

In-situ polymerization of n-butyl acrylate in poly(vinyl chloride)

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The *in situ* polymerization of n-butyl acrylate with poly(vinyl chloride) has been studied. Butyl acrylate was polymerized using a peroxydicarbonate initiator and a thiol chain transfer agent in the presence of poly(vinyl chloride) beads suspended in water. The products were examined, after pressing into sheets, for optical clarity and by dynamic mechanical analysis. It was found that if 10% butyl acrylate was present in the mixture homogeneous blends were formed but if 15% or more butyl acrylate was present two phase mixtures were formed. If homogeneous blends prepared as above were reswollen in butyl acrylate, and the latter then polymerized, homogeneous blends containing more poly(butyl acrylate) could be prepared. The interaction parameters between both poly(vinyl chloride) and poly(butyl acrylate) and butyl acrylate were estimated by inverse gas chromatography. Using these and an estimate of the polymer/polymer interaction parameter the three component phase diagram could be qualitatively explained.

(Keywords: poly(vinyl chloride); poly(butyl acrylate); miscibility; compatibility; polymerization *in situ*)

INTRODUCTION

At one time it was thought that very few polymers were miscible but the list of miscible pairs is now large and still growing. Lists of such pairs can be found in a variety of books and reviews^{1,2}. Poly(vinyl chloride) (PVC) has been found to be miscible with a wide range of polymers containing electron donor groups such as esters. This has been attributed to the formation of specific interactions involving the methine hydrogen of PVC^{3,4}.

We have previously shown PVC to be miscible with a wide range of polyacrylates and polymethacrylates⁵. In the particular case of poly(n-butyl acrylate) (PBA), this polymer was found to be miscible with PVC but 50/50 mixtures were found to phase separate when heated to temperatures above 120°C.

There are three main methods for the preparation of homogeneous polymer blends: mechanical mixing, mixing in a common solvent followed by precipitation or evaporation, and *in-situ* polymerization. Mechanical mixing is not suitable for many pairs due to the low diffusion rates in bulk polymers, the poor thermal stability of many polymers, and the fact that many pairs are thermodynamically immiscible at higher temperatures. Mixing in a common solvent is the commonest method for producing blends but in some cases miscible pairs can produce heterogeneous blends. This is more likely when there is a large difference between the two individual polymer/solvent interaction parameters⁶. Mixing in a common solvent also could have only limited practical applicability. *In-situ* polymerization is the polymerization of one monomer in the presence of another polymer. It was widely used to produce heterogeneous polymer blends, for example in high impact polystyrene. It is also a very attractive method of producing homogeneous blends.

In-situ polymerization of vinyl chloride in chlorinated polyethylene has been used to prepare PVC blends⁷. More recently we have described the *in-situ* polymerization of vinyl chloride in poly(n-butyl acrylate)⁸. In this case a two phase region existed within the vinyl chloride/PVC/PBA three component phase diagram as shown in Figure 1. Polymerization of a mixture from point A to B produces a homogeneous blend whereas polymerization from E to F passing through the two phase region produces a heterogeneous blend. If the blend at composition B is reswollen with vinyl chloride to C and then polymerized, using a route avoiding the two

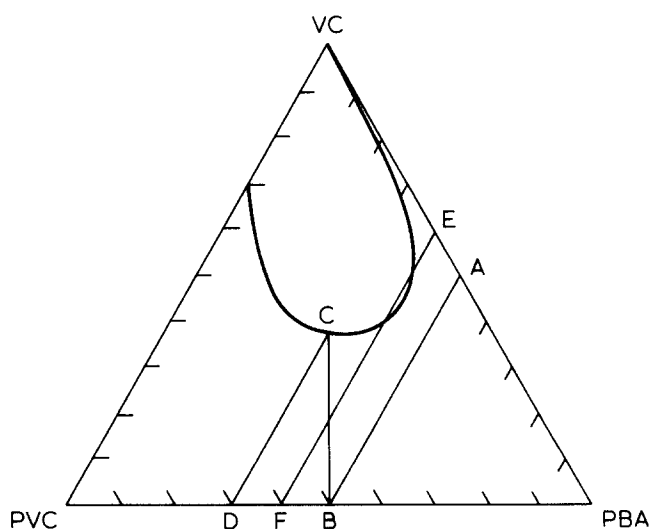


Figure 1 The three component phase diagram for vinyl chloride/poly(vinyl chloride)/poly(n-butyl acrylate). The solid lines represent polymerization pathways

