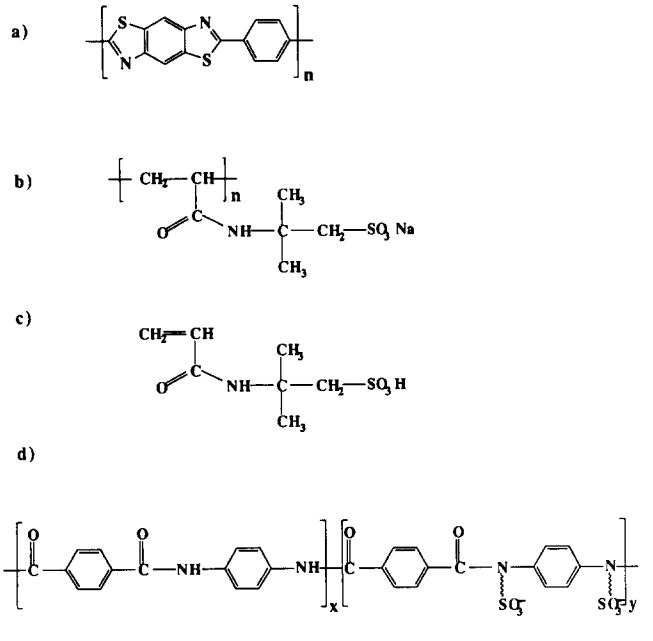

Figure 1 Chemical structures of components: (a) PBZT, (b) NaAMPS polymer, (c) HAMPS monomer, and (d) PPTA-PS

For the flexible molecules, four different compounds were used: nylon, NaAMPS polymer, HAMPS monomer and PPTA-PS. The nylon (Zytel™ 330), obtained from DuPont, was an amorphous polymer with a molecular weight of 14 000. NaAMPS polymer (Lubrizol), the trade name of poly(sodium 2-acrylamido-2-methylpropanesulphonate) from Lubrizol Co. (*Figure 1b*), is a linear polymer (with molecular weight about $(3–4) \times 10^6$) containing sulphonated side groups and is soluble in both MSA and H_2O. 'Lubrizol 2420' as received was a milky white, viscous, aqueous liquid. It was precipitated into a mixture of toluene and methanol yielding a wax-like substance. After filtering, washing and drying, NaAMPS polymer was a powder[3]. NaAMPS polymer was known to degrade after long-term exposure in acid. After two weeks in MSA, the inherent viscosity of NaAMPS polymer/MSA solution was found to decrease by 15%[3]. The HAMPS monomer was also obtained from Lubrizol Co. and the chemical structure is shown in *Figure 1c*. Poly((*p*-phenyleneterephthalamido)propanesulphonate) (PPTA-PS), a sulphonated version of Kevlar, with an average molecular weight of 25 000, was provided by J. Reynolds[11]. PPTA-PS was prepared by reacting poly(*p*-phenyeleneterephthalamide) with 1,3-propane sulphone[12]. Its chemical structure is shown in *Figure 1d*. PPTA-PS is soluble in both water and MSA. Elemental analysis showed that 66% of the PPTA polymer backbone was sulphonated[12].

Ternary phase diagrams

The ternary phase diagram of the rod/coil/solvent system was studied by varying the rod/coil polymer composition from 100/0 to 10/90. For a given rod/coil composition, the critical concentration was determined by slowly titrating an anisotropic solution of known concentration until the solution became isotropic. For each concentration, the ternary solution was stirred at room temperature under dry nitrogen for one to two days to assure achieving a homogeneous solution. Most isotropic solutions were optically transparent and dark green, while the anisotropic solutions were opaque and yellowish green. The isotropic phase was confirmed by using optical microscopy under crossed polarizers. The concentration at which the anisotropic phase disappeared was chosen to be the critical concentration for a given composition. The weight fraction of polymers at the critical point was then calculated from the weight of solvent added.

RESULTS AND DISCUSSION

Flory's analysis of rod/coil/solvent ternary systems

The theory developed by Flory[1] described the phase behaviour of a ternary system consisting of an isodiametrical solvent, a rigid-rod polymer and a flexible-coil polymer. It assumes an athermal condition in which there is no interaction between the rod and the coil components. This theory is characterized by three geometrical factors, X_1, X_2 and X_3, which are related to the solvent, the rod and the coil molecules, respectively. Assuming the cross-sectional areas of all three components are the same, the molecular volume ratio of the three components are in the ratio of $1:X_2:X_3$. The parameters X_2 and X_3 represent the aspect ratio of the rod molecule and the contour length of the coil molecule, respectively.

