Compatibility of polyacrylates and polymethacrylates with poly(vinyl chloride): 2. Measurement of interaction parameters

D. J. Walsh and J. G. McKeown
Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London SW7, UK

(*Received* 23 *January* 1980)

Interactions of various solvents with poly(vinyl chloride) and a series of polyacrylates and polymethacrylates have been studied by inverse gas chromatography. Values of the interaction parameters χ_{12} have been calculated and show the importance of specific interactions between the polymers and the solvents. Low values of χ_{12} indicating a strong interaction were found for the polyacrylates and polymethacrylates with a proton donating solvent, chloroform, and for the poly(vinyl chloride) with some proton accepting solvents, especially butan-2-one. Interactions of solvents, with mixtures of poly(vinyl chloride) with some compatible polyacrylates and polymethacrylates, have also been studied. From this, and using the values of χ_{12} found above, values of the polymer-polymer interaction parameters χ_{23} have been calculated. Low values of χ_{23}, indicating a strong interaction were found, especially for polymethacrylates and polyacrylates with shorter ester side chains. Lower values were obtained for polymethacrylates than polyacrylates again indicating greater interactions. These results fit in well with the results of a previous paper where we found that the polymers with longer ester side chains were not compatible with PVC or phase separated on heating, and that fewer acrylates than methacrylates are compatible with PVC.

INTRODUCTION

Inverse gas chromatography can be used to measure the interactions between a polymer and a solvent or between two polymers. The absolute values of the interactions are subject to some doubt but comparative measurements within a series of experiments can give information about trends within that series.

The basic experiment is performed by spreading the polymer as a thin film onto an inert support which is then packed into a column. Injections of various solvents are made into the columns and the volume of gas required to 'sweep' the solvent through the column is measured. This volume is indicative of the interaction between the polymer and solvent. Similarly if two polymers are used as a stationary phase and they interact with one another, this will reduce their ability to interact with the solvent and hence retention will be lower relative to the pure homopolymers.

The quantities measured are the time taken for a pulse of solvent to pass through the column and the volume flowrate or carrier gas. These are related to the specific retention volume at 273.15K by[1]

$$V_g=(t_r-t_{gas})Q\frac{273.15f_p}{T\ W} \tag{1}$$

where V_g = retention volume at 0°C, cm^3; t_r = retention time for solvent, s; t_{gas} = retention time for a non-interacting air sample, s; Q = volume flowrate of carrier gas, cm^3 s^{-1}; T = operating temperature of the column, K; W = weight of stationary phase; f_p = is a correction for the pressure drop along the column and is given by[2]

$$f_p=2\left[\left(\frac{P_i}{P_o}\right)^3-1\right]\Big/3\left[\left(\frac{P_i}{P_o}\right)^2-1\right] \tag{2}$$

where P_i = inlet pressure; P_o = outlet pressure. The retention volume is extrapolated to zero flowrate to give V_g^o.

The theory of inverse gas chromatography has been described elsewhere[3,4]. The partition coefficient of the solvent is related to the activity coefficient in the liquid phase which can be described by the Flory-Huggins equation. The Flory-Huggins interaction parameter between the polymer and the solvent χ_{12} is then given by

$$\chi_{12}=\ln\left(\frac{273.15\ R\ v_2}{P_1^0V_g^0V_1}\right)-\left(1-\frac{V_1}{\bar{M}_2v_2}\right)-\frac{P_1^0}{RT}(B_{11}-V_1) \tag{3}$$

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

Since χ_{12} is concentration dependent the value obtained will not be the value for infinite dilution of the solvent. This has prompted some workers to replace the normal combinatorial contribution in the Flory-Huggins equation by one which uses core volumes v^*. The non-combinatorial contribution then contains all the contributions to χ and the combinatorial part will be temperature independent. Equation (3) then becomes

$$\chi^*{}_{12}=\ln\left(\frac{273.15\ R\ v_2^*}{P_1^0V_g^0V_1^*}\right)-\left(1-\frac{V_1^*}{\bar{M}_2v_2^*}\right)-\frac{P_1^0}{RT}(B_{11}-V_1) \tag{4}$$

