Closed-loop immiscibility in a ternary mixture of homopolymers

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Light scattering and calorimetric techniques were used to investigate the isothermal phase behaviour of a ternary polymer blend consisting of three pairwise miscible homopolymers. These homopolymers, polystyrene (PS), poly(2-chlorostyrene) (P2ClS) and polycyclohexylacrylate (PCHA), are apparently the first known examples of homopolymers that form a closed loop in the ternary isothermal phase diagram. The phase diagram of the ternary blend was determined by light scattering at 433 K, where all three pairs are below their respective lower critical solution temperature (*LCST*). The miscible compositions exhibit a single glass transition temperature (T_g) which follow a simple volume additivity relationship. Inside the immiscible closed-loop region, single T_gs are also observed, but these are shown to be consistent with the presence of two phases. Two binary interaction parameters (for the pairs PS–P2ClS and PS–PCHA) were determined from the locations of *LCST*s. The interaction parameter between P2ClS–PCHA was determined by approximating the observed closed-loop region of immiscibility by the Flory–Huggins lattice model. In analogy with systems comprised of a mixture of two polymers and a solvent, the closed-loop immiscibility gap results from an asymmetry in the interaction parameters between the three pairs (a '$\Delta\chi$' effect). The following ordering was observed: $\chi_{\mathrm{PCHA-P2ClS}} < \chi_{\mathrm{PCHA-PS}} \approx \chi_{\mathrm{PS-P2ClS}}$. This trend is consistent with the curvatures of the composition-dependent glass transition $T_g(\phi)$ plots.

(Keywords: ternary blends; closed loop; phase diagram)

INTRODUCTION

With the rapidly growing application of multiphase polymers[1–5], intense interest has been recently directed toward ternary polymer blends[6,7]. Research in this field, although still in its infancy, has been quite successful and there is now extensive literature on the subject[7]. In comparison with binary blends, ternary polymer systems can be viewed technologically as the 'next generation' in multiphase polymers. This is so because of the obvious advantage of an extra degree of freedom offered by the third component. From a fundamental viewpoint, ternary polymer mixtures offer unique opportunities to investigate multiphase behaviour, where four degrees of freedom are present in the system: temperature, pressure, and the concentrations of two components. Experiments in ternary blends have focused primarily on two types of systems[7]:

1. Two pairs of miscible polymers (*Figure 1a*). Incompatibility between two chemically different homopolymers A and B arises, as is well known, from the fact that the vanishingly low entropy of mixing of the macromolecules is usually not sufficient to overcome the unfavourable enthalpy of mixing of the different type of segments. In a close analogy with a good solvent, the role of a third component C (miscible with A and with B), which may be either a homopolymer or a random copolymer (but not a block copolymer), is to reduce the number of unfavourable contacts between the A–B segments. Above a critical concentration of C, the ternary system is expected to become homogeneous[8,9]. An example of this sort of system is given by the immiscible poly(methyl methacrylate)–poly(ethyl methacrylate) (PMMA–PEMA) pair which can be solubilized by poly(vinylidene fluoride) (PVF_2)[10] or styrene/acrylonitrile copolymers[11]. Several aliphatic or aromatic polyesters are also very effective in solubilizing the immiscible poly(vinyl chloride)–chlorinated poly(vinyl chloride) (PVC–CPVC) pair[12]. A random copolymer of the partly miscible pair has also been used as a solubilizing component[13], for example, in polystyrene/polybutadiene (PS/PB)[14].
2. Three pairs of miscible polymers (*Figure 1b*). When all three binary pairs are miscible, a completely homogeneous phase diagram is possible. An example is the ternary blend of PMMA–poly(epichlorohydrin)–poly(ethylene oxide) (PMMA–PECH–PEO)[15]. However, disparities in the interaction parameters of the binary system A–B and A–C, the so-called '$\Delta\chi$ effect', can lead to a closed loop for the boundary between miscible and immiscible regions[16–18]. Indeed such behaviour has been demonstrated in the ternary PMMA–PEO–SAA blend[19] where SAA is a random copolymer of styrene and acrylic acid. By varying the composition of the acrylic acid in the