phase region, then a homogeneous blend of composition D can be produced.

In this paper we describe an alternative route to this blend by the *in-situ* polymerization of *n*-butyl acrylate in PVC. This has some advantages in the laboratory due to the well-known dangers of vinyl chloride monomer. The blends produced by these two methods may be different in certain ways. Firstly, residual *n*-butyl acrylate may be more difficult to remove than vinyl chloride. Secondly, the problems associated with any possible grafting between the phases may be different. Thirdly, the detailed morphology of the blend may be different because of the particle structure and partial crystallinity of PVC. We also expect a difference in the monomer/polymer/polymer three component phase diagram when *n*-butyl acrylate replaces vinyl chloride due to the different interactions of the two monomers with the polymers.

EXPERIMENTAL

Materials

Poly(vinyl chloride): suspension polymerized 'flexible grade', I.C.I. *n*-Butyl acrylate: BDH, A.R. grade, was washed twice with (10%) sodium hydroxide solution and twice with distilled water before use. *t*-Butyl cyclohexyl peroxydicarbonate: Laporte. This material was recrystallized from methanol and stored at below 0°C until required. Dodecane-1-thiol: Aldrich chemical. Carboxymethyl cellulose: (Natrosol), Hercules.

Preparation

Blends were prepared by *in-situ* suspension polymerization of *n*-butyl acrylate in poly(vinyl chloride) using *t*-butyl cyclohexyl peroxydicarbonate initiator (0.4% based on *n*-butyl acrylate), and dodecane-1-thiol as a chain transfer agent (0.15 mol% based on *n*-butyl acrylate). Carboxymethyl cellulose was added to the mixture as a stabilizing agent at 0.5% of the total weight.

An example preparation follows. (90 PVC/10 PBA). A 5 litre flanged reaction vessel was fitted with a stirrer, nitrogen bleed, dropping funnel, and condenser. Distilled water (2,500 cm³), carboxymethyl cellulose (1.75 g previously dissolved in some of the hot water) and poly(vinyl chloride) (beads 90 g) were placed into the vessel and stirred. *n*-Butyl acrylate (100 gm); dodecane-1-thiol (0.25 g), and *t*-butyl cyclohexyl peroxydicarbonate (0.4 g) were mixed, placed in the dropping funnel and added dropwise to the flask while stirring the contents. The mixture was gently stirred at room temperature for 24 h in order to achieve equilibrium swelling and then the temperature was increased to 40°C ($\pm 1^\circ\text{C}$) for 24 h when the *n*-butyl acrylate polymerized. The resulting beads were washed several times with water and then with methanol in order to remove the impurities and residual monomer. They were then partially air dried and finally dried in a vacuum oven at 30°C for 96 h.

In the case of multi-step polymerizations the above polymerization procedure was repeated with further additions of initiator, monomer and chain transfer agent after the reaction mixture was allowed to cool to room temperature.

Gel permeation chromatography

This was carried out using a Waters machine with tetrahydrofuran as a solvent. Molecular weights were determined relative to polystyrene standards.

Dynamic mechanical analysis

This was carried out using a 'Dynamic Mechanical Thermal Analyser' (Model PL-DMTA, Polymer Laboratories Ltd.). A strip of the sample was subjected to an imposed oscillatory frequency of 10 Hz. A temperature range of -45° to 150°C was scanned at 3°C min^{-1} heating rate. A plot of $\tan \delta$ against temperature was obtained. A maximum in $\tan \delta$ was taken as a measure of the glass transition temperature (T_g). A single peak suggests a homogeneous blend whereas two separate peaks suggest a two phase structure.