0032 3861/80/111335 06$02.00

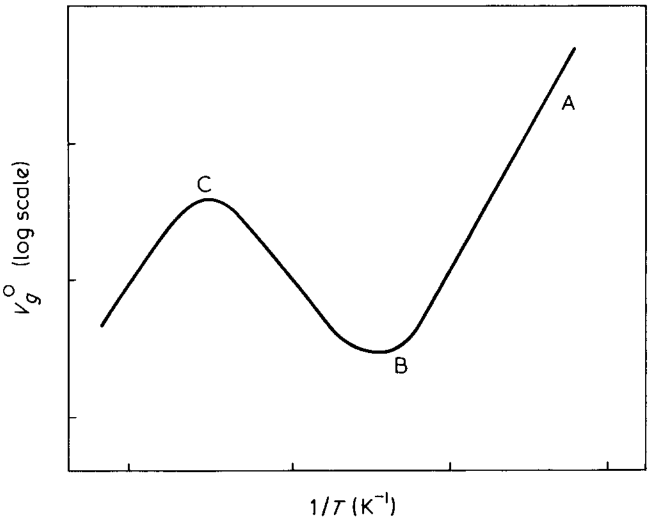

Figure 1 Form of plot for variation of the logarithm of retention volume (log V_g^0) against the reciprocal temperature ($1/T$) for a polymer in the region of its glass transition temperature

In a similar way, Flory-Huggins theory can be applied to a mixed stationary phase of two polymers (2), (3) with a probe solvent (1) to obtain[5]

$$\ln\left(\frac{273.2\,R}{P_1^0 V_g^0 M_1}\right)-\frac{P_1^0}{RT}(B_{11}-V_1)=\ln\left(\frac{V_1}{w_2v_2+w_3v_3}\right)$$
$$+1+\chi_{12}\varphi_2+\chi_{13}\varphi_3-\chi_{23}\varphi_2\varphi_3 \qquad (5)$$

where M_1 is the molecular weight of the solvent; φ_1, φ_2, and φ_3 are the volume fractions of the components; w_2 and w_3 are the weight fractions of the polymers; χ_{12} and χ_{13} are the separate polymer-solvent interaction parameters; χ_{23} is the polymer-polymer interaction parameter. If the core volumes are used again χ_{23}^* is obtained.

In practice this calculation based on equilibrium adsorption of solvent is not sufficient to describe the behaviour of the system. The retention volume is found to vary with temperature in a similar way to that shown in *Figure* 1[6].

In the region *AB* the polymer is below its glass transition temperature and retention is caused by adsorption on the surface of the polymer. Between *B* and *C* penetration of solvent into the polymer increase and at *C*, usually about $Tg+50$°C, equilibrium is observed. Above *C* both bulk absorption and surface adsorption occur. The value of retention volume also depends on the weight of polymer on the support in a similar way to that shown in *Figure* 2.

As the surface area changes very little with coating thickness, the surface adsorption contribution causes V_g^0 to increase sharply at low loadings. At high coverages the coating thickness becomes large enough for non-equilibrium diffusion of the solvent to occur. The weight loading used in the calculation of V_g^0 is thus artificially large, since not all the polymer is contributing to the partitioning process, and the value of V_g^0 falls.

Some authors have decided that the opposite effects of surface adsorption and non-equilbrium diffusion are small and nearly equivalent at a volume loading of 8% w/w[7]. Other authors have tried to eliminate the surface contribution by extrapolation to infinite loading of polymer[8]. This is a difficult extrapolation when non-equilibrium diffusion occurs and at high coverages V_g^0 values become very sensitive to small changes in the gas flowrate making extrapolation to zero flowrate difficult. Yet another method[9] is based on extrapolation of surface adsorption figures from below the glass transition temperature. This assumes that the surface of glass is equivalent to the surface of a rubber above the glass transition.

In this paper values of V_g^0 at 8% coverage have been used. The values of interaction parameters so obtained are not believed to be reliable in an absolute sense but comparisons between values from a series of similar experiments can justifiably be made.