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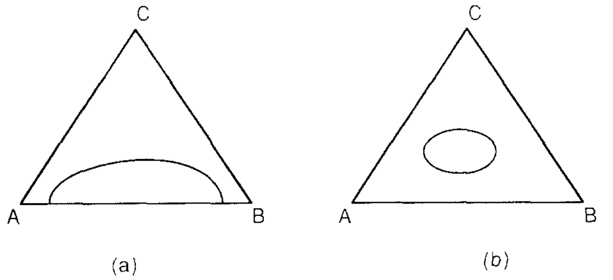

Figure 1 Schematic representation of two possible ternary phase diagrams: (a) two pairs are completely miscible, one pair is partially miscible; (b) all three pairs are miscible, but there is a region where the three polymers together are immiscible

copolymer AA, it was possible to observe a closed-loop region of immiscibility. Brannock and Paul have identified a number of ternary systems where all three pairs are miscible[7]. The phase behaviour of a series of ternary blends based on styrene/acrylonitrile (SAN) and styrene/maleic anhydride copolymers (SMA), and either PMMA, PEMA, or a methyl methacrylate/acrylonitrile copolymer have also been experimentally mapped by calorimetric and optical methods[7].

The phase relationships for ternary mixtures where one component is a solvent and two are polymers have been described by Scott[20] and Tompa[21] using the lattice theory of Flory and Huggins. Robard and Patterson[16] have demonstrated the existence of the $\Delta\chi$ effect in ternary polymer solutions. A salient example is the closed-loop region of immiscibility in the PS–poly(vinyl methyl ether)–chloroform solution. The extension of the model to ternary polymer melts has been conducted by Su and Fried[22]. They computed spinodal curves and critical points for different combinations of the binary interaction parameters, thus providing some useful observations on trends in the phase diagrams of ternary polymers. They did not calculate any coexistence curves or tie-lines, however. The effect of the asymmetry in the interaction parameters as well as the difference in molecular weight on the coexistence curves have been simulated by Hsu and Prausnitz[23].

In this paper, we investigated the isothermal phase diagram of a ternary homopolymer blend of PS, poly(cyclohexylacrylate) and poly(2-chlorostyrene) (PS–PCHA–P2ClS). The three pairs were found to be miscible at 433 K. Light scattering was used to determine the phase diagram. The data were subsequently analysed within the framework of the Flory–Huggins–Scott model.

EXPERIMENTAL

PCHA was prepared from cyclohexylacrylate (Polysciences, Inc.) in an ethyl methyl ketone solution at 60°C using 2,2-azobisisobutyronitrile as the initiator. The molecular weight was determined by size exclusion chromatography on a Waters 840 with three microstyrogel column sets (10^3 Å, 10^4 Å and 10^5 Å). Five monodisperse PS materials were used for the molecular weight calibration, using tetrahydrofuran (THF) as the elution solvent. The number-average molecular weight of PCHA was measured to be 60000 g mol^{-1} with a polydispersity of 2.2. PS ($M_w = 35000$ g mol^{-1}, $M_w/M_n = 1.04$) and P2ClS ($M_w = 65000$ g mol^{-1}, $M_w/M_n = 1.4$) were obtained from Polysciences, Inc.

All of the blends were prepared by dissolution in THF followed by precipitation into a 10-fold excess of non-solvent (methanol). The precipitated samples were washed with fresh methanol several times to remove the remaining THF and then dried in a vacuum oven at 373 K for 24 h. These blends were directly used for the thermal studies. For light scattering measurements, thin polymer films ($\sim$50–70 μm) were prepared by casting from a THF solution onto a glass plate. The films were further annealed at 373 K under vacuum to ensure that all residual solvent was removed. The samples were sandwiched between cover glass slides prior to measurement. All cast films were transparent, a necessary (but not sufficient) indication of single phase.

The thermal measurements were obtained on a Seiko DSC model 220C at a heating rate of 10°C min^{-1} under a nitrogen blanket. Indium and tin were used as calibration standards. Approximately 10 mg of sample were employed in each experiment. The glass transition temperature (T_g) was determined as the temperature of the midpoint of the heat capacity change. Each sample was annealed at 433 K for 1 h prior to measurements.