Inverse gas chromatography

This was used to study the interaction of the *n*-butyl acrylate with PVC or PBA. It was carried out using a PYE 104 gas chromatograph equipped with a thermal conductivity detector. The chromatograph was fitted with a 1.5 metre coiled pyrex column which was packed with PTFE (30-60 mesh, Phase Separation) on which the polymers were spread as a thin film. The polymers were weighed and dissolved in butanone (A.R.) at 80% w/w. The PTFE beads were added and the solvent evaporated with stirring to produce a powder which was dried in a vacuum oven for 24 h. The coating weights were 0.12 g per gram of support.

The column was installed and heated to 120°C . Nitrogen was then passed through the column for 6 h in order that it should come to equilibrium. Helium was finally used as the carrier gas. Samples of *n*-butyl acrylate (1 μl , stabilizer removed) were injected into the column using a syringe. Retention times were measured 4 times each at 5 carrier gas flow rates (30 cm³ min⁻¹ max). The non-interacting peak elution time was obtained by injecting a sample of air.

RESULTS AND DISCUSSION

Samples of PVC/PBA were prepared at 90/10, 85/15 and 80/20 compositions using a one-step, two-step and three-step *in-situ* polymerization route respectively. Samples of 85/15 and 80/20 composition were also prepared by a one-step route for comparison.

Samples were analysed by elemental analysis and the compositions determined from the carbon content of the blends accurate to $\pm 1\%$. The actual values PVC/PBA found were 89.2/10.8; 84.6/15.4 and 80.0/20.0 for the one phase blends and 85.0/15.0, 77.2/22.8 for the two phase blends.

A sample of the 84.6/15.4 one phase blend was extracted with cyclohexane (a solvent for PBA but not for PVC) in a Soxhlet extractor for 120 h (after which no further weight loss takes place). The weight extracted was 13.6% of the total weight which represents 88% ($\pm 6\%$) of the poly(*n*-butyl acrylate). This suggests that some grafting might take place during the polymerization.

The three component phase diagram for the system PVC/PBA/*n*-butyl acrylate is shown in Figure 2. A polymerization from A to B produced a product which can be pressed (at 150°C for 4 mins) to give a clear sheet. Polymerization from C to G and H to J produce cloudy products. If a blend of composition B is reswollen to F, after polymerization from F to G a clear product results. If this is again reswollen to I, again on polymerization from I to J, a clear product results. All of the samples were

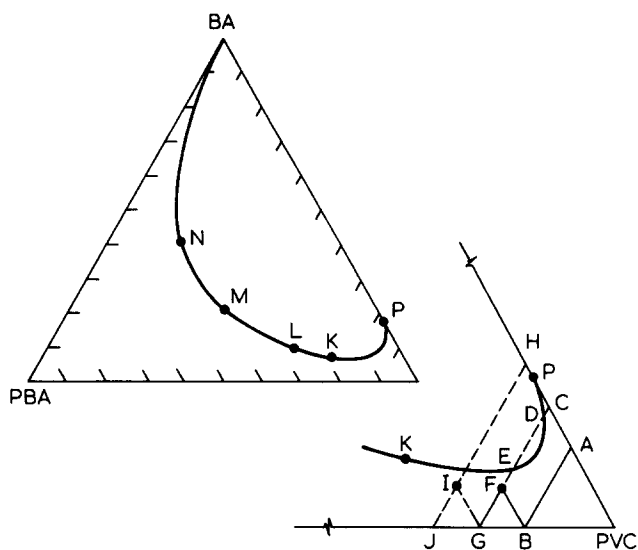


Figure 2 The three component phase diagram for *n*-butyl acrylate/poly (vinyl chloride)/*n*-butyl acrylate). Also shown is an expansion of the bottom, right corner of the diagram showing the polymerization pathways used in this work