Attempts have been reported to compare χ_{12} values found from gas chromatography with values found from conventional methods. For solvents with poly(dimethyl siloxane)[10] and natural rubber[11] it was found that absolute values were not exact but the trend within a series of solvents was the same. Other experiments with poly(dimethyl siloxane)[12], however, obtained lower interaction parameters than the above, which was put down to different column packing procedures. This highlights the unreliability of absolute values of χ_{12} obtained in this way. The system poly(vinyl chloride)/dioctyl phthalate has been studied recently[13,14], and it was observed that the interaction parameter, χ_{23} varied with the solvent probe used. This was explained as due to non-random mixing and/or the effect of preferential solvation of one of the components.

In this paper results are reported of experiments using poly(vinyl chloride) and a series of polyacrylates and polymethacrylates with a range of different solvents. By using the polymers separately, and together as the stationary phases we have also been able to estimate values of the interaction parameters between the two polymers.

EXPERIMENTAL

The apparatus consisted of a Pye 104 gas chromatograph. A schematic is shown in *Figure* 3. It contains a 1.5 metre coiled pyrex column packed with polytetrafluoroethylene

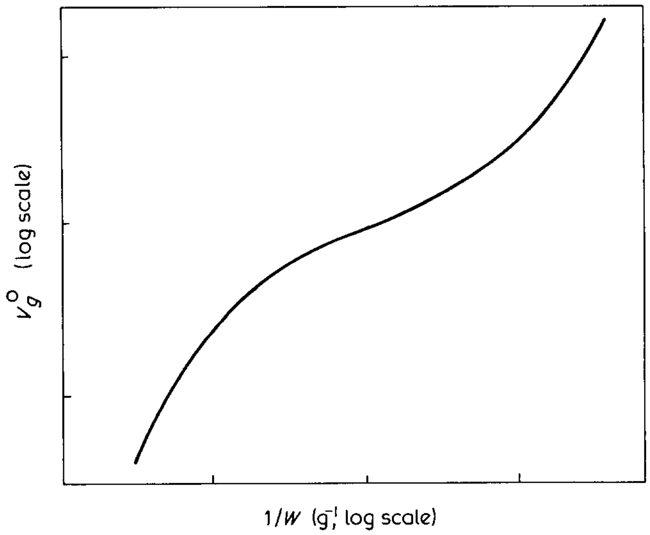

Figure 2 Form of plot for variation of the logarithm of retention volume (log V_g^0) against the logarithm of the reciprocal of the polymer loading on the support, log ($1/W$), for a temperature within the non-equilibrium region

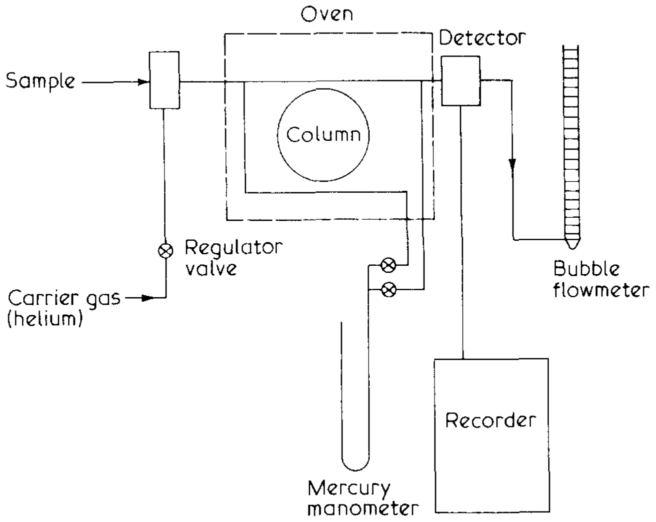

Figure 3 Diagram of g.l.c. apparatus

Table 1 Physical properties of solvents

Solvent	Saturated vapour pressure (atm)	Molar volume (cm^3)	$-\frac{P_1^0}{RT}(B_{11}-V_1)$
Hexane	3.923	153.9	0.123
Butan-2-one	3.172	103.71	0.094
Acetonitrile	2.9134	61.03	0.1427
Chloroform	4.887	83.57	0.1016
n-Propanol	2.236	84.57	0.058
Acetone	6.115	84.89	0.162
Ethyl acetate	3.402	114.53	0.112

(60/80 mesh) on which the polymer was spread as a thin film. A uniform flow of helium carrier gas is passed through the column which is kept at constant temperature in an air circulating oven. A pulse of solvent is injected at one end and is detected at the other by a thermal conductivity detector.

