Compatibility of polyacrylates and polymethacrylates with poly(vinyl chloride): 1. Compatibility and temperature variation

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Mixtures of a series of polymethacrylates and polyacrylates with PVC were prepared by solvent casting from methyl ethyl ketone. Some mixtures were also prepared by mechanical mixing and *in situ* polymerization (polymerization of vinyl chloride monomer in the presence of the other polymer). The mixtures were assessed for compatibility by dynamic mechanical measurements and optical clarity. It was found that all polymethacrylates from poly(methyl methacrylate) to poly(n-hexyl methacrylate) were compatible with PVC as were poly(n-propyl acrylate) and poly(n-butyl acrylate). Higher chain polyacrylates are incompatible. Poly(methyl acrylate) and poly(ethyl acrylate) appear incompatible with PVC when mixtures are prepared by solvent casting, but compatible when prepared by *in situ* polymerization, and mechanical mixtures show some sign of compatibility. It seems possible that in this case the solvent interferes with the compatibility. Mixtures of PVC with poly(n-hexyl methacrylate), poly(n-butyl acrylate) and poly(n-propyl acrylate) phase separate when heated in the region between 100°C and 160°C indicating the existence of a lower critical solution temperature.

INTRODUCTION

In recent years there has been a lot of interest in polymer blends and polymer compatibility, and several reviews have been written on the subject[1,2]. Compatibility between polymer pairs is fairly rare as can easily be understood from considerations of the thermodynamics of the system. The entropy of mixing, ΔS_m, of two polymers is very small; it is given by the Flory-Huggins treatment[3] as,

$$\Delta S_m = -k(n_1 \ln \varphi_1 + n_2 \ln \varphi_2) \tag{1}$$

where φ_1 and φ_2 are the volume fractions, and n_1 and n_2 the number of molecules, of the two components. Because n_1 and n_2 are small for high molecular weight polymers ΔS_m must also be small. Thus even a very small unfavourable heat of mixing is sufficient to produce phase separation.

The Flory-Huggins treatment predicts a favourable entropy of mixing and thus polymers should be more compatible at higher temperatures and exhibit upper critical solution temperatures (*UCST*). This, however, is only observed for low molecular weight polymers. High molecular weight, compatible polymers, which show phase boundaries, are less compatible at higher temperatures and often exhibit lower critical solution temperatures (*LCST*). An *LCST* can only arise if the entropy of mixing is unfavourable (-ve), and the enthalpy of mixing is favourable (-ve).

The phase diagram will have the general form shown in *Figure* 1. The solid line is the curve of equilibrium phase separation, called the binodal, and on this curve,

$$\left(\frac{\partial \Delta G}{\mathrm{d}\varphi}\right)_{T,P} = 0$$

where ΔG is the free energy mixing and φ the volume fraction of one component. Inside the binodal there is a region of metastability, the limit of which is shown by the dotted line, called the spinodal. On this curve,

$$\left(\frac{\partial^2 \Delta G}{\mathrm{d}\varphi^2}\right)_{T,P} = 0$$

At the critical temperature, T_c, a homogeneous mixture is produced at all compositions, and at this point

$$\left(\frac{\partial^3 \Delta G}{\mathrm{d}\varphi^3}\right)_{T,P} = 0$$

Negative entropies and enthalpies of mixing can be caused by volume changes on mixing, or by specific interactions between the polymers such as hydrogen

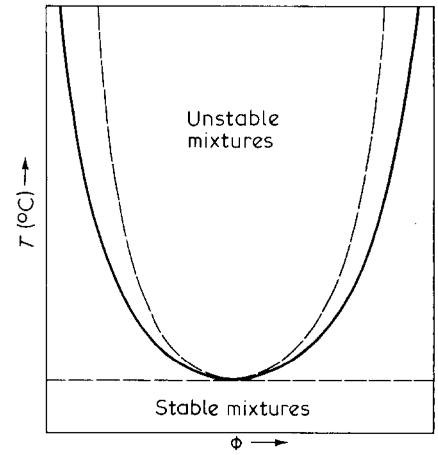

Figure 1 Phase diagram

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bonds. An examples of the former is the system poly(vinyl chloride), (PVC), with solution chlorinated polyethylene[4]. An example of the latter is PVC with polycaprolactone[5], where a weak hydrogen bond probably exists between the hydrogen on the same carbon as the chlorine of PVC and the carbonyl of polycaprolactone. This type of interaction has been shown to exist for a series of haloalkanes with electron donors, such as ketones, ethers, esters, tertiary amines and tertiary amides[6,7,8]. Another example of this type is PVC with poly(methyl methacrylate)[9] which has been found to be compatible at all temperatures and compositions tested.

