

Miscibility and phase diagrams for poly(vinyl methyl ether) and polyacrylate blend systems

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The miscibility of binary polymer blend systems consisting of poly(vinyl methyl ether) (PVME) and polyacrylates has been studied. Based on film clarity, glass transition temperature and cloud-point studies, PVME is found to be miscible with poly(ethyl acrylate), poly(*n*-propyl acrylate) and poly(*n*-butyl acrylate) but not with poly(methyl acrylate). The phase diagrams of some of these blends are reported.

(Keywords: compatibility; poly(vinyl methyl ether); polyacrylates; glass transition temperature; cloud point; lower critical solution temperature)

INTRODUCTION

The combinatorial entropy of mixing in polymer-polymer systems being negligibly small, a stable polymer-polymer mixture usually results when the components of the mixture interact specifically with each other, leading to an exothermic heat of mixing¹. A well studied homogeneous polymer blend is that formed from polystyrene (PS) and poly(vinyl methyl ether) (PVME), for which a negative value of the exchange interaction parameter (X_{12}) as defined in the Prigogine-Flory theory^{2,3} (implying exothermic mixing) has been determined by a number of methods, viz. small-angle neutron scattering (SANS)^{4,5}, inverse gas chromatography (i.g.c.)⁶⁻⁸, vapour sorption⁹ and osmotic pressure measurement¹⁰.

To our knowledge, no homopolymer other than PS has been reported to be miscible with PVME. The specific interaction in the PS-PVME system is of the donor-acceptor type, the π -electron systems in the benzene rings of PS acting as donors and the ether oxygens in PVME acting as acceptors^{6,11}. On the other hand, it has been reported in the literature that poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc), all containing ester functional groups, are miscible with poly(ethylene oxide) (PEO)¹²⁻¹⁴, which contains ether linkages in the polymer chain backbone. The PEO-PMMA system has been studied in some detail¹⁵⁻¹⁷. For this system, neutron scattering¹⁵ and melting-point depression¹⁶ studies give a negative value of X_{12} , whereas Fourier-transform infra-red spectroscopy (FTi.r.)¹⁷ does not indicate the existence of specific interactions. These results led us to investigate the miscibility of PVME (which contains ether functions as pendent groups in the polymer chain instead of being present in the chain backbone as in PEO) with polyacrylates. In an earlier communication we

briefly reported that PVME is indeed miscible with a number of polyacrylates¹⁸ and poly(vinyl ester)s¹⁹. In this paper we present the results of our detailed studies on the miscibility of PVME and polyacrylates. The appearance of cast films and the glass transition temperature behaviour have been used to judge miscibility. Furthermore, phase diagrams have been constructed from cloud-point studies.

EXPERIMENTAL

Materials

PVME ($\bar{M}_v = 5.25 \times 10^4$, $D = 2.59$) was an Aldrich product supplied as 50% aqueous solution. On warming the solution, the polymer separated out, and was then dried in a vacuum oven at 90°C for 72 h.

All the acrylate monomers except *n*-propyl acrylate were commercial products. These were washed with alkali (5%) to free them from inhibitors, washed free of alkali, dried and distilled before polymerization. *n*-Propyl acrylate was synthesized following the method of Rehberg *et al.*²⁰.

High-molecular-weight poly(methyl acrylate) (designated PMA(H); $\bar{M}_v = 8.00 \times 10^5$, $D = 1.78$), poly(ethyl acrylate) (PEA; $\bar{M}_v = 2.10 \times 10^5$, $D = 1.75$) and poly(*n*-propyl acrylate) (PPrA; $\bar{M}_v = 1.10 \times 10^6$, $D = 1.71$) samples were prepared by solution polymerization of the respective monomers at 60°C using 2,2'-azobisisobutyronitrile (AIBN, 0.1% w/v) initiator to about 20% conversion. In the preparation of PEA, *n*-propyl mercaptan was used as chain transfer agent. A low-molecular-weight PMA (designated PMA(L); $\bar{M}_v = 3.20 \times 10^4$, $D = 2.04$) was also prepared in a similar way using dodecyl mercaptan as chain transfer agent. Poly(*n*-butyl acrylate) (PBA; $\bar{M}_v = 1.01 \times 10^6$, $D = 2.04$) was prepared by emulsion polymerization of butyl acrylate at 80°C using sodium dodecyl sulphate (0.5% w/v) as emulsifier and potassium persulphate