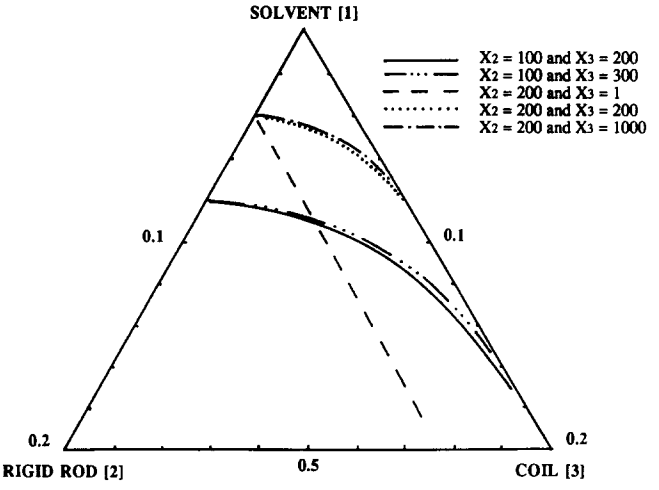

Figure 2 Theoretical critical concentration of ternary system based on Flory's theory

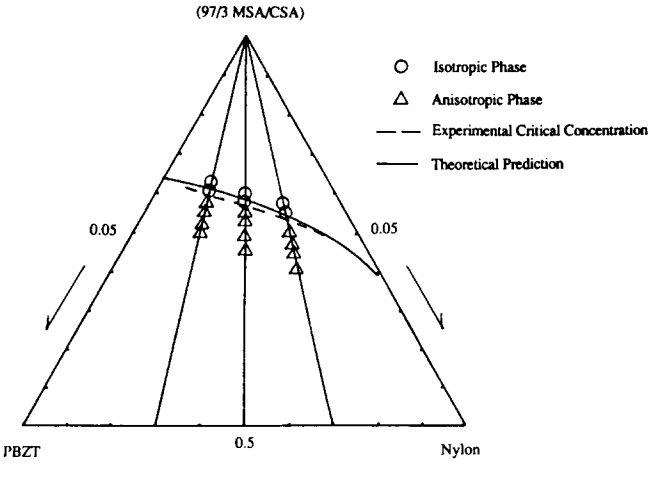

Figure 3 Ternary phase diagram of PBZT/nylon/(97/3 MSA/CSA)

According to Flory's theory of a rod/coil/solvent ternary system, the phase boundary varies depending upon the value of X_2 and X_3. The sensitivity of the phase boundary to values of X_2 and X_3 is shown in *Figure 2*. It shows that the phase boundary moves towards lower concentration when X_2, the aspect ratio of the rod molecule, increases from 100 to 200. The critical concentration remains relatively unchanged when X_3 is changed from 200 to 300. When X_3 decreases, the critical concentration of the binary mixture of the rod and solvent remains unchanged but the phase boundary of the ternary solution moves towards higher concentration. However, when the coil molecule is short ($X_3 < 10$), the phase boundary is very sensitive to the value of X_3. In the extreme case where $X_3 = 1$, there is no distinction between the coil and the solvent, and the reduced rod concentration remains constant through the whole range of the rod/coil composition. Therefore, the phase boundary is more sensitive to the rod's aspect ratio but is relatively insensitive to the coil's contour length when the molecular weight of the coil is relatively high.

PBZT/nylon/MSA system

With the molecular weight of PBZT ($M_w = 27\,000$) and the repeat unit length and width as 12.2 Å and 4.69 Å respectively, the aspect ratio of the rod component was estimated to be 256. In the region of large X_3, the phase boundary is insensitive to the actual value of X_3. Following a previous analysis of another ternary system[2], the value of 300 is used in the study for nylon. With the mixed solvent of 97/3 wt% ratio of MSA/CSA, the phase behaviour of PBZT/nylon/solvent system was studied and is shown in *Figure 3*. The critical concentration vs. composition are listed in *Table 1*. The experimentally determined critical concentration shows an increasing trend from 3.6% to 4.7% with increasing amount of coil content (up to 70%). The theoretical phase boundary calculated using X_2 and X_3 values of 256 and 300, respectively, is also shown in *Figure 3* as a full curve. The experimental results for the PBZT/nylon/MSA–CSA system are in excellent agreement with the theoretical prediction. This confirms that the PBZT/nylon/MSA system represents a model system satisfying Flory's athermal condition in ternary solution and the X_2 and X_3 values used are appropriate for the analysis of this study.