There are three main methods for mixing polymers, mixing in the melt, mixing in solution, and *in situ* polymerization (the addition of an alternate monomer to a preformed polymer, followed by polymerization). Mixing in the melt is difficult to achieve due to the low diffusion coefficients of polymers, even at elevated temperatures. Equilibrium may never be achieved in a reasonable time, which is limited by the thermal degradation of the polymers. Also any attempt to mix polymers above an *LCST* would always result in two phases.

The low diffusion coefficient can be overcome by dissolving the two polymers in a common solvent at low concentration followed by precipitation into a non-solvent or evaporation. This method can sometimes fail in situations where the solvent strongly interacts with one of the polymers. For instance, the compatible system polystyrene/poly(vinyl methyl ether)[10] separates into two phases when cast from chloroform whereas one phase is formed from toluene solutions[11].

In situ polymerization involves swelling the preformed polymer with another monomer followed by polymerization, initiated chemically or by radiation[4]. This can lead to grafting, but does not prevent phase separation if the polymers are incompatible[12]. The monomer, acting as a solvent for the two polymers, may also cause phase separation in some cases.

Several methods of measuring compatibility are available. Optical clarity is often used as a criterion, but this is open to misinterpretation if the refractive indices of the two polymers are similar or if the size of the dispersed phase is too small to scatter a significant amount of light. One of the most sensitive methods of determining whether a two phase structure exists in a polymer blend is by measuring the glass transitions within the mixture. If mixing has occured then one glass transition, usually intermediate between those of the two components is found. If the polymers exist in separate domains then the separate transitions of the two phases are obtained.

The glass transition can be detected using a number of methods[13]. Among the most commonly used are dynamic mechanical measurements. In these, the samples are subjected to a periodic stimulus stress and the response or strain is measured. If a sinusoidal stress is applied, a sinusoidal strain is produced which lags the stress by a phase angle δ. When the frequency of molecular rearrangements and the applied stress match each other then a peak in the loss factor obtained.

In this paper the compatibility of a series of polyacrylates and polymethacrylates with PVC is described and examples given of those which exhibit an *LCST*. The polyacrylates and polymethacrylates used were the methyl, ethyl, n-propyl, n-butyl, n-pentyl, and n-hexyl esters, plus poly(n-octyl acrylate) and poly(t-butyl acrylate).

EXPERIMENTAL

Preparation of monomers and polymers

The propyl, pentyl, and hexyl, acrylates and methacrylates were prepared by condensing acryloyl chloride or methacryloyl chloride with the corresponding alcohol. All materials used were AR grade and were used as supplied.

Triethylamine (2 moles) and the alcohol (1 mole) were charged into a round-bottomed flask fitted with a condenser, dropping funnel, and stirrer. An equivalent volume of benzene was added and the flask and contents cooled in an ice bath. The acid chloride (1 mole) was added in drops from the funnel over one hour and the mixture was then left to stir overnight. The precipitate of triethylamine hydrochloride was filtered from the solution and washed with benzene to remove the last traces of monomer. One percent, by weight of monomer, of the stabilizer, tertiary butyl catechol, was added to the solution and the mixture was fractionally distilled under reduced pressure. The benzene was removed first and the monomer distilled. A first and last fraction were discarded and the middle fraction used in the preparation of the polymer.

The methyl, ethyl and butyl acrylates were obtained commercially; before use they were distilled as above.

The polymers were prepared by emulsion polymerization. The formulation used for the preparation was: distilled water — 100 parts by weight; monomer — 50 parts by weight; potassium persulphate — 0.003 parts by weight; sodium lauryl sulphate — 1 part by weight. Water and the water soluble ingredients were charged into a round-bottomed flask equipped with a stirrer, reflux condenser, and thermometer. The flask was flushed with nitrogen and the monomer added. The mixture was heated to 90°C and stirred for six hours under nitrogen.

The latex was coagulated and purified according to the method of Haslam[14]. 100 cm^3 of the emulsion was shaken with 5 cm^3 of ether, and 30 cm^3 of 5% magnesium chloride solution added. The emulsion was added by drops to a ten-fold volume of methanol with constant stirring. The polymer came out of suspension and was washed with hot methanol to remove the last traces of emulsifier. The polymer was dissolved in butanone, centrifuged at 10 000 rpm to remove any gel particles and reprecipitated into a ten-fold volume of methanol. It was dried in a vacuum oven at 80°C and 0.1 mm Hg pressure for 24 hours.