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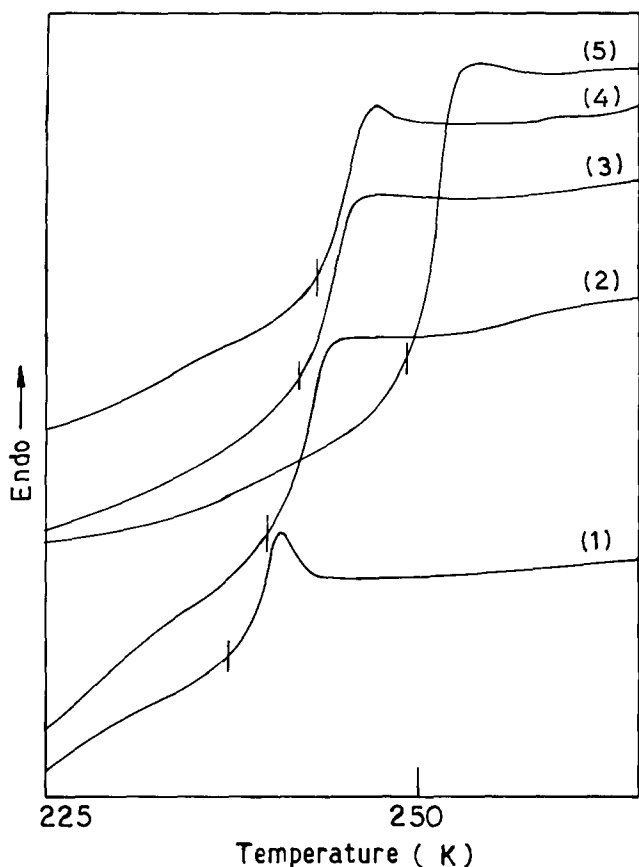


Figure 1 The d.s.c. traces of pure polymers PVME and PPrA and their blends. The weight fractions of PPrA in the blends are 0.00, 0.26, 0.50, 0.68 and 1.00 for curves 1–5 respectively

(0.035% w/v) as initiator. The viscosity-average molecular weights (\bar{M}_v) were obtained viscometrically using benzene as the solvent at 30°C. The K and α data for the Mark–Houwink equation were obtained from the literature²¹. The dispersity index (D) of the polymers was determined from gel permeation chromatography (g.p.c.) using polystyrene as calibration standard.

Method

The blend films were cast from 2% solution of the polymers in benzene or acetone. Film clarity at room temperature was examined visually. The films were dried in a vacuum oven at 80°C for 72 h. The T_g values were measured using a Perkin–Elmer differential scanning calorimeter (DSC-2) calibrated with indium. The samples were annealed at 343 K in the d.s.c. apparatus for 10 min and then quenched to 190 K and scanned at a heating rate of 20 K min⁻¹.

Cloud-point determination

The cloud point was determined by measuring the relative intensity of light transmitted through the film of a polymer that was placed in a hot stage sandwiched between two microscope coverslips and under a N₂ atmosphere. The temperature was measured by a chromel–alumel thermocouple placed in a hole drilled through the hot stage below the sample. The transmitted light intensity was measured by a photodiode. The output of the photodiode and that of the thermocouple (after suitable amplification) was fed into an X–Y recorder. The arrangement provided a direct recording of light intensity vs. temperature irrespective of its rate of change.

Steps were taken to eliminate stray light. The polymer sample was introduced in the hot stage at a temperature about 15°C below the cloud point and annealed for 20 min²². The temperature was then increased at a rate of 1–2°C min⁻¹. The cloud point was taken as the onset temperature of the change in intensity of light. The experiment was repeated three or four times with each sample and the cloud temperatures were averaged.

RESULTS AND DISCUSSION

Blend films of all compositions cast from benzene or acetone were opaque for PVME–PMA(H) as well as for PVME–PMA(L) blend systems, whereas those of PVME–PEA, PVME–PPrA and PVME–PBA were clear. This result gave an indication that PVME forms miscible blends with PEA, PPrA and PBA but not with PMA. However, the refractive indices of the polyacrylates are close to that of PVME. The refractive index values are 1.4670, 1.4800, 1.4685 and 1.4660 respectively for PVME, PMA, PEA and PBA at 20°C²³. So the conclusion about the miscibility from the film clarity test for the blends using the higher acrylates may be suspect.

However, evidence in support of the conclusion reached from the film clarity test was obtained from T_g studies. D.s.c. thermograms of the blends over a wide range of compositions revealed two T_g values (i.e. immiscibility) for the PVME–PMA system even using the low-molecular-weight PMA, but a single T_g value (i.e. miscibility) for the PVME–PPrA (Figure 1) and PVME–PBA (Figure 2) systems. Owing to the closeness of T_g values for PVME (249 K) and PEA (249 K)²⁴, miscibility for this blend system could not be studied by T_g measurements. However, cloud-point studies described later in this paper gave convincing proof that PEA is miscible with PVME, as are the other two polyacrylates PPrA and PBA.