Small-angle laser light scattering experiments were performed using a two-dimensional 14-bit charge-coupled detector (OMAIII from EG&G Princeton Applied Research). The incident light was a 0.5 mW He–Ne laser ($\lambda = 6328$ Å). The scattered light was made parallel with two large aperture lenses and subsequently collected on the detector. The geometry of the detector was selected so that the entire scattering pattern could be observed at once. This mode of detection permits the measurement of the scattered light at different angles simultaneously. Data processing was performed with an on-line computer. The coexistence curves were constructed by using data from isothermal experiments. If no apparent increase in light scattering intensity was observed within a 6 h period at a specified temperature, then the sample was considered to be outside the immiscibility region (or below the coexistence curve in the binary blends). If an increase in scattering intensity was observed, then the blend was taken to be in the multiphase region.

RESULTS AND DISCUSSION

Qualitative phase behaviour

Figure 2 displays the isothermal phase diagram of the ternary PS–PCHA–P2ClS blend at 433 K obtained from light scattering. Although a large region of miscibility occupies much of the triangle, a closed region of immiscibility is located near the PS apex and slightly shifted toward the PS–P2ClS line. From the location and shape of the closed-loop region, numerical studies, as well as reasoning by analogy with ternary polymer solution behaviour[22,23] indicated that the magnitude of three binary interactions follows the order:

$$\chi_{\text{PCHA-P2ClS}} < \chi_{\text{PCHA-PS}} \approx \chi_{\text{PS-P2ClS}} \qquad (1)$$

Glass transition temperature

A simple, although qualitative, way to confirm this is to compare the curvature of the compositional dependence of the glass transition of the three pairs. For this purpose, the glass transition of the mixture can be expressed simply as the volume fraction average of the components. This relation is a natural consequence

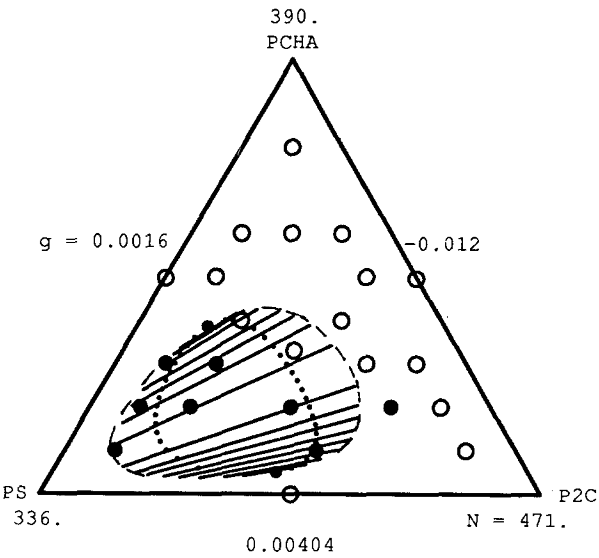

Figure 2 Ternary phase diagram of PS–PCHA–P2ClS blends at T=433 K. The open circles represent compositions in which only a single phase was observed; the large closed circles have two phases; the smaller closed circles are the two calculated critical points. The calculated spinodal is shown by the dotted line

Table 1 Glass transition temperature (K) of the three miscible pairs

Weight fraction (first component)	PS–PCHA	P2ClS–PS	P2ClS–PCHA
0	303	378	303
0.2	317	380	316
0.3	322	381	326
0.5	336	386	347
0.7	350	391	368
0.8	361	394	376
1	378	403	403

of the Kelley–Bueche relation[24], derived from the assumption of additivity of free volume:

$$T_g=\frac{\phi_1 T_{g1}+k\phi_2 T_{g2}}{\phi_1+k\phi_2} \tag{2}$$

where ϕ_i and T_{gi} are the volume fraction and glass transition of component i, respectively. Although the constant k has a well defined molecular significance[25], it can be used as a fitting parameter[26]. In this case, the parameter k provides a qualitative comparison of the strength of the intersegmental interaction. It has been shown that the concavity of the T_g–composition is inversely proportional to the strength of the intersegmental interaction between the two polymers[27]. D.s.c. thermograms of all three pairs exhibit single, composition-dependent T_gs which are shown in *Table 1* and plotted in *Figures 3–5*. The dashed lines were obtained from the fits of the data to equation (2). Values of k=0.5, 0.75 and 0.85 were obtained for PS–P2ClS, PS–PCHA and P2ClS–PCHA, respectively. The consistency of those values with equation (1) is gratifying.