Poly(vinyl chloride) and poly(methyl methacrylate) were commercial samples. They were purified in a soxhlet apparatus by refluxing with methanol and ether[14], and dried in a vacuum oven at 0.1 mm Hg, at 40°C for 48 hours. Poly(ethyl methacrylate), poly(n-butyl acrylate) and poly(n-octyl acrylate) were obtained from Aldrich Chemical Co. as secondary standards.

The polymers were characterized by membrane osmometry. This gives a number average molecular weight which is the average necessary for the calculation of interaction parameters. A Melabs SCM2 osmometer was used in conjunction with a Sartorius cellulose membrane. Four concentrations were used with two readings at each concentration, c, together with three readings for the pure solvent, dimethyl formamide. The osmotic pressure, π, was obtained by the difference between the solution and pure solvent readings. π/c was then plotted against c and the number average molecular weight obtained from the intercept at $c=0$. The results are shown in *Table* 1. The polymers, which were obtained as secondary standards,

Table 1 Number average molecular weights of polymer

Poly(methyl methacrylate)	100 000
Poly(ethyl methacrylate)	40 000
Poly(n-propyl methacrylate)	70 000
Poly(n-butyl methacrylate)	35 000
Poly(n-pentyl methacrylate)	80 000
Poly(n-hexyl methacrylate)	72 000
Poly(methyl acrylate)	90 000
Poly(ethyl acrylate)	80 000
Poly(n-propyl acrylate)	95 000
Poly(n-butyl acrylate)	100 000
Poly(t-butyl acrylate)	50 000
Poly(n-pentyl acrylate)	73 000
Poly(n-hexyl acrylate)	75 000
Poly(n-octyl acrylate)	30 000
Poly(vinyl chloride)	35 000

had quoted values of *Mn*. These are included in the table for completeness.

Preparation of polymer mixtures

Samples of mixed polymers were prepared by solvent casting, *in situ* polymerization, and mechanical mixing. Solvent cast mixtures were prepared by dissolving varying amounts of the polyacrylates and polymethacrylates in methyl ethyl ketone (AR) at 3% by weight concentration. These were then added to different volumes of a 3% by weight poly(vinyl chloride) solution in methyl ethyl ketone and stirred overnight. The solutions were poured into petri dishes and left for one week at room temperature to evaporate. The petri dishes were partly covered during this time to slow down the rate of evaporation of solvent, a procedure which produced better films. The resulting films were dried to constant weight in a vacuum oven for three days at 50°C and 0.1 mm Hg pressure. The films produced were optically clear, except for mixtures of PVC with poly(methyl acrylate), poly(ethyl acrylate), poly(t-butyl acrylate), poly(octyl acrylate) and poly(hexyl acrylate), which suggests that these are not compatible. Films were also produced from solutions in tetrahydrofuran but these were always cloudy.

In situ polymerization was carried out by swelling the polyacrylate or polymethacryalte with vinyl chloride and polymerizing to produce a polymer mixture. 0.5 ml of a 0.1% solution of benzoyl peroxide in methanol was introduced into a glass ampoule. The methanol was evaporated leaving the benzoyl peroxide. A 0.5 g sample of the solid polyacryalte or polymethacrylate was then placed in the ampoule. Vinyl chloride monomer (0.5 g measured using a manometer knowing the volume of the system) was distilled into the ampoule which was in a liquid nitrogen bath. The ampoule was sealed under vacuum, allowed to warm to room temperature, the contents mixed and left to equilibrate overnight. The ampoule was heated in an oven at 85°C for twelve hours in order to polymerize the vinyl chloride. The ampoule was broken, and the conversion found from the weight loss to be around 98% in each case. This procedure was carried out for poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), poly(pentyl acrylate) and poly(hexyl methacrylate). All samples were optically clear except for the poly(pentyl acrylate)/poly(vinyl chloride) mixture. The samples were found to swell but not dissolve in methyl ethyl ketone showing them to have crosslinked during the polymerization.

Mechanical mixing was carried out using a Brabender Plastograph with the 30 cm^3 mixing head, at 160°C and 60 rpm for 15 minutes. Samples of poly(methyl acrylate) and poly(ethyl acrylate) were mixed with poly(vinyl chloride) in the ratio 70:30 by weight.