Figures 3 and 4 show the variation of T_g values of the blends with composition for PVME–PPrA and PVME–PBA respectively. Several theoretical equations have been proposed to describe the variation of T_g with blend composition^{25–28}. Our data fit well with the

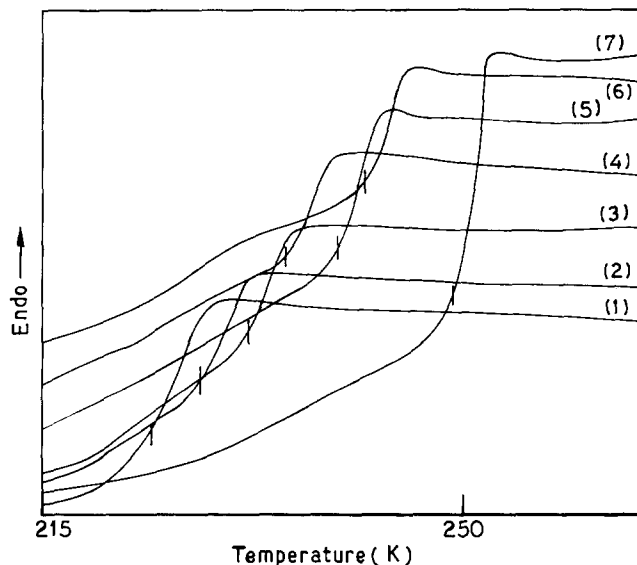


Figure 2 The d.s.c. traces of the pure polymers PVME and PBA and their blends. The weight fractions of PBA in the blends are 0.00, 0.17, 0.25, 0.51, 0.75, 0.83 and 1.00 for curves 1–7 respectively

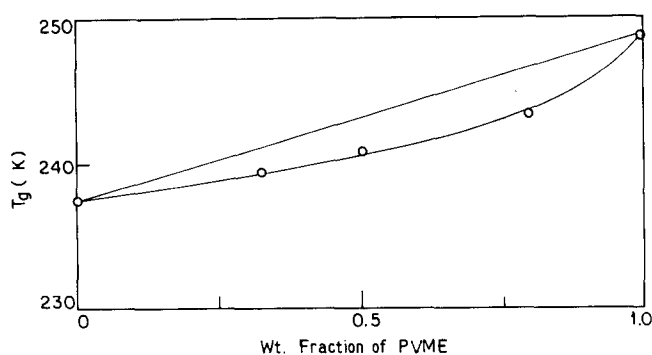


Figure 3 The T_g -composition diagram for the PVME-PPrA system. The points represent the experimental results. The curve is drawn using the Gordon-Taylor equation with $k = 0.606$

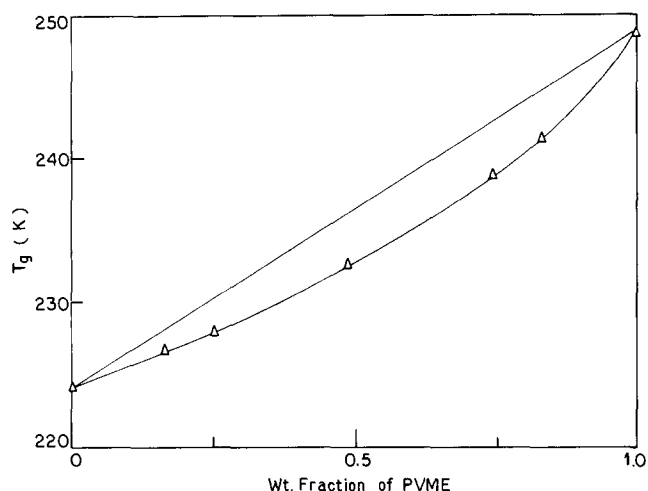


Figure 4 The T_g -composition diagram for the PVME-PBA system. The points represent the experimental results. The curve is drawn using the Gordon-Taylor equation with $k = 0.636$