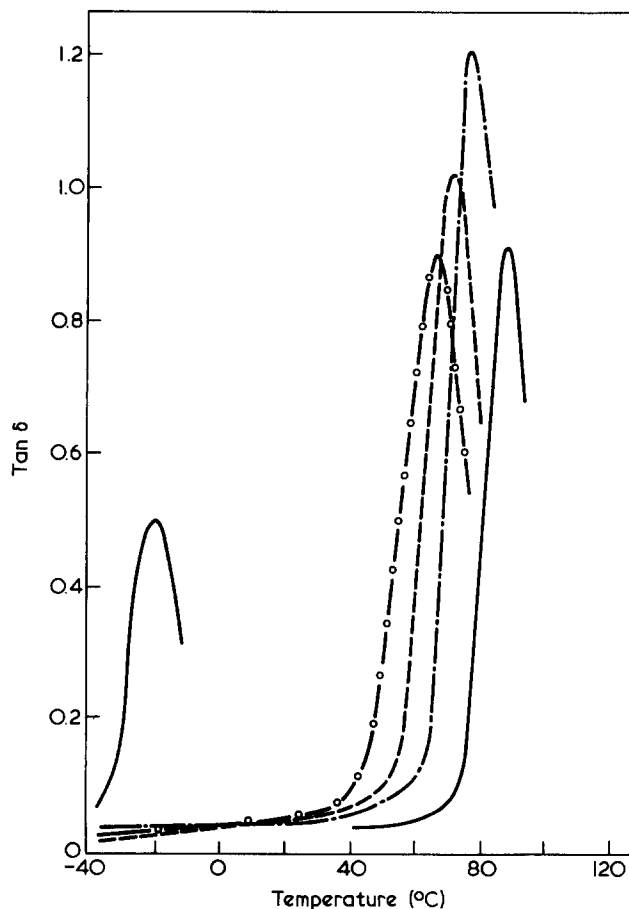


Figure 3 Plots of $\tan \delta$ against temperature for PVC, PBA and blends of PVC/PBA at 90/10 (-----), 85/15 (-----), and 80/20 (-----). The glass transition temperatures (T_g) of samples are 89°C, -20°C, 78°C, 72°C, and 67°C respectively

pressed at temperatures below the expected phase separation temperatures of the blend reported earlier⁸.

The cloud point curve was obtained by swelling various PVC/PBA blends with *n*-butyl acrylate. Points N, M, and L were obtained by swelling blends prepared in the *in-situ* polymerization of vinyl chloride in PBA, the preparation

of which was described in a previous paper⁸. Point K was obtained by swelling the blend at point J. Point P was obtained by swelling PVC itself. All of these points are obtained by a crude visual observation of maximum *n*-butyl acrylate uptake and the errors are probably of the order of $\pm 3\%$ in the degree of swelling. Point P may be the most inaccurate due to the structure of PVC. Thus polymerization from C produces a heterogeneous blend probably because at some point D it passes into the two phase region. When it leaves the two phase region at E the mobility of the polymers and sizes of the phase separated regions are such that the polymers do not remix. This explanation however relies on the accuracy of the cloud point diagram. It might be possible that composition C was never homogeneous.

The homogeneity of the blends was confirmed by using dynamic mechanical analysis. *Figure 3* shows plots of $\tan \delta$ against temperature for PVC, PBA and PVC/PBA blends at 90/10, 85/15 and 80/20 compositions prepared by one, two and three-step *in-situ* polymerizations. Single glass transitions are observed at temperatures intermediate between those of the component polymers.

Figure 4 shows a comparison of 85/15 PVC/PBA blends prepared by one-step and two-step routes. The two-step blend shows a single peak whereas the one-step blend shows two peaks, one close to that of the 90/10 homogeneous blend and the other close to that of pure PBA. It would be expected from theoretical considerations that one component would be pure PBA as will be described later.