Dynamic mechanical measurements

A direct reading visco-elastometer, the rheovibron, was used for the dynamic mechanical measurements. Small sample sizes, approximately 0.5 x 2 x 0.1 cm are required. The sample was held in the machine under slight tension and a strain was applied at a fixed frequency of 11 Hertz. The stress and strain are measured by transducers and the two readings processed to give a direct reading of tan δ.

The heating rate was set at 10°C min^{-1}. ($\pm$0.1°C) and the temperature was scanned from 0°C to 100°C, or in some cases from -100°C to $+100$°C. Measurements below 0°C are obtained by blowing air over liquid nitrogen into the sample chamber.

In order to measure the phase separation temperature of a compatible blend showing an *LCST* the following procedure was used. The sample was first scanned on the rheovibron up to 100°C in order to measure the glass transition of the mixture. Next, it was placed in an oven at a known temperature for 30 minutes after which it was removed and quenched quickly to room temperature by placing it on a metal sheet. The sample was reloaded into the rheovibron and again scanned up to 100° in order to observe any movement in the glass transition or the appearance of a discrete phase of poly(vinyl chloride) indicated by a peak at 100°C. The temperature of the oven was raised in steps between 100°C and 160°C and the process repeated at each temperature interval. The maximum temperature used was 160°C due to the degradation of PVC above this temperature. Since the appearance of the PVC homopolymer peak is enough to confirm phase separation, only the hot stage, 0°C upwards, was used for phase separation studies.

RESULTS AND DISCUSSION

Samples of the various polymers mixed with PVC in the ratios 70:30, 50:50, and 30:70, cast from solution in methyl ethyl ketone were examined on the rheovibron. Two phase mixtures showed two glass transitions and one phase mixture one glass transition. The results are shown in *Table* 2 along with their observed optical clarity.

Table 2 Rheovibron results

Polymer (with PVC)	Rheovibron result	Optical clarity
Poly(methyl methacrylate)	One phase	Clear
Poly(ethyl methacrylate)	One phase	Clear
Poly(n-propyl methacrylate)	One phase	Clear
Poly(n-butyl methacrylate)	One phase	Clear
Poly(n-pentyl methacrylate)	One phase	Clear
Poly(n-hexyl methacrylate)	One phase	Clear
Poly(methyl acrylate)	Two phases	Cloudy
Poly(ethyl acrylate)	Two phases	Cloudy
Poly(n-propyl acrylate)	One phase	Clear
Poly(n-butyl acrylate)	One phase	Clear
Poly(n-pentyl acrylate)	Two phases	Clear (except 70% PVC)
Poly(n-hexyl acrylate)	Two phases	Cloudy
Poly(n-octyl acrylate		Cloudy
Poly(t-butyl acrylate)		Cloudy

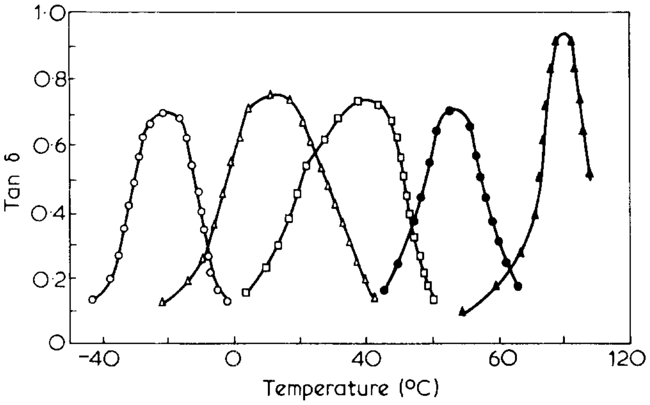

Figure 2 Plots of tan δ against temperature for mixtures of poly(n-propyl acrylate) and PVC: ▲ – pure PVC; ● – 70% (w/w) PVC; □ – 50% PVC; △ – 30% PVC; ○ – pure poly(n-propyl acrylate)

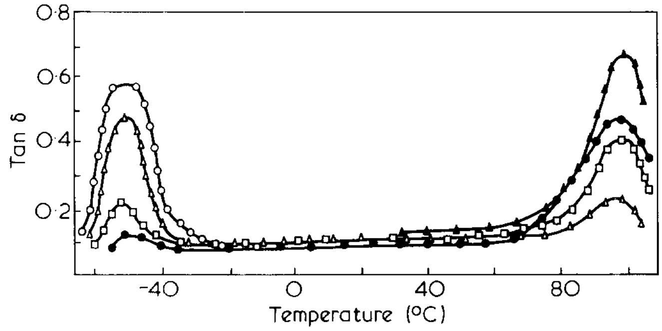

Figure 3 Plots of tan δ against temperature for mixtures of poly(n-hexyl acrylate) and PVC: ▲ – pure PVC; ● – 70% (w/w) PVC; □ – 50% PVC; △ – 30% PVC; ○ – pure poly(n-hexyl acrylate)