Some measurements of T_g inside the ternary were also made. None of the d.s.c. curves gave two T_gs, and this contrasts with the observations that samples 2, 3 and 10 separated into two phases as determined from light scattering. This may be due to the different rates used in the two sorts of measurement, or due to the relatively small differences in the compositions of the separated phases. The proper expression for the dependence of the T_g as a function of composition when the composition is inside the ternary is somewhat problematic. An expression, that reduces to (2) when the composition is on one of the sides of the simplex is:

$$\begin{aligned} T_g=&\frac{(w_1w_2)}{s}\left[\frac{w_1T_1+k_{12}(1-w_1)T_2}{w_1+k_{12}(1-w_1)}\right]\\ &+\frac{(w_1w_3)}{s}\left[\frac{w_1T_1+k_{13}(1-w_1)T_3}{w_1+k_{13}(1-w_1)}\right]\\ &+\frac{(w_3w_2)}{s}\left[\frac{w_3T_3+k_{23}(1-w_3)T_2}{w_3+k_{23}(1-w_3)}\right] \end{aligned} \tag{3}$$

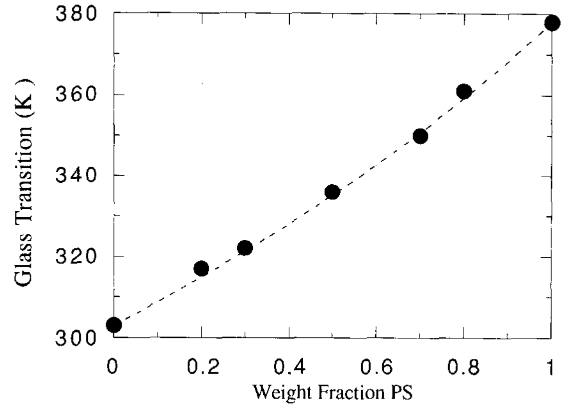

Figure 3 Glass transition temperature of PS–PCHA as a function of PS content

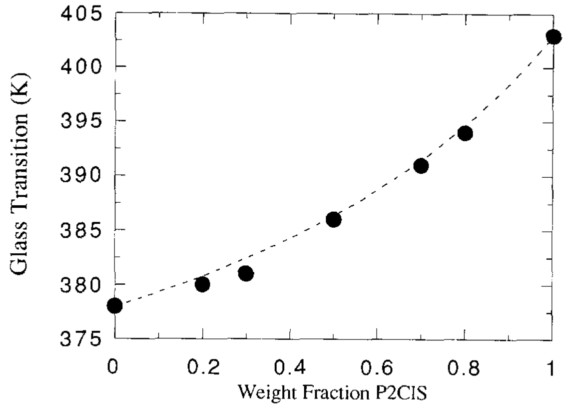

Figure 4 Glass transition temperature of PS–P2ClS as a function of PS content

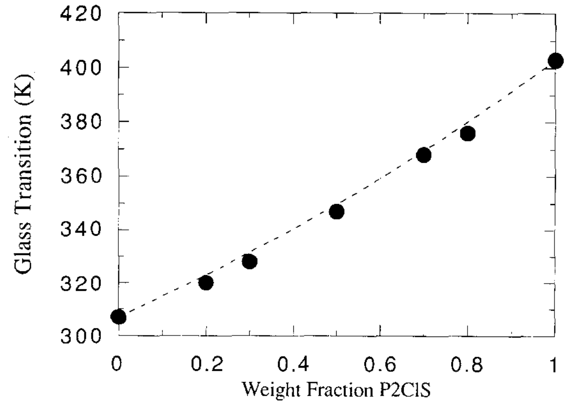

Figure 5 Glass transition temperature of PCHA–P2ClS as a function of P2ClS content

