Influence of chlorination of poly(vinyl chloride) on miscibility with poly(methyl methacrylate)

E. J. Vorenkamp and G. Challa

Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

(Received 12 June 1987; accepted 21 July 1987)

The improvement of the miscibility of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) with moderate chlorination of PVC was demonstrated by determination of cloud-point curves and glass transitions of the mixtures. Heats of mixing of low-molar-mass analogues for PMMA and for the various structural units present in chlorinated PVC (CPVC) were determined in a microcalorimeter along with Fourier transform infra-red spectroscopy of these mixtures. The results show that the improvement of miscibility is caused by a specific interaction between the carbonyl group of PMMA and predominantly the CHCl group of CPVC. The specific interactions present in these systems are best described as a Lewis acid–base type of interaction, considering the carbonyl oxygen of the ester as an electron donor and the hydrogen of the CHCl group as an electron acceptor: C=O . . . HC–Cl. The decrease in miscibility observed when more strongly chlorinated PVC is used can be ascribed to the relatively high concentration of CCl_2 groups, which have a less favourable interaction with the carbonyl groups.

(Keywords: polymer blends; miscibility; poly(methyl methacrylate); poly(vinyl chloride); Fourier transform infra-red spectroscopy; heats of mixing; specific interactions)

INTRODUCTION

In a previous paper[1] we reported that poly(vinyl chloride) (PVC) is more compatible with syndiotactic (s-) poly(methyl methacrylate) (PMMA) than with isotactic (i-) PMMA. Atactic (a-) PMMA, having a microstructure that is closer to s- than i-PMMA, behaves very similarly to s-PMMA and shows (as reported before) typically a lower critical solution temperature (*LCST*) at 190°C.

In binary blends of high-molar-mass polymers the condition for miscibility is that the second derivative of the Gibbs free energy of mixing is positive, which means that the free energy of mixing has to be negative. As the entropy of mixing in such high-molar-mass blends is very small, this implies that the enthalpy of mixing should be negative. Two basically different ways to obtain exothermic mixing can be distinguished. First, miscibility between homopolymers can be considered to be the result of the occurrence of specific intermolecular interactions, for example in a blend of polycaprolactone (PCL) and polyvinylphenol (PVPh)[2], where an intermolecular hydrogen bridge type of interaction is present between the carbonyl oxygen and the hydroxyl group. Secondly, in blends consisting of one or two random copolymers, miscibility can be considered to be the result of an intramolecular 'repulsion' between the component monomer units of the copolymer, which 'out-ranges' the intermolecular repulsion eventually present. In a paper by Woo, Barlow and Paul[3] this treatment was extended to mixtures of homopolymers, which were considered as alternating copolymers of the component units, e.g. aliphatic and O–CO groups in polyesters. The miscibility between PMMA and PVC is in line with reports on other systems consisting of carbonyl-containing polymers, like polyesters (e.g. PCL), and complementary polymers, like PVPh[2], PVC[4,5], styrene–acrylonitrile copolymers[6], poly(vinylidene chloride-*co*-acrylonitrile)[7], poly(vinylidene chloride-*co*-vinyl chloride)[8,9], poly(bisphenol A carbonate)[10] and poly(hydroxy ether of bisphenol A)[11]. Other examples are ethylene–vinyl acetate (EVA) copolymers with PVC[12] or chlorinated polyethylene[13]. In all these systems, shifts to lower frequency and asymmetric broadening of the carbonyl stretching vibration are observed and taken as an indication for specific intermolecular interactions involving the carbonyl bond. In mixtures containing polymers with hydroxyl groups, such as PVPh[14], or poly(hydroxy ether of bisphenol A)[11], red shifts of the OH stretching vibration due to specific interaction have been observed. In such cases an explanation of the nature of this interaction in terms of a hydrogen bridge between OH and CO groups seems correct.

In blends like PVC/PMMA, however, there is less certainty about the precise nature of the interacting moiety in PVC. For such blends, two types of interactions have been mentioned[7,15]: interactions involving the carbonyl group either with the methyne proton, which is also considered to be a type of hydrogen bridge interaction, or with the carbon–chlorine bond of PVC, which has been described as a dipole–dipole interaction.