Detailed examples of the results for one compatible system (poly(n-propyl acrylate)/poly(vinyl chloride)) and one incompatible system (poly(n-hexyl acrylate)/poly(vinyl chloride)) are shown in *Figure* 2 and *Figure* 3.

For the series of polymethacrylates the peaks in the loss tangent versus temperature plots widen as the series from methyl to hexyl is ascended. This might be expected since the difference between the glass transition temperatures of the two polymers is increasing. However in the case of poly(n-hexyl methacrylate) the peak is very much broader (*Figure* 4). This could be an indication that this mixture is less miscible than the other methacrylates which correlates with the temperature of phase separation discussed later in this paper. One can also observe that the 50:50 mixture gives the broadest peak as might be expected if this was nearest to the critical composition.

The result for poly(n-pentyl acrylate) is ambiguous. This could be due to the fact that phase separation occurs in all samples but does not produce domains of the polymer large enough to scatter a lot of light. It could also be an indication that a phase boundary exists close to room temperature. An inherent problem in the method used to determine compatibility is that one must scan between 0 and 100°C in order to obtain a result. If a phase boundary exists within this region anomalous results could be produced.

It might be possible to interpret the results as showing that the short chain esters of the polyacrylates and polymethacrylates are more compatible than the long chain esters due to a higher concentration of carbonyl groups and less steric hindrance to the formation of hydrogen bonds with the PVC. However the results for poly(methyl acrylate) and poly(ethyl acrylate) mixtures run counter to this argument. It was thought possible that the solvent used for casting (methyl ethyl ketone) might be interfering with the compatibility in this case. Two different methods of preparing mixtures with these polymers were therfore tried. The polymers were mechanically mixed with PVC using a Brabender plastograph. In both cases there was evidence of intermixing though two peaks were always visible. The second method was *in situ* polymerization. With both polymers this produced clear samples and only one peak was produced on the rheovibron. The results for solvent casting, mechanical mixing, and *in situ* polymerization of poly(methyl acrylate) with PVC are shown in *Figure* 5.

The results show that poly(methyl acrylate) and poly(ethyl acrylate) are, in fact, compatible with PVC. The samples prepared by *in situ* polymerization were, however, crosslinked during polymerization and it could be argued that this affects the compatibility. *In situ* mixtures of poly(n-butyl acrylate), poly(n-pentyl acrylate), and poly(n-hexyl methacrylate) with PVC were therefore prepared. These showed results to that found in solvent cast mixtures in each case.

A search was made for polymer mixtures exhibiting lower critical solution temperatures. *Figure* 6 shows the results of heating a 50:50 poly(vinyl chloride)/poly(butyl acrylate) mixture to a series of temperatures between 100 and 160°C on the rheovibron results. As the temperature

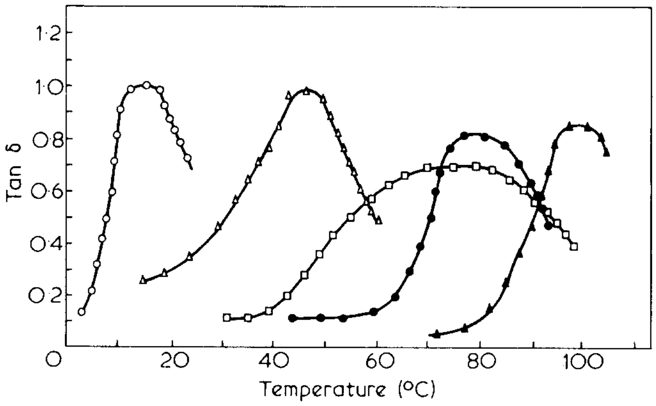

Figure 4 Plots of tan δ against temperature for mixtures of poly(n-hexyl methacrylate) and PVC: ▲ – pure PVC; ● – 70% (w/w) PVC; □ – 50% PVC; △ – 30% PVC; ○ – pure poly(n-hexyl methacrylate)