The base polymer and the blends were analysed by gel permeation chromatography and the results are shown in *Table 1*. These values are relative to polystyrene standards and take no account of the different values of refractive

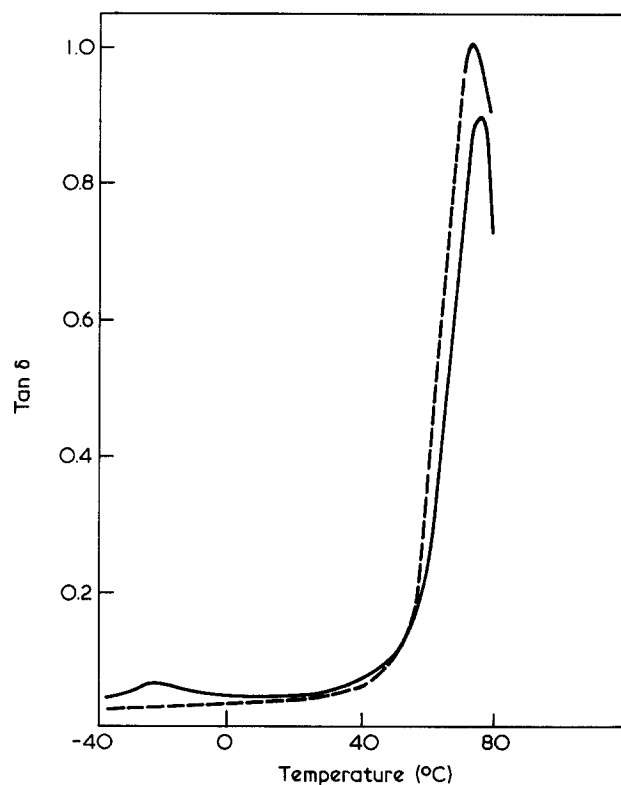


Figure 4 Plots of $\tan \delta$ against temperature for blends of PVC/PBA at 85/15 composition prepared by a one-step (—), and a two-step (---) process

Table 1 G.p.c. results for polymers and blends

Polymer	\overline{M}_n	\overline{M}_w	$\overline{M}_w/\overline{M}_n$
PBA	320 000	992 000	3.1
PVC	88 000	202 000	2.3
90/10	93 000	223 200	2.4
85/15	95 000	228 000	2.4
80/20	95 000	228 000	2.4

index for the two polymers (dn/dc in THF, PBA=0.065 and PVC=0.11) which means that the PBA will make a smaller contribution. It does however show that there is no overall change in the molecular weight which means that the new polymer prepared has the same order of molecular weight as the base PVC. If no chain transfer agent has been included, a much higher molecular weight PBA would have been synthesized. The properties of pure PBA as used in dynamic mechanical analysis are shown in Table 1.

The origins of three component phase diagram can be understood in terms of the three interaction parameters χ_{12} (PVC/*n*-butyl acrylate), χ_{13} (PBA/*n*-butyl acrylate) and χ_{23} (PVC/PBA). This was done in the same way as reported previously for the vinyl chloride/PVC/PBA phase diagram⁸. χ_{12} and χ_{13} were estimated by using inverse gas chromatography and a value χ_{23} was inferred also from inverse gas chromatography results reported previously⁵. We did not believe inverse gas chromatography to be a reliable method for reasons discussed elsewhere⁹, but it does give a first order approximation of the interaction parameter. The technique has been reviewed in detail by Braun and Guillet¹⁰.

From the measurement we can determine the specific retention volume at 273.15 K by:

$$V_g = (t_s - t_m) Q \frac{j273.15}{WT}$$

where t_m is the retention time for a non-interacting material, air, W is the weight of stationary phase, T is the operating temperature, and j is the correction factor gas compressibility, given by:

$$j = \frac{3[(P_i/P_0)^2 - 1]}{2[(P_i/P_0)^3 - 1]}$$

where P_i is the inlet pressure and P_0 is the outlet pressure. The values of V_g are extrapolated to zero flow rate to give V_g^0 .