The packing was prepared by coating from a solvent. The polymer was dissolved in butan-2-one and the solution added to 15 g of the support which had been dried in an oven at 80°C prior to use. The volatile solvent was evaporated slowly with heating, and frequent stirring, to prevent coagulation of the particles. The powder was then sieved (60/80 mesh) to remove any large particles and packed into the glass column, applying a vacuum to one end. After measurement of the retention volumes the coated support was unpacked, loaded into a soxhlet thimble and extracted with tetrahydrofuran for 48 hours. The support was dried in an oven at 80°C for 24 hours and in a vacuum oven at 80°C and 0.1 mm Hg for 24 hours and weighed in order to calculate the true polymer loading.

The packed column was loaded into the g.l.c. oven and left for 6 hours at 120°C, while nitrogen was flushed through the column, in order that it should come to equilibrium. The retention volumes were measured for several solvents (hexane, butan-2-one, acetonitrile, chloroform, ethyl acetate, n-propanol and acetone). Samples of solvent (0.1 μl) were injected with a 1μl Hamilton syringe. The time to peak retention volume was measured using a stopwatch calibrated in 0.2 s. The dead time (t_{gas}) was measured by injecting a sample of air. All measured retention times were taken in triplicate and an average taken. Five flowrates from 30 ml min^{-1} to 5 ml min^{-1} were taken and the net retention volume extrapolated to zero flowrate.

The polymers used singly were poly(vinyl chloride), the ethyl, n-propyl, n-butyl, n-pentyl and n-hexyl polymethacrylates, and the methyl, ethyl, n-propyl, n-butyl, and n-hexyl polyacrylates. The mixed polymer systems used were poly(vinyl chloride), in 50/50 mixtures, with the ethyl, n-propyl, n-butyl, and n-pentyl polymethacrylates, and with the n-propyl and n-butyl polyacrylates. In the previous paper these have been shown to produce one phase mixtures when cast from butan-2-one. The preparation and molecular weights of the polymers used are as given in the previous paper of this series.

RESULTS AND DISCUSSION

The values of the physical properties necessary for the calculation of the interaction parameters are shown in *Table* 1. Saturated vapour pressures[15], densities[16], and second virial coefficients[17], were obtained from the literature.

Expansion coefficients for the solvents, necessary for the calculation of the specific core volumes were derived from the literature[16]. Densities of the polymers and their expansion coefficients, where available, were taken from the literature[18]. The values of v^* and V^* so derived are shown in *Table* 2. The values of V_g^0 for the various polymer/solvent systems are shown in *Table* 3, and the values of χ_{12} calculated from them are shown in *Table* 4.

The solvents may be classified as non-polar (hexane), proton accepting (butan-2-one, acetone, and ethyl acetate) and proton donating (chloroform). Acetonitrile and propanol, while included, may give anomalous results due to self-association phenomena[19,1].

The results for poly(vinyl chloride) are generally high, indicating the general insolubility of the polymer at 120°C. The hexane value is marginally within the experimental error in V_g^0 considered to be about ± 0.05, and hence will give a very inaccurate value of χ_{12}. χ_{12} is, however, certainly very large. The best solvent, indicated by the lowest χ_{12} value is butan-2-one, a good proton acceptor and a known solvent for PVC at room temperature.

The results for the polyacrylates and polymethacrylates with solvents other than hexane and chloroform show a general tendency for the solvents to interact more

Table 2 Core volumes of the components

Material	v^* (cm^3 g^{-1})	V^* (cm^3)
Hexane	1.246	107.17
Butan-2-one	1.106	79.63
Acetonitrile	1.130	46.35
Chloroform	0.561	59.55
n-Propanol	1.044	62.69
Acetone	1.105	64.09
Ethyl acetate	0.926	81.52
Poly(vinyl chloride)	0.63	
Poly(butyl acrylate)	0.82	
Poly(ethyl acrylate)	0.76	
Poly(n-propyl methacrylate)	0.77	
Poly(n-butyl methacrylate)	0.79	