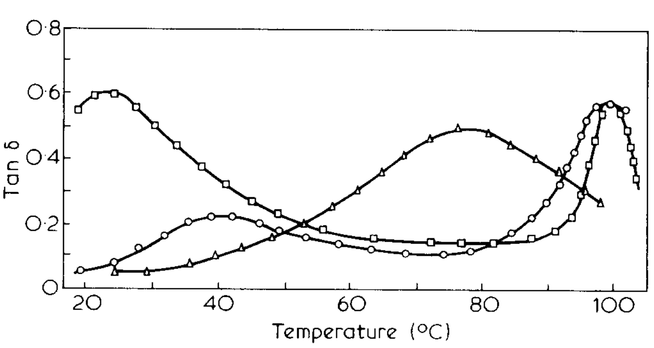

Figure 5 Plots of tan δ against temperature for mixtures of poly(methyl acrylate) and PVC: □ – solvent cast from butan-2-one; ○ – mechanically mixed; △ – *in situ* polymerized

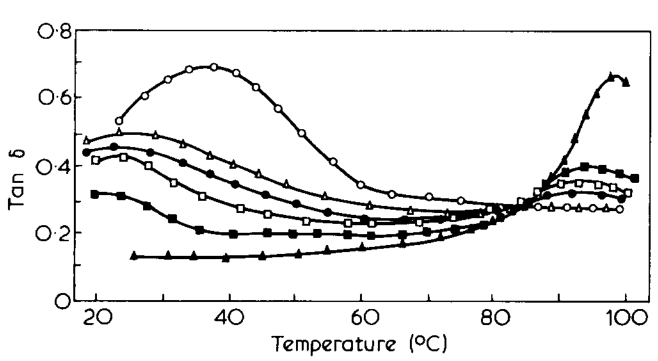

Figure 6 Plots of tan δ against temperature for mixtures of poly(n-butyl acrylate and PVC, which have been heated to the indicated temperatures prior to testing: ○ – room temperature standard; △ – 112°C; ● – 120°C; □ – 125°C; ■ – 140°C; ▲ – 160°C

is increased the peak moves slowly in composition. Only between 140 and 160°C does a large poly(vinyl chloride) peak appear, and only at 160°C does the sample become turbid. It may be concluded that phase separation occurs somewhere within this temperature range. The extent to which the processes involved are thermodynamically controlled, and to what extent they are kinetically controlled is difficult to assess. Phase separation was also observed for a mixture of poly(n-propyl acrylate) with PVC at around 140°C, and for mixtures of poly(n-hexyl methacrylate) below 125°C. No other compatible, solvent cast mixtures show phase separation.

None of the *in situ* prepared, compatible mixtures show phase separation on heating. This is presumably due to the effect of crosslinking on the phase separation temperature and throws some doubt on the earlier conclusion that poly(methyl acrylate) and poly(ethyl acrylate) are compatible with PVC. To explain the fact that no phase separation was observed for poly(n-butyl acrylate) and poly(n-hexyl acrylate) mixtures with PVC a 20–40°C change in phase boundary caused by the different method of preparation would have to be assumed. To explain the results with poly(methyl acrylate) and poly(ethyl acrylate) mixtures with PVC a 140°C change in phase boundary would have to be assumed if they were not in fact compatible at room temperature. *In situ* polymerization did not make one phase mixtures of poly(n-pentyl acrylate) with PVC and it is difficult to explain how *in situ* polymerization could have a very large effect on the properties. It therefore seems more likely on balance that poly(methyl acrylate) and poly(ethyl acrylate) are thermodynamically compatible with PVC at room temperature. It must also be borne in mind that all the results will depend on the molecular weights of the polymers used, especially the specific temperatures of phase separation.

CONCLUSION

It has been found that all polymethacrylates up to poly(n-hexyl methacrylate), and poly(n-propyl acrylate) and poly(n-butyl acrylate) are compatible with poly(vinyl chloride). Higher chain polyacrylates are incompatible. Poly(methyl acrylate) and poly(ethyl acrylate) are incompatible with PVC when prepared by solvent casting but compatible when prepared by *in situ* polymerization. It seems probable that they are in fact thermodynamically compatible at room temperature but that the solvent, methyl ethyl ketone, interferes with their compatibility. Poly(n-hexyl methacrylate), poly(n-propyl acrylate) and poly(n-butyl acrylate) phase separate when heated to temperatures between 100 and 160°C. These results suggest a general picture of polyacrylates and polymethacrylates with shorter ester chains being more compatible.

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