The interaction parameter χ is given by:

$$\chi = \ln \left(\frac{273.15 R v_2}{V_g^0 P_1^0 V_1} \right) - \left(1 - \frac{V_1}{(\overline{M}_2)_n v_2} \right) - \frac{P_1^0}{RT} (B_{11} - V_1)$$

where v_2 = specific volume of polymer; V_1 = molar volume of solvent; $(\overline{M}_2)_n$ = number average molecular weight of polymer; P_1^0 = saturated vapour pressure of solvent; and B_{11} = second virial coefficient.

V_1 was estimated for *n*-butyl acrylate by the relationship of molecular weight and specific volume to be $142.63 \text{ cm}^3 \text{ mol}^{-1}$ under the conditions of the experiment (120°C).

B_{11} was estimated to be $-1905.54 \text{ cm}^3 \text{ mol}^{-1}$ ¹¹ using

the critical properties V_c , and T_c estimated by the Lyderson Method¹². P_1^0 was taken as 0.156 atm ¹³. For PVC, v_2 was taken as $0.722 \text{ cm}^3 \text{ g}^{-1}$ ¹⁴ and \overline{M}_n was measured as 88 000 by g.p.c. relative to polystyrene standards. For PBA, v_2 was taken as $0.893 \text{ cm}^3 \text{ g}^{-1}$ ¹⁴ (based on the group contribution) and \overline{M}_n was measured as above to be 320 000. The measured values of V_g^0 and the calculated χ values are shown in Table 2. It should be pointed out that these values are calculated for 120°C , the temperature of the inverse gas chromatography experiment, whereas the polymerization was actually carried out at 40°C . We have no way of knowing whether the values at 40°C will be higher or lower and these values should therefore only be considered as a rough guide.

They show a very unfavourable interaction for *n*-butyl acrylate/PVC. The value for *n*-butyl acrylate/PBA must be too high as we know PBA is completely soluble in *n*-butyl acrylate at room temperature. This must therefore be at or below the critical value of $\chi = 0.5$. χ_{23} (PVC/PBA) is estimated as before⁸ to have a small negative value and we choose an initial estimate of -0.1 .

Calculating binodals from interaction parameters is usually very difficult but in this case, as previously⁸, it is relatively simple. As the molecular weights of the two polymers tend toward infinity, the critical point tends towards the apex of the triangle. The tie lines thus must radiate from the apex. The binodal thus represents a line joining compositions where the chemical potential is equal to that of pure monomer (*n*-butyl acrylate) thus since¹⁵,

Table 2 Results of inverse gas chromatography

	V_g^0 ($\text{cm}^3 \text{ g}^{-1} \text{ K}^{-1}$)	χ
PVC/ <i>n</i> -butyl acrylate	20.79	1.51
PBA/ <i>n</i> -butyl acrylate	60.86	0.65