Table 3 Values of V_g^0 (cm^3) for single polymer systems

Polymer	Hexane	Butan-2-one	Acetonitrile	Chloroform	n-Propanol	Acetone	Ethyl acetate
Poly(vinyl chloride)	0.1	8.1	7.9	4.8	3.7	3.5	4.7
Poly(ethyl methacrylate)	2.4	13.5	17.8	25.9	15.5	8.1	11.5
Poly(n-propyl methacrylate)	6.3	13.6	11.9	20.6	16.1	7.6	11.5
Poly(n-butyl methacrylate)	6.7	14.1	11.7	19.1	15.6	7.0	12.0
Poly(n-pentyl methacrylate)	8.0	12.0	12.5	19.2	13.5	5.8	10.3
Poly(n-hexyl methacrylate)	6.3	10.6	7.4	16.7	11.8	5.6	9.6
Poly(methyl acrylate)	1.8	11.5	15.8	13.5	14.3	6.7	9.1
Poly(ethyl acrylate)	2.7	12.7	14.3	16.5	15.7	7.4	10.5
Poly(n-propyl acrylate)	5.0	13.1	12.4	17.5	16.3	8.0	11.5
Poly(n-butyl acrylate)	4.8	11.5	11.4	19.1	15.4	6.5	11.1
Poly(n-hexyl acrylate)	6.5	12.3	9.7	19.3	13.4	6.1	11.0

Table 4 Values of χ_{12} for polymer/solvent systems

Polymer	Hexane	Butan-2-one	Acetonitrile	Chloroform	n-Propanol	Acetone	Ethyl acetate
Poly(vinyl chloride)	4.7	0.89	1.57	1.20	2.19	1.34	1.28
Poly(ethyl methacrylate)	1.75	0.60	0.98	−0.25	0.98	0.72	0.61
Poly(n-propyl methacrylate)	0.82	0.63	1.42	0.01	0.98	0.82	0.65
Poly(n-butyl methacrylate)	0.78	0.62	1.40	0.10	1.01	0.93	0.67
Poly(n-pentyl methacrylate)	0.62	0.79	1.41	0.11	1.19	1.13	0.79
Poly(n-hexyl methacrylate)	0.91	0.81	1.47	0.22	1.36	1.20	0.90
Poly(methyl acrylate)	1.95	0.68	1.02	0.30	0.97	0.82	0.76
Poly(ethyl acrylate)	1.63	0.66	1.32	0.19	0.97	0.81	0.70
Poly(n-propyl acrylate)	1.10	0.70	1.42	0.20	1.00	0.81	0.68
Poly(n-butyl acrylate)	1.17	0.87	1.54	0.15	1.10	1.05	0.76
Poly(n-hexyl acrylate)	0.87	0.95	1.70	0.14	1.24	1.11	0.76

Table 5 V_g^0 values for mixed columns of PVC with the indicated polyacrylate or polymethacrylate

Polymer	Hexane	Butan-2-one	Acetonitrile	Chloroform	n-Propanol	Acetone	Ethyl acetate
Poly(ethyl methacrylate)	3.5	5.2	5.5	4.7	4.3	2.7	3.9
Poly(n-propyl methacrylate)	3.0	7.5	7.3	7.3	5.5	4.2	4.5
Poly(n-butyl methacrylate)	3.7	8.5	7.5	8.6	5.4	4.6	6.5
Poly(n-pentyl methacrylate)	3.7	9.9	8.0	11.4	9.0	4.5	10.3
Poly(n-propyl acrylate)	3.3	10.7	11.7	11.3	9.7	6.6	8.3
Poly(n-butyl acrylate)	3.8	10.6	10.3	13.7	11.0	7.4	10.0