The sensitivity of the phase behaviour of the ternary system can be easily observed by using 'as-received' MSA solvent instead of the 97/3 MSA/CSA mixed solvent. The same phase diagram was constructed for PBZT/nylon/MSA system (*Figure 4*) where the MSA used was the 'as-received' 99% MSA from Aldrich Chemicals. The critical concentrations were determined for different compositions of PBZT/nylon blends in 'as-received' MSA. The experimental critical concentration results are shown in *Table 1*. These experimental critical concentrations are slightly higher than those predicted by Flory's theory, as shown in *Figure 4*. This discrepancy can be rationalized as a decrease of the X_2 value due to the aggregation of rod molecules. Owing to the presence of a small amount of moisture in MSA, the PBZT molecules form a small degree of aggregation[3]. The result is a decrease of the effective aspect ratio of the rod

Table 1 Critical phase concentration of PBZT/nylon/MSA

PBZT/nylon composition	C_{Cr} in MSA (wt%)	C_{Cr} in 97/3 MSA/CSA (wt%)	Calculated C_{Cr} (wt%)
100/0	4.0	–	3.6
70/30	4.4	4.0	3.9
50/50	4.8	4.3	4.2
30/70	5.3	4.7	4.5
15/85	5.8	–	4.9

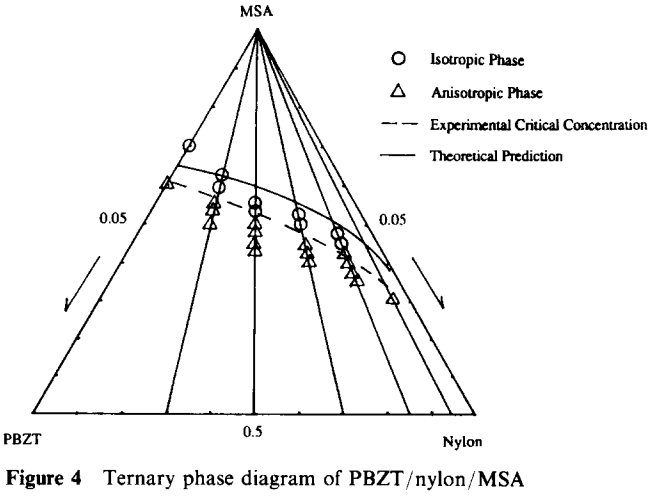

Figure 4 Ternary phase diagram of PBZT/nylon/MSA

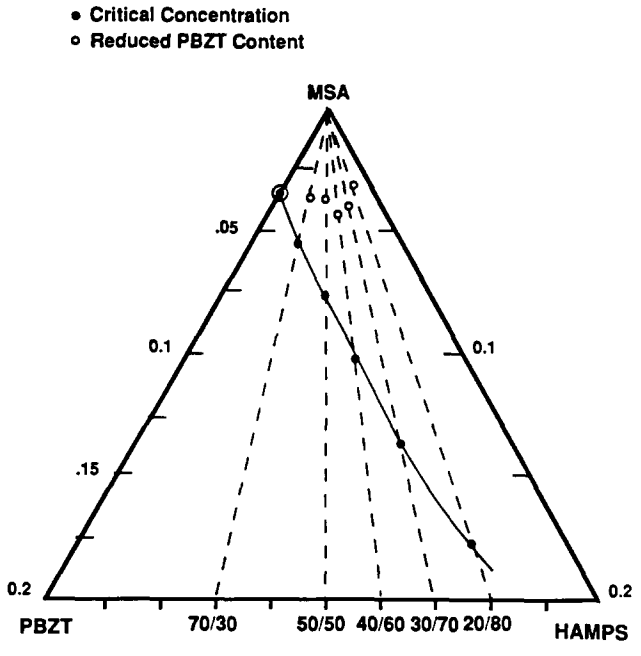

Figure 5 Ternary phase diagram of PBZT/HAMPS monomer/MSA

molecule in the solution, leading to a higher critical concentration value in the ternary phase diagram. When the 'as-received' MSA phase diagram is used to back-calculate the aspect ratio of the rigid-rod molecules, the effective aspect ratio of the PBZT molecules in the 'as-received' MSA solution is found to be 220, a decrease of 14%.