In this paper miscibility of PMMA with chlorinated PVC (CPVC) was investigated. In varying the degree of chlorination, CHCl and CCl_2 group contents are varied, which may cause a difference in miscibility with PMMA. In using moderately chlorinated PVC, an improvement of the miscibility with PMMA was observed. The effects are explained by studying the interactions between low-molar-mass analogues for PMMA and (C)PVC.

0032–3861/88/010086–07$03.00

Table 1 Molar masses of polymers used, and Mark–Houwink constants

Mark–Houwink constants for g.p.c.			
PVC	$K=1.5\times10^{-4}$ $a=0.77$	PS	$K=1.14\times10^{-4}$ $a=0.72$
PMMA	$K=8\times10^{-4}$ $a=0.75$	CPVCs	as PVC

Sample	$\bar{M}_w$	$\bar{M}_n$
PMMA	100000	45000
PVC	75000	36000
CPVC-63	70000	37000
CPVC-65	60000	32000
CPVC-67	85000	43500

EXPERIMENTAL

Materials

The polymer samples used are all commercially available: poly(methyl methacrylate) (PMMA) was obtained from ICI (Diakon M0900); poly(vinyl chloride) (PVC) was obtained from Péchiney et St Gobain (Lucovyl RB8010); the chlorinated PVCs were purchased from Nobel (Rhenoflex-CPVC63) and B. F. Goodrich Temprite (Geon 647X532-CPV65 and Geon 674X571-CPVC67). The molar masses were determined by g.p.c. (Waters ALC/GPC 150C) using tetrahydrofuran (THF) as eluent, relative to polystyrene standards. *Table 1* contains the molar masses of the samples used, together with the Mark–Houwink constants.

Polymer blends

Blends of (C)PVC and PMMA were prepared in three different ways: solution blending, melt mixing and precipitation from a common solvent. Solution blending was performed by casting 3 wt% mixed solutions in butan-2-one on a warm glass plate (30°C). The films obtained were used after drying in vacuum for studying optical clarity. Melt mixing was performed at 180–190°C on a two-roll mill, using 1 wt% stabilizer (di-n-octyltin-5,5'-bis(iso-octylmercaptoacetate)). The samples used for the d.s.c. experiments were precipitated from butan-2-one solution into hexane.

Glass transitions

The glass transition temperatures were measured with a Perkin–Elmer DSC-2 differential scanning calorimeter at a heating rate of 10°C min^{-1}, using an Apple-II^{e} microcomputer for the data handling.

Cloud-point curves

The cloud points were determined by light scattering at an angle of 30° on thin films that were directly cast onto glass microscope slides. A modified Cenco-TNO light scattering photometer was equipped with a heating block, which could be controlled electrically, and was used at a heating rate of 4°C min^{-1}.

Heats of mixing

The heats of mixing of low-molar-mass analogues were measured at 30°C with a Setaram Calvet type microcalorimeter.

Infra-red spectroscopy

The infra-red spectra were recorded with a Bruker IFS-88 *FT* i.r. spectrophotometer at a resolution of 2 cm^{-1}, using a solution cell with a pathlength of 15 μm or 0.1 mm to study the mixtures of analogues and the 1 g dl^{-1} polymer solutions, respectively. Polymer films with traces of solvent were used to study interaction effects of the polymer on the solvent.

RESULTS

Our previous study[16] of the phase behaviour in blends of normal PVC with a-PMMA showed that PVC and PMMA can form homogeneous blends with a single glass transition temperature (T_g), if prepared from suitable solution. Heating of these blends resulted in phase separation above 190°C. However, subsequent annealing at temperatures below 190°C did not result in remixing of the separated phases, probably because of the high viscosity of the blend. By choosing a PMMA sample of a somewhat lower molar mass, Vorenkamp *et al.*[1] were able to observe an equilibrium behaviour, i.e. reversible mixing and demixing upon cooling and heating, respectively, which enabled them to measure a real cloud-point curve (*Figure 1*).