Table 6 χ_{23} values for mixtures of PVC

Polymer	Hexane	Butan -2-one	Aceto- nitrile	Chloro- form	n- Propanol	Acetone	Ethyl acetate	Average excluding hexane
Poly(ethyl methacrylate)	7.25	−2.9	−3.26	−3.84	−2.57	−2.9	−2.72	−3.03
Poly(n-propyl methacrylate)	4.73	−1.45	−1.22	−1.59	−1.72	−0.99	−2.18	−1.52
Poly(n-butyl methacrylate)	5.00	−1.03	−1.07	−0.78	−1.72	−0.44	−0.70	−0.96
Poly(n-pentyl methacrylate)	4.59	−0.04	−1.97	0.34	0.65	−0.10	−1.01	−0.02
Poly(n-propyl acrylate)	5.18	0.07	0.06	0.52	0.52	0.71	0.43	0.38
Poly(n-butyl acrylate)	5.75	0.33	0.27	1.06	1.13	1.66	1.12	0.98

strongly with the lower alkyl chain length polymers. Hexane, which would be expected to interact more strongly with the less polar, longer alkyl chain length polymers shows the opposite effect. The very low values obtained for chloroform may be interpreted in terms of the hydrogen bonding of the proton of chloroform to the ester group. This type of interaction is known to exist in many similar systems[20,21,22].

The V_g^0 values for mixed columns of 50/50 by weight poly(vinyl chloride) with various polyacrylates and polymethacrylates are shown in *Table* 5 and the values of χ_{23} calculated from them (using values of χ_{12} and χ_{13} appropriate from *Table* 4 are shown in *Table* 6.

The values of χ_{23} obtained when using hexane as a probe are unreliable as they depend on the unreliable χ_{12} value with PVC and have therefore been left out of the average value. The values of χ_{23} found when using all other solvents show the same trends. The polyacrylates and polymethacrylates with the smallest ester group chains have the lowest χ_{23} values, and hence have greater interactions with PVC, and can be expected to be more compatible. The polymethacrylates also have greater

Table 7 Values of χ^*_{12} for various polymer/solvent systems

Polymer	Hexane	Butan-2-one	Acetonitrile	Chloroform	n-Propanol	Acetone	Ethyl acetate
Poly(vinyl chloride)	4.95	1.04	1.73	1.42	2.73	1.51	1.51
Poly(ethyl methacrylate)	1.96	0.71	1.11	–0.07	1.12	0.85	0.79
Poly(n-propyl methacrylate)	1.01	0.72	1.52	0.17	1.10	0.93	0.81
Poly(n-butyl methacrylate)	0.97	0.70	1.56	0.27	1.15	1.03	0.79
Poly(n-butyl acrylate)	1.34	0.95	1.63	0.31	1.21	1.15	0.91

Table 8 Values of χ^*_{23} for PVC with the indicated polymers

Polymer	Hexane	Butan -2-one	Aceto-nitrile	Chloro-form	n-Propanol	Acetone	Ethyl acetate	Average excluding hexane
Poly(ethyl methacrylate)	7.38	–2.88	–3.18	–3.76	–2.51	–2.86	–2.69	–2.98
Poly(n-propyl methacrylate)	6.22	–1.42	–1.16	–1.51	–1.63	–0.95	–2.12	–1.47
Poly(n-butyl methacrylate)	5.21	–1.01	–1.02	–0.71	–1.66	–0.41	–0.75	–0.92
Poly(n-butyl acrylate)	6.49	0.33	0.31	1.13	1.19	1.66	1.14	0.96

interactions with PVC than the acrylates. One can also compare the low values of χ_{23} for the lower polymethacrylates with the low values of χ_{12} shown for the same polymers with chloroform in *Table* 4 where a similar interaction is postulated.

The values of χ_{23} measured for the acrylates are above the critical values of χ_{23} which should be approximately zero. The results in the previous paper suggest that at 120°C these polymers are close to their lower critical solution temperature and that χ_{23} should therefore be around zero. A positive χ_{23} suggests a value above the lower critical solution temperature which is only possible if the phase diagram is asymmetric with respect to composition. This is quite possible, especially if the two polymers have different molecular weights.

The scatter of χ_{23} values around the average value, when determined using various solvent probes, may represent to some extent an accumulation of random errors in the various experiments. It is, however, more likely to be largely due to a failing in the theory which is based on a lattice model with the inclusion of a heat of mixing term. This cannot hope to account for specific interactions between the various components such as hydrogen bonding and steric restrictions.

In the cases where the data is available values of χ^*_{12} have been calculated for the single polymer/solvent systems, and these are shown in *Table* 7. Using these, values of χ^*_{23} have been calculated for the mixed polymer systems, and these are shown in *Table* 8.