Gordon-Taylor equation, which is represented as follows²⁸:

$$T_g = \frac{(w_1 T_{g1} + k w_2 T_{g2})}{w_1 + k w_2} \quad (1)$$

where w_i represents the weight fraction of the component polymers in the blends and k is a constant equal to $\Delta\alpha_2/\Delta\alpha_1$, $\Delta\alpha$ being the difference in volume expansion coefficients of the polymers between the liquid and the glassy states. T_{g1} and T_{g2} are the glass transition temperatures of the blend components. The T_g -composition diagrams (Figures 3 and 4) gave smooth curves that are concave upwards with $k = 0.606$ and 0.636 respectively for PVME-PPrA and PVME-PBA systems. These best k values were arrived at following Prud'homme *et al.*²⁹⁻³¹. Rearranging the Gordon-Taylor equation one obtains:

$$T_g = T_{g1} + k w_2 \frac{(T_{g2} - T_g)}{w_1}$$

Thus plotting T_g as a function of $(w_2/w_1)(T_{g2} - T_g)$, the straight line that gives the best fit has a slope of the value of k . The value of k has been used as a rough guide for the strength of polymer-polymer interaction in blends. For a value of $k = 1$, the Gordon-Taylor equation gives rise to the weight-average T_g line, i.e.:

$$T_g = w_1 T_{g1} + w_2 T_{g2}$$

The lower the value of k , the lower is the degree of miscibility³¹⁻³³. When the interaction between blend components is very strong, such as effected by H bonds, blend T_g values turned out to be greater than the weight-average T_g values of pure components³⁴, and in those cases k assumes values greater than 1. The values found for the present systems given above indicate that the interactions between the blend components are not very strong.

Figure 5 shows the phase diagrams of some of these blend systems. The lower critical solution temperature ($LCST$) for the PVME-PEA system is estimated to be 221°C . The existence of an $LCST$ indicates that PEA and PVME form miscible blends at all compositions below this temperature. For the PVME-PBA blend system, cloud points (T_p) were obtained for some compositions, whereas for other compositions T_p could not be determined with any accuracy. This may be due to the closeness of the refractive indices (r_i) of the polymers, which has been discussed earlier in the paper. For the PVME-PPrA system, no T_p for any of the compositions could be determined even when the blends were heated up to the decomposition temperatures of the polymers (ca. 300°C). It may be concluded that either the T_p values are located above this temperature or the instrument could not detect T_p because of the very small Δr_i for this blend system. Thus, from the r_i data quoted in this paper, we find that the ambient-temperature Δr_i (r_i (polyacrylate) - r_i (PVME)) values are $+0.013$, $+0.0015$ and -0.001 when the polyacrylates are PMA, PEA and PBA respectively. The r_i for PPrA was not available. However, the Δr_i for the PVME-PPrA system is expected to lie between $+0.0015$ and -0.001 , i.e. Δr_i is the lowest for this system, which makes the determination of phase separation by the present method very difficult. An $LCST$ in polymer blend systems may arise from two effects: (i) exothermic mixing and (ii) large difference in free volumes^{1,35}. Since the T_g values of the acrylate polymers used here are within $0-25^\circ\text{C}$ of that of PVME, the contribution of free-volume differences to the $LCST$ must be small. The $LCST$ for the present miscible systems may therefore be attributed to originate from exothermic

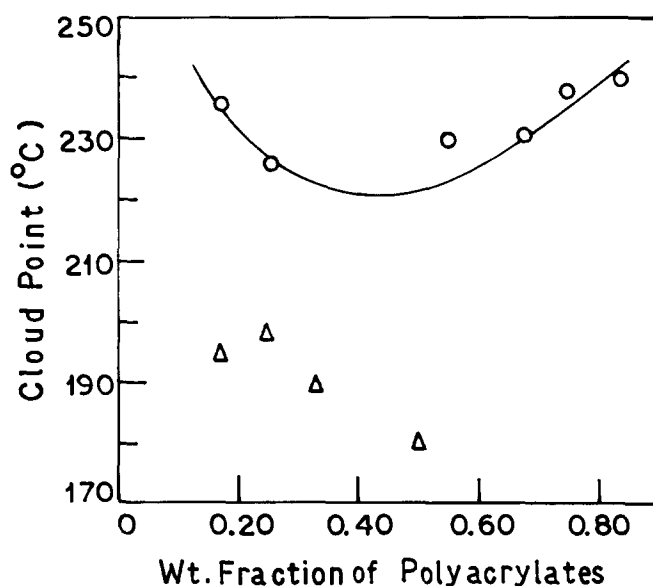


Figure 5 Cloud point-composition diagram for PVME-PEA (O) and PVME-PBA (Δ) systems

mixing. Although the *LCST* for the PVME–PBA system could not be estimated, the cloud-point data that were available at some of the compositions and are reported in *Figure 5* indicate that the *LCST* for this system will be at a lower temperature than for the PVME–PEA system. So it can be concluded that between PVME–PEA and PVME–PBA systems the mixing is better achieved for the former system.

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