PBZT/HAMPS monomer/MSA and PBZT/NaAMPS polymer/MSA systems

The ternary phase diagram of PBZT/HAMPS monomer/distilled MSA was made by varying the composition of PBZT/HAMPS monomer from 100/0, 70/30, 50/50, 40/60, 20/80 and 0/100. By titrating the anisotropic solution, the critical concentration was determined. As shown in *Figure 5*, the critical concentration increases drastically from 3.65% up to 18% with increasing NaAMPS polymer content. In comparison, the critical concentration was much higher than that of the PBZT/Zytel 330/mixed solvent (MSA/CSA) system (*Figure 3*). When the reduced PBZT concentration was calculated from C_{cr}, the reduced PBZT content is almost constant regardless of the HAMPS monomer content. Using Flory's theory to analyse this phase behaviour, one can see that this ternary phase diagram is consistent with the case of $X_3 = 1$. This is not too surprising because the HAMPS monomer is a small molecule and the X_3 parameter for this component can be justifiably approximated as unity.

The phase behaviour was also studied by using the ultra-high-molecular-weight NaAMPS polymer. As shown in *Figure 6*, the critical concentration ranges from 3.65% to over 16.9%. In spite of its high molecular weight, the phase behaviour of the polymer system is very similar to that of HAMPS monomer ternary system. The critical concentrations at high NaAMPS polymer content are slightly less than the corresponding value for the HAMPS monomer, indicating that the X_3 parameter of NaAMPS polymer is only slightly higher than that of HAMPS monomer, but is remarkably close to unity. Besides, the reduced PBZT concentration exhibits almost a constant value, just like the PBZT/HAMPS monomer/MSA system.

This is a surprising result in view of the fact that NaAMPS polymer is a linear polymer with very high molecular weight; its X_3 should have been in the order of 10^3–10^4. According to Flory's theory, its phase diagram should exhibit phase behaviour closer to amorphous nylon than HAMPS monomer. However, the ionic interaction between the protonated PBZT and the anions on the NaAMPS polymer must have played a role here. Over a wide composition range, the ternary system behaves just like a binary system of rod and solvent. The effect of the long coil-like NaAMPS molecules is not shown. The protonated PBZT is 'seeing' NaAMPS polymer as if it were a low-molecular-weight solvent and is unable to distinguish NaAMPS polymer from MSA in the ternary solution.

Flory's theory takes into account the excluded-volume effect but, by assuming an athermal condition, does not consider any possible interaction between the coil and the rod. The ionic interaction between the protonated PBZT and the anionic NaAMPS polymer chain seems to negate the excluded-volume effect. Clearly, the meanings of X_1, X_2 and X_3 as derived by Flory are not applicable in this case where the coil–rod interaction is present. A modified version of the theory will be needed to account for the coil–rod interaction. An accurate description of the ternary phase diagram using Flory's formalism must be able to reduce the calculated X_3 value from the contour length of the coil to a value close to unity in the presence of such interaction. Another plausible explanation is that the solubility parameters of the MSA solvent and the NaAMPS coil polymer are very close and the interaction between the coil polymer and the solvent is very strong. Therefore, they behave just like a single component. The solution is behaving like a binary system instead of a ternary one. Studying other systems may help in addressing this issue.

PBZT/PPTA-PS/MSA system

The ternary phase diagram of the PBZT/PPTA-PS/MSA system is shown in *Figure 7*. The critical concentration of this ternary system lies between that of the corresponding systems of amorphous nylon and