There is no way of saying which of the two values χ_{23} or χ^*_{23} is most valid. Both, however, show a similar trend and are not very different. The exact values of interaction parameters may also show some variation with the molecular weights of the polymers though at the molecular weights used (as given in the first paper of this series) the effect is not expected to be large.

CONCLUSIONS

Measurement of polymer-solvent interaction parameters, χ_{12}, and polymer-polymer interaction parameters, χ_{23}, by inverse gas chromatography, has been found to give reproducible, comparative values within a series of experiments. The variation in values of χ_{23} found using different solvent probes, however, suggests that the absolute values are not reliable.

The values of χ_{12} calculated show the importance of specific interactions between polymers and solvents. Low values of χ_{12}, indicating a strong interaction were found for the polyacrylates and polymethacrylates with a proton donating solvent, chloroform, and for the poly(vinyl chloride) with some proton accepting solvents, especially butan-2-one. This suggests the existence of a 'complementary dissimilarity' between PVC and the other polymers which can lead to compatibility.

The values of χ_{23} found were often very low indicating a strong interaction between the polymers. This was especially true for polymethacrylates and polyacrylates with shorter ester side chains. Lower values were obtained for polymethacrylates than polyacrylates indicating again greater interactions.

These results fit in well with the results of the previous paper in this series where it was found that the polymers with longer ester side chains either were not compatible with PVC or phase separated on heating, and that fewer acrylates were compatible with PVC than methacrylates.

REFERENCES

1 Newman, R. D. and Prausnitz, J. M. *J. Phys. Chem.* 1972, **76**, 1492
2 James, A. T. and Martin, J. P. *Biochem J.* 1952, **50**, 679
3 Porter, P. E., Deal, C. H. and Stross, F. H. *J. Am. Chem. Soc.* 1956, **78**, 2999
4 Patterson, D., Tewari, Y. B., Schreiber, H. P. and Guillet, J. E. *Macromolecules* 1971, **4**, 356
5 Olibisi, O. *Macromolecules* 1975, **8**, 316
6 Martin, R. L. *Anal. Chem.* 1961, **33**, 347
7 Galin, M. and Rupprecht, M. C. *Polymer* 1978, **19**, 506
8 Conder, J. R., Locke, D. C. and Purnell, J. H. *J. Phys. Chem.* 1972, **76**, 1492
9 Braun, J. M. and Guillet, J. E. *Macromolecules* 1975, **8**, 892
10 Summers, W. R., Tewari, Y. B. and Schreiber, H. P. *Macromolecules* 1972, **5**, 12
11 Tewari, Y. B. and Schreiber, H. P. *Macromolecules* 1972, **5**, 329
12 Lichtenthaler, R. N., Newman, R. D. and Prausnitz, J. M. *Macromolecules* 1973, **6**, 650

13 Patterson, D. and Schreiber, H. P. *Soc. Plast. Eng. Tech.* 1975, Paper **21**, 120

14 Su, C. S., Patterson, D. and Schreiber, H. P. *J. App. Pol. Sci.* 1976, **20**, 1025

15 Dreisbach, R. R. 'Physical Properties of Chemical Compounds' American Society Press, Washington, 1965

16 Timmermans, I. 'Physico-Chemical Constants of Pure Organic Compounds' Elsevier, New York, 1960

17 Dymond, J. and Smith, E. B. 'The Virial Coefficients of Gases, a Critical Compilation' Clarendon Press, Oxford, 1969

18 Van Krevlin, D. W. 'Correlation between Structure and Physical Properties of Polymers', Van Nostrand, 1976

19 Covitz, F. H. and King, J. W. *J. Pol. Sci., Pol. Chem. Ed.* 1972, **10**, 689

20 Sheridan, J. P., Martire, D. E. and Tewari, Y. B. *J. Am. Chem. Soc.* 1972, **94**, 3294

21 Sheridan, J. P., Martire, D. E. and Banda, F. P. *J. Am. Chem. Soc.* 1973, **95**, 4788

22 Liao, H. L., Martire, D. E. and Sheridan, J. P. *Anal. Chem.* 1973, **45**, 2087