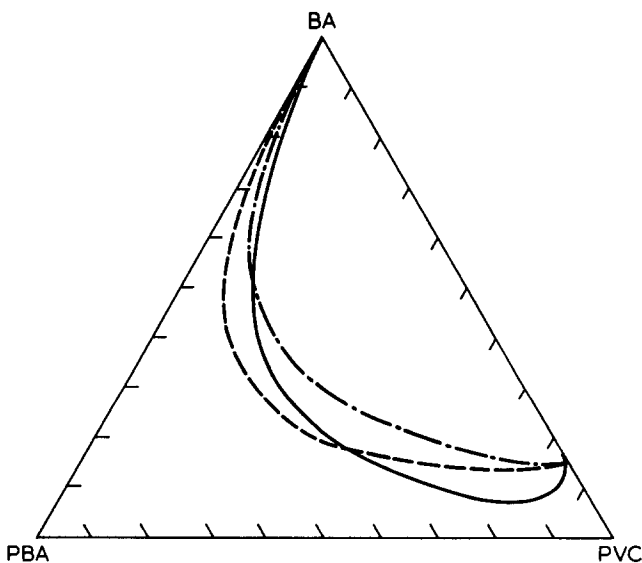


Figure 5 The theoretical three component phase diagram for *n*-butyl acrylate/poly(vinyl chloride)/poly(*n*-butyl acrylate); component 1/2/3, using values of (—) $\chi_{12}=1.51$, $\chi_{13}=0.5$, and $\chi_{23}=-0.1$; (---) $\chi_{12}=1.51$, $\chi_{13}=0.5$, and $\chi_{23}=-2.0$. The solid line shows the experimental phase diagram

$$\begin{aligned} \frac{\Delta\mu_i}{RT} &= \ln \phi_1 + 1 - m_1 \sum \frac{\phi_i}{m_i} + m_1 \sum \chi_i \phi_i \\ &\quad - m_1 \sum \chi_{ij} \phi_i \phi_j \\ &= \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right) \phi_2 + \left(1 - \frac{m_1}{m_3}\right) \phi_3 \\ &\quad + [\chi_1(\phi_2 + \phi_3)^2 + \chi_2 \phi_2^2 + \chi_3 \phi_3^2] m_1 \end{aligned}$$

where μ_i = chemical potential of component i ; m_i = number of segments of species i ; ϕ_i = volume fraction of component i ; $2\chi_1 = \chi_{12} + \chi_{13} - \chi_{23}$; and χ_2, χ_3 similarly.

Putting $m_1 = 1$ and letting m_2 and m_3 tend to infinity, simplifying, eliminating ϕ_3 (since $\phi_1 + \phi_2 + \phi_3 = 1$), and collecting terms we obtain:

$$\begin{aligned} \ln \phi_1 + 1 + \chi_{13} - (1 - 2\chi_{13})\phi_1 + \chi_{13}\phi_1^2 \\ - 2\chi_3(1 - \phi_1)\phi_2 + \chi_{23}\phi_2^2 = 0 \end{aligned}$$

This gives a quadratic for ϕ_2 for any chosen value of ϕ_1 and the phase boundary can be easily calculated. The resulting phase diagram using our initial values of $\chi_{12} = 1.51$, $\chi_{13} = 0.5$, and $\chi_{23} = -0.1$ is shown in *Figure 5* and is a good match considering the approximations made. The main difference lies in the curvature near to the PVC corner of the triangle. In order to try and simulate this feature, we varied the interaction parameters but we were not able to simulate it. Even with a value of $\chi_{23} = -2$ it could not be reproduced as shown in *Figure 5*. (It is a paradox that a lower value of χ_{23} , which means that the polymers are more miscible, makes the area of immiscibility in the three component diagrams larger, but if the polymers have a strong interaction they then have a greater tendency to push out the third component.) The fact that we cannot simulate this feature does not however necessarily mean that it does not exist. Our calculations are based on a simple Flory-Huggins approximation which may not be appropriate for a complex system with free volume changes and specific interactions between the components.

CONCLUSION

Homogeneous blends of poly(vinyl chloride) and poly(*n*-butyl acrylate) can be prepared by the *in-situ* polymerization of *n*-butyl acrylate with PVC. If less than 10% *n*-butyl acrylate is present in the mixture a homogeneous blend can be formed by direct polymerization. If more than 10% *n*-butyl acrylate is present the polymerization route passes through a two-phase region in the *n*-butyl acrylate/PVC/PBA three component phase diagrams and inhomogeneous blends result. Homogeneous blends within these compositions can be prepared by polymerization with less than 10% *n*-butyl acrylate followed by re-swelling with *n*-butyl acrylate and repolymerization, thus avoiding the two phase region. The three component phase diagram can be qualitatively explained in terms of the interaction parameters between the components.

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