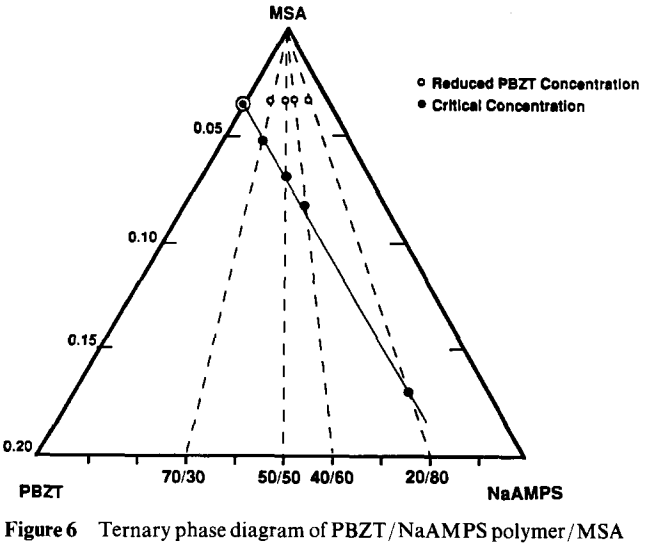

Figure 6 Ternary phase diagram of PBZT/NaAMPS polymer/MSA

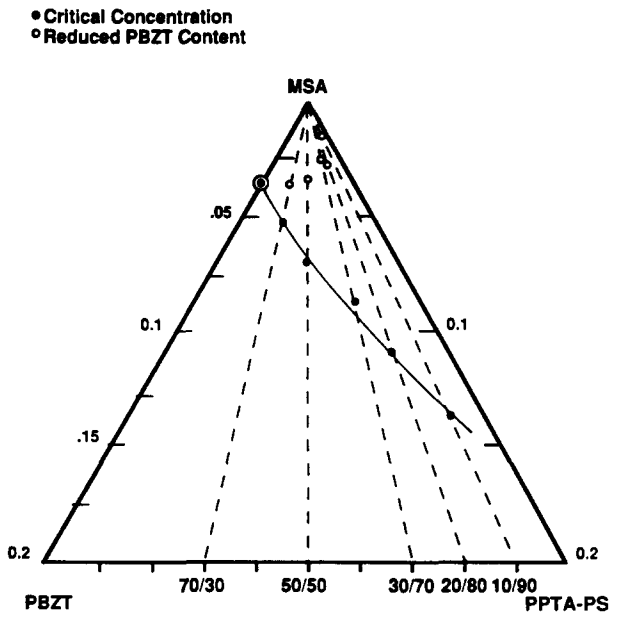

Figure 7 Ternary phase diagram of PBZT/PPTA-PS/MSA

Table 2 Critical concentration of PBZT/PPTA-PS/MSA system

PBZT/PPTA-PS composition	C_{cr} (wt%)	Reduced PBZT conc. (wt%)
100/0	3.65	3.65
70/30	5.28	3.69
50/50	6.90	3.45
30/70	8.60	2.58
20/80	10.90	2.72
10/90	13.60	1.36

NaAMPS polymer. The critical concentrations for this system at various PPTA-PS composition are listed in *Table 2*. The calculated reduced PBZT concentration showed a relatively constant value up to 50/50 PBZT/PPTA-PS composition and the reduced PBZT concentration showed a slight decrease at higher PPTA-PS composition. This suggests that the contour length effect of PPTA-PS component is not shown in the ternary phase diagram, similar to the behaviour of NaAMPS polymer system. The deviation from Flory's theory can again be attributed to the ionic association between the protonated PBZT and the anionic sulphonate group in PPTA-PS.

When Flory's theory was applied to the phase behaviour of the PPTA-PS ternary system by using an X_2 value of 256, the X_3 of this system corresponds to a value less than 5, but not unity like NaAMPS polymer ternary system. Assuming that X_3 corresponds to the contour length of the coil when there is no coil–rod interaction and that X_3 becomes unity when strong coil–rod interaction exists, these PPTA-PS system data suggest that sufficiently strong coil–rod interaction exists, but not as strong as in the NaAMPS polymer case. Based on the molecular structure of the various sulphonate groups used in this study, the sulphonate group of MSA is expected to be most acidic while those of PPTA-PS and NaAMPS are expected to be about the same. The fact that PPTA-PS polymer is only 66% sulphonated may have weakened the coil–rod interaction and caused the effective X_3 to be larger than one.

CONCLUSIONS

The PBZT/nylon/MSA–CSA ternary system was found to obey Flory's prediction. When no coil–rod interaction is present, the X_3 parameter in Flory's theory corresponds directly to the contour length of the coil polymer. When an interaction between rod and coil exists, the phase transition between the isotropic and the anisotropic region occurs at much higher concentration and Flory's theory is no longer applicable. The X_3 value approaches unity as shown in the results of the ternary systems containing NaAMPS, HAMPS component and PPTA-PS in this study. Both NaAMPS polymer and HAMPS monomer exhibited similar phase behaviour, leading to a constant reduced PBZT concentration in the ternary system, even though the molecular weight of NaAMPS polymer and HAMPS monomer are significantly different. Although the X_3 parameter is used as a fitting parameter in this study, its original derivation in Flory's theory is based on the geometrical structure of the coil polymer.