Chlorination of PVC in solution increases primarily the number of CHCl groups and only at a relatively high degree of chlorination does the number of CCl_2 groups become significant[17,18]. From *Table 2*, showing the contents of CHCl and CCl_2 groups in the CPVCs used, it is clear that by using CPVC-63 instead of PVC the

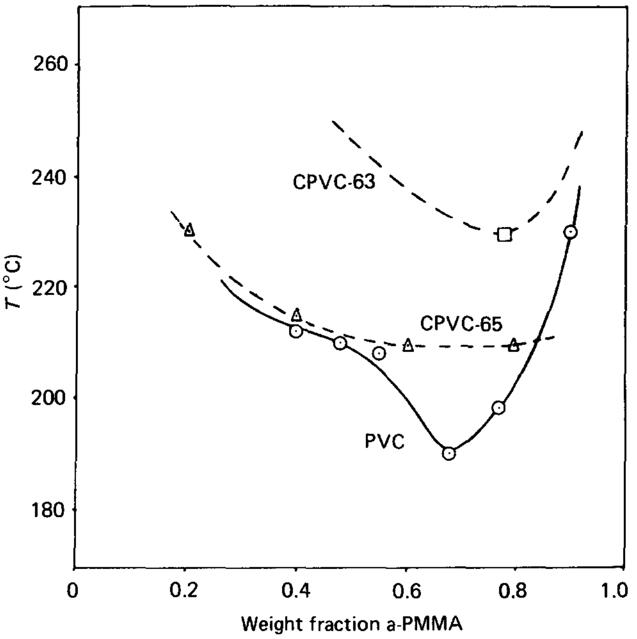

Figure 1 Cloud-point curves for blends of PMMA and (C)PVCs

Table 2 Properties of CPVCs used in blending[a]

Sample	Cl (wt%)	CH_2 (mol%)	CHCl (mol%)	CCl_2 (mol%)
PVC	56.8	50	50	
CPVC-63	63	39.6	57.9	2.5
CPVC-65	65.5	32.5	63.6	3.9
CPVC-67	67	29.6	63.9	6.5