Table 2 Glass transition temperature (K) of the ternary mixtures

	Weight fraction			No. of	T_g		
Sample	PS	PCHA	P2ClS	phases	Exp.	Eqn (4)	Eqn (3)
1	0.3	0.3	0.3	1	358	360	363
2	0.6	0.2	0.2	2	369	364	371
3	0.2	0.2	0.6	2	375	373	379
4	0.2	0.6	0.2	1	340	333	338
5	0.5	0.5	0.0	1	339	336	346
6	0.5	0.0	0.5	1	386	390	395
7	0.0	0.5	0.5	1	349	346	349
8	0.2	0.4	0.4	1	354	352	358
9	0.4	0.4	0.2	1	352	348	355
10	0.4	0.2	0.4	2	371	369	376

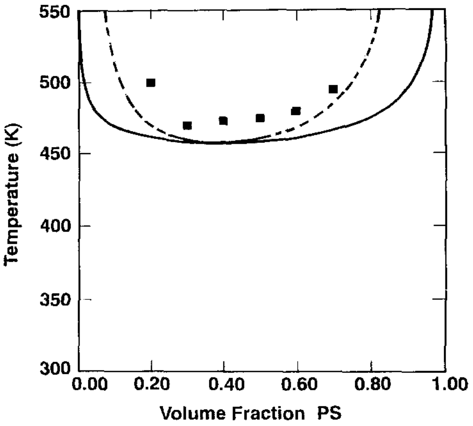

Figure 6 Phase diagram for the PS–PCHA system observed as a function of temperature. The dashed line is the calculated spinodal and the solid line is the calculated coexistence curve

where

$$s = w_1w_2 + w_2w_3 + w_1w_3$$

Obviously this expression is not unique, and others might be readily contrived. A Fox–Flory expression, on the other hand, would predict for the miscible blends that:

$$1/T_g = \sum_{i=1}^{3} w_i/T_i \tag{4}$$

Table 2 shows a comparison of the experimental values with those calculated according to these two expressions. The Fox–Flory expression gave results in closer agreement with the experimental values: the average deviation was 2.2°C for the former, as opposed to -3.7°C for the latter. Neither formula gave results that were more in error for the two-phase compositions than for the miscible cases.

Binary phase behaviour

The actual magnitude of the χ_{ij}s may be determined from the measurement of the coexistence curve of each binary *ij* pair. The phase behaviour of the PS–P2ClS system was extensively investigated by Zacharius *et al.*[28] and Kwak *et al.*[29]. The interaction parameter has been found to be very weak and almost independent of temperature. Kwak *et al.* have determined the temperature dependence of $\chi_{\text{PS–P2ClS}}$ to be:

$$\chi_{\text{PS–P2ClS}} = 0.0078 - 1.63/T \tag{5}$$

For the interaction parameter between PS and PCHA we made similar observations on the coexistence curve for the binary. In order to observe a lower critical solution temperature (*LCST*) within a reasonable temperature range (<473 K), we used a PS with a molecular weight of 180000 g mol^{-1}. *Figure 6* displays the measured coexistence curve. The blend exhibits a *LCST* with a critical point at $T_c = 463$ K and $\phi_c = 0.35$. The dashed and solid curves represent the spinodal and coexistence curve, respectively, obtained from the best fit of the data using the Flory–Huggins model. The interaction parameter obtained from the data-fitting gave:

$$\chi_{\text{PS–PCHA}} = 0.02 - 7.97/T \tag{6}$$

For the PCHA–P2ClS pair, it was not possible to determine the interaction parameter by this method because the *LCST* (within the range of available molecular weights) is probably located above 563 K which is above the limit imposed by degradation of the sample. We therefore estimated this interaction parameter from the observed ternary phase diagram (see below).

Ternary phase diagram

For mixtures containing only polymeric components, mean field theory provides an adequate framework for analysis of its phase relation[30]. For a ternary system, the Flory–Huggins free energy of mixing, $\Delta G_{123}^{\mathrm{M}}$, per unit volume of the mixture may be approximated by:

$$\beta\Delta G_{123}^{\mathrm{M}} = \sum_{i=1}^{3} \frac{\phi_i}{N_i} \ln \phi_i + \sum_{i<j} g_{ij}\phi_i\phi_j \tag{7}$$

where $\beta = (k_bT)^{-1}$, g_{ij} is the binary interaction parameter (taken to be independent of composition) between polymer *i* and polymer *j*, ϕ_i is the volume fraction and N_i is the degree of polymerization. Differentiation with respect to the volume fraction leads to the chemical potential for the three components:

$$\begin{aligned}\beta\Delta\mu_1 = \ln\phi_1 + \left(1 - \frac{N_1}{N_2}\right)\phi_2 + \left(1 - \frac{N_1}{N_3}\right)\phi_3 \\ + N_1[g_{12}\phi_2^2 + g_{13}\phi_3^2 + (g_{12} + g_{13} - g_{23})\phi_2\phi_3)]\end{aligned} \tag{8}$$

$$\begin{aligned}\beta\Delta\mu_2 = \ln\phi_2 + \left(1 - \frac{N_2}{N_1}\right)\phi_1 + \left(1 - \frac{N_2}{N_3}\right)\phi_2 \\ + N_2[g_{12}\phi_1^2 + g_{23}\phi_3^2 + (g_{12} + g_{23} - g_{13})\phi_1\phi_3)]\end{aligned} \tag{9}$$

$$\begin{aligned}\beta\Delta\mu_3 = \ln\phi_3 + \left(1 - \frac{N_3}{N_1}\right)\phi_2 + \left(1 - \frac{N_1}{N_3}\right)\phi_1 \\ + N_3[g_{13}\phi_1^2 + g_{23}\phi_2^2 + (g_{13} + g_{23} - g_{12})\phi_1\phi_2)]\end{aligned} \tag{10}$$

The spinodal is given by the condition:

$$J \equiv \begin{vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{vmatrix} = 0 \tag{11}$$

where

$$G_{ij} = \frac{\partial^2 \Delta G_{\mathrm{M}}}{\partial\phi_i \partial\phi_j} \tag{12}$$

The critical point is required to satisfy condition (11) as well as:

$$U_{\mathrm{cr}}=\begin{vmatrix} \dfrac{\partial J}{\partial \phi_1} & \dfrac{\partial J}{\partial \phi_2} \\ G_{21} & G_{22} \end{vmatrix}=0 \qquad (13)$$

With only two phases present, the compositions of the coexisting phases are determined by equating the chemical potentials of each component in both phases. Choosing the two independent components to be 1 and 3, and equating weight and volume fractions, gives three non-linear equations:

$$\begin{aligned} \mu_1(\phi_1', \phi_3') &= \mu_1(\phi_1'', \phi_3'') \\ \mu_2(\phi_1', \phi_3') &= \mu_2(\phi_1'', \phi_3'') \\ \mu_3(\phi_1', \phi_3') &= \mu_3(\phi_1'', \phi_3'') \qquad (14) \end{aligned}$$

where the primes and double primes refer to the two phases. The isothermal phase diagram of the ternary system is therefore completely determined by the knowledge of the three binary interaction parameters χ_{ij} and the molecular weight of the components N_i. Thus, the spinodal, the critical points and the tie-lines of the ternary blend can all be computed. This was carried out in our case by a program written using Mathematica. Its built-in function 'FindRoot' was used to construct the tie-lines from the three simultaneous non-linear equations for the equality of the chemical potential. The functions 'Solve' were used to obtain the spinodal and critical points.

Figure 2 displays the experimental results obtained by light scattering on the PS–PCHA–P2ClS blends. A region of incompatibility in the interior of the simplex clearly exists. A phase diagram was constructed using values of the binary interaction parameters obtained from equations (5) and (6) at $T=433$ K, and with the binary interaction parameter $\chi_{\mathrm{PCHA-P2ClS}}$ adjusted to approximate the observed closed-loop region. The experimentally determined closed-loop region of *Figure 2* is satisfactorily reproduced for values of $\chi_{\mathrm{PCHA-P2ClS}} \cong -0.012$. The two-phase closed loop first appears for $\chi_{\mathrm{PCHA-P2ClS}}$ at ~ -0.008 and is clearly too large when it is ~ -0.020. The calculated tie-lines and critical points using the parameters shown in *Figure 2* are also displayed for comparison to the experimental results. The agreement between the calculated and experimental results, while not perfect, is probably satisfactory considering the well-known shortcomings of the Flory–Huggins model. From the calculated phase diagram, one may infer that inside the closed-loop region and away from the two critical points the mixture separates into two phases: one phase is dominated by the strongly interacting PCHA–P2ClS and the other phase consists predominantly of PS. The calculated tie-lines are seen to slope upward to the axis representing the binary system with the larger interaction parameter (P2ClS–PCHA). This is a natural consequence of the asymmetry in the binary interaction parameters. The calculated phase diagram also exhibits two critical points at PS:PCHA = {0.50:0.05} and {0.474:0.038}. Experimental data on these predictions are not currently available but would be informative.