The PPTA-PS result showed that the corresponding X_3 value is larger than 1, but less than 5. The deviation from the value of unity could be due to the partial sulphonation of PPTA polymer. Alternatively, the sulphonate group in PPTA-PS has less acidic power, resulting in a lesser degree of interaction with PBZT molecules. A modification of Flory's theory is needed to describe the phase behaviour of a ternary system with rod–coil interaction. The X_3 parameter in the modified theory should not only correspond to the value of the contour length in the absence of coil–rod interaction, but also reduce to unity in the presence of strong coil–rod interaction.

Another manifestation of the deviation from Flory's theory can be viewed in terms of the reduced PBZT content at the critical concentrations. The reduced PBZT content from the experimental critical concentrations of ternary systems (PBZT/nylon/MSA, PBZT/NaAMPS polymer/MSA, PBZT/HAMPS monomer/MSA and PBZT/PPTA-PS/MSA) is shown as a function of rod/coil composition in *Figure 8*. When strong inter-

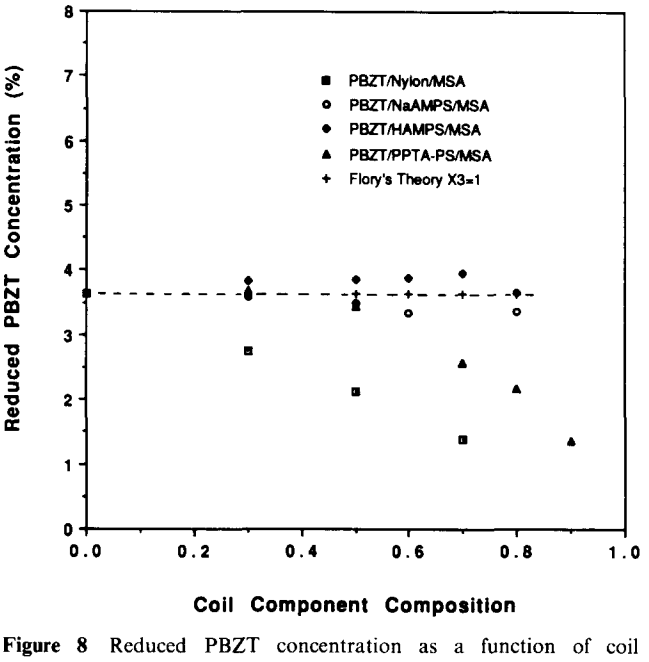

Figure 8 Reduced PBZT concentration as a function of coil components

molecular interaction exists, it exhibits a constant reduced content regardless of rod/coil composition, as shown in the PBZT/NaAMPS/MSA system. Depending upon the degree of intermolecular interaction between the rod and the coil in the ternary system, the reduced PBZT content varies with rod/coil composition. Another possible explanation of the deviation is that the compatibility between the sulphonated polymer and the MSA solvent is so strong that the sulphonated polymer and the acid are acting as one component. The solution is behaving as a binary system instead of a ternary system. Studying other ternary systems with different types of coil–rod interaction can give further insight into this question.

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REFERENCES

1 Flory, P. J. *Macromolecules* 1978 **11**, 1138
2 Helminiak, T. E., Wellman, M., Hwang, W. F., Wiff, D., Rodgers, V. and Benner, C. Report, AFWAL-TR-80-4163, 1980
3 Tan, L. S., Arnold, F. E. and Chuah, H. *Polymer* in press
4 Helminiak, T., Husman, G., Adams, W., Wiff, D. and Benner, C. *ACS Polym. Prepr.* 1975, **16**, 659
5 Hwang, W. F., Wiff, D. R. and Verschoore, C. *Polym. Eng. Sci.* 1983, **23**, 789
6 Gabriel, C. University of Massachusetts, Technical Report of Contract No. 33615-83-K-5001, 1984
7 Chuah, H., Lee, C. Y.-C. and Helminiak, T. E. Technical Report, AFWAL-TR-87-4127, 1988
8 Kim, C. S. and Berry, G. C. *J. Rheol.* 1990, **34**, 1011
9 Welsh, W. J., Bhaumik, D. and Mark, J. E. *Macromolecules* 1981, **14**, 947
10 Gabriel, C. A. Ph.D. Thesis, University of Massachusetts, 1987
11 Courtesy of Professor John Reynolds, University of Texas at Arlington, 1990
12 Gieselman, M. B. and Reynolds, J. *Macromolecules* 1990, **23**, 3118