[a] From ref. 17

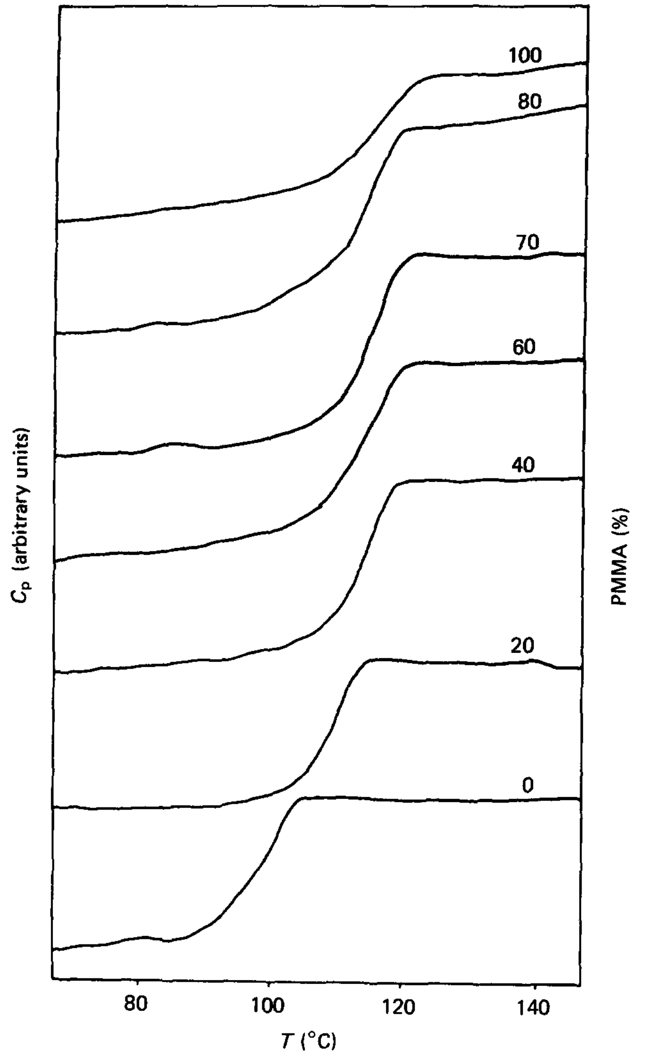

Figure 2 Thermograms for blends of PMMA and CPVC-63

possibilities for interaction through CHCl groups between the polymers are enhanced. This improves the miscibility, as can be concluded from *Figure 1*, showing the cloud-point curves for blends of PMMA with different (C)PVCs, made from mixed solutions. In fact, the cloud-point curve of the blend CPVC-63/PMMA could not be drawn, because of the large degree of degradation above 240°C. Only one point of the cloud-point curve showing reversible mixing and demixing on cooling and heating, respectively, at 80 wt% PMMA could be determined. *Figure 1* also shows the cloud-point curve of the PMMA/CPVC-65 blend, indicating that the compatibility decreased again. As the molar masses of the different (C)PVCs are more or less identical, we may assume that the cause of the difference in miscibility behaviour must be found in the contents of CHCl and CCl_2 groups in the chlorinated PVCs.

Blends of PMMA with (C)PVC were also made by direct melt mixing at 180°C. Heating of the blends of PMMA with CPVC-65 above 220°C resulted in a sudden increase of the turbidity, which did not disappear again during annealing at temperatures below 220°C. This irreversible behaviour means that the cloud-point curve for blends of PMMA with CPVC-65 (and CPVC-67) is probably drawn at too high temperatures, presumably because of the high viscosity of these blends below 220°C.

Homogeneous blends of PMMA with CPVC-63, when investigated by d.s.c., showed only one composition-dependent T_g (*Figure 2*). In *Figure 3* the temperatures of the onset and the end of the T_g jump are plotted against the composition of these blends, showing an above-additive behaviour. From the literature, only a few examples of such behaviour are known. Walsh *et al.*[19] mentioned similar effects in blends of normal PVC with polyacrylates or polymethacrylates and ascribed these to favourable interactions. Kwei *et al.*[20] explained the positive deviation from the additive T_g value by the occurrence of either steric hindrance or a closer packing, both restricting the motion of molecules at the transition point.

Blends of PMMA and CPVC-65 or CPVC-67 also showed only one composition-dependent T_g, which means that at low temperatures these blends are indeed miscible.

To obtain more or less quantitative thermodynamic information on the polymer blends, the heat of mixing of low-molar-mass analogues of the component polymers was measured using a mixing microcalorimeter. Methyl isobutyrate, $CH_3CH(CH_3)COOCH_3$ (MIB), was used as a model for PMMA, and various chlorinated propanes or butanes were used to simulate (C)PVC. From the results in *Figure 4* it can be concluded that on using 1,2,3-