CONCLUSIONS

The system PS, PCHA and P2ClS has a phase diagram in which each polymer pair is separately miscible and apparently has a closed loop miscibility gap in the ternary at 433 K. From the position of the miscibility gap compared to that calculated from the Flory–Huggins mean field model, we infer that the PCHA–P2ClS pair has a negative interaction parameter, smaller than the other two pairwise interaction parameters.

REFERENCES

1 Utracki, L. A. 'Polymer Blends and Alloys', Hanser, New York, 1989

2 Wignal, G. D. in 'Encyclopedia of Polymer Science and Engineering' Vol. 10, 2nd edn, Wiley, New York, 1987, p. 112

3 Paul, D. R. and Newman, S. 'Polymer Blends', Vol. 2, Academic Press, New York, 1978

4 Walsh, D. J., Higgins, J. S. and Maconnachie, A. in 'Polymer Blends and Mixtures', Nato ASI Series, Series E, No. 89, Applied Science, London, 1985

5 Olabisi, O., Robeson, L. M. and Shaw, M. T. in 'Polymer–Polymer Miscibility', Academic Press, New York, 1979

6 Leibler, L. *Makromol. Chem. Rapid Commun.* 1981, **2**, 393

7 Brannock, G. R. and Paul, D. R. *Macromolecules* 1990, **23**, 5240

8 Tseng, H. S., Lloyd, D. R. and Ward, T. C. *J. Polym. Sci.* 1991, **29**, 161

9 Keitz, J. D., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1984, **29**, 3131

10 Kwei, T. K., Frisch, H. L. and Radigan, W. *Macromolecules* 1977, **10**, 157

11 Goh, S. H., Siow, K. S. and Yap, K. S. *Thermochim. Acta* 1986, **105**, 191

12 Ameduri, B. and Prud'homme, R. E. *Polymer* 1988, **29**, 1052

13 Shah, V. S., Keitz, J. D., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1986, **32**, 3863

14 Rigby, D., Lin, J. L. and Roe, R. J. *Macromolecules* 1985, **18**, 2269

15 Kim, K. E., Chiou, J. S., Barlow, J. W. and Paul, D. R. *Polymer* 1987, **28**, 1721

16 Robard, A. and Patterson, D. *Macromolecules* 1977, **10**, 1021

17 Su, C. S. and Patterson, D. *Macromolecules* 1977, **10**, 709

18 Bhattacharyya, C., Maiti, N., Mandal, B. M. and Bhattacharyya, S. N. *Macromolecules* 1989, **22**, 487

19 Jo, W. H., Kwon, Y. K. and Kwon, I. H. *Macromolecules* 1991, **24**, 4708

20 Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279

21 Tompa, H. *Trans. Faraday Soc.* 1949, **45**, 1142

22 Su, A. C. and Fried, J. R. *Polym. Eng. Sci.* 1987, **27**, 1657

23 Hsu, C. C. and Prausnitz, J. M. *Macromolecules* 1974, **7**, 320

24 Kelley, F. N. and Bueche, F. *J. Polym. Sci.* 1961, **50**, 549

25 Schneider, H. A. *Makromol. Chem.* 1988, **189**, 1941

26 Belorgey, G. and Prud'homme, R. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 191

27 Ting, S. P., Pearce, E. M. and Kwei, T. K. *J. Polym. Sci., Polym. Lett. Edn* 1980, **18**, 20

28 Zacharius, S. L., ten Brinke, G., MacKnight, W. J. and Karasz, F. E. *Macromolecules* 1983, **16**, 381

29 Kwak, K. D., Okada, M. and Nose, T. *Polymer* 1991, **32**, 864

30 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979, Ch. 4