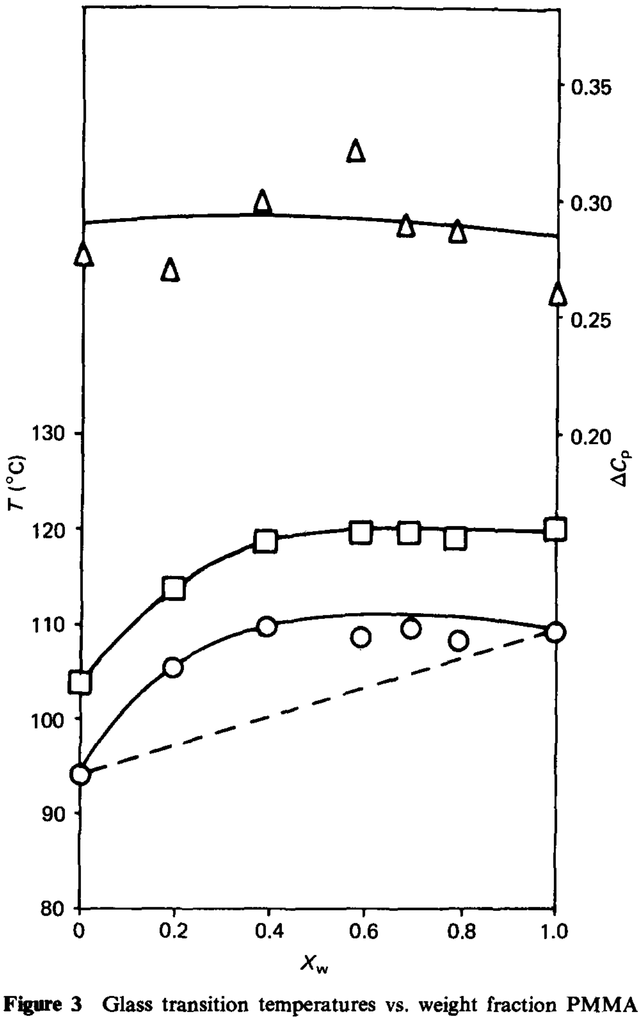

Figure 3 Glass transition temperatures vs. weight fraction PMMA (X_w) for blends of PMMA and CPVC-63: ○, T_g onset; □, T_g end; △, ΔC_p

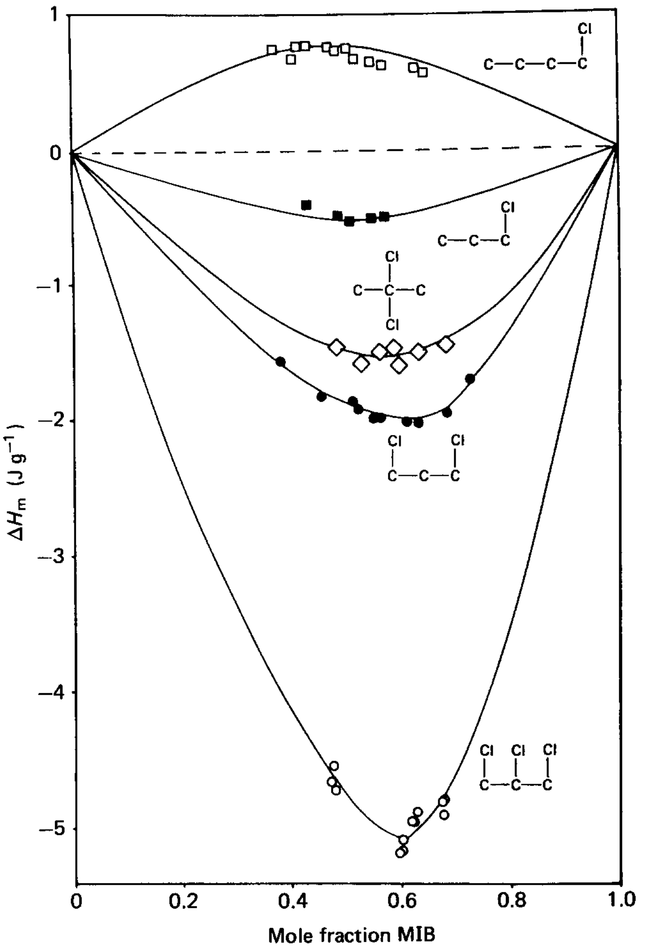

Figure 4 Heat of mixing against composition for mixtures of methyl isobutyrate with chlorobutanes or propanes as indicated

trichloropropane instead of 1,3-dichloropropane (model compounds for CPVC-63 and PVC, respectively) much more heat of mixing is evolved. The observed improvement in miscibility of PMMA with CPVC-63 compared to PVC is in line with this increased heat of mixing due to extra CHCl groups. On the other hand it is also clear from *Figure 4* that the introduction of CCl_2 units does not result in an equal improvement of the interaction. This means that it is not to be expected that the introduction of CCl_2 units into (C)PVC favours miscibility with PMMA. A first reason for this weaker interaction between the CCl_2 units and PMMA compared to the interaction with CHCl units is probably a steric one. The possibilities for a good fit of polymer chains, which are irregularly interrupted by bulky CCl_2 units, are expected to be much less.

The observed specific interactions between MIB and the various chloroalkanes are also reflected in a shift of the carbonyl oxygen stretching vibration to lower frequency, as can be measured by *FT*i.r. (*Figure 5*). The same tendency as above is observed; the mixture of MIB with 1,2,3-trichloropropane shows the largest shift of the C=O band, followed by 1,3-dichloropropane and 2,2-dichloropropane in that order. A combination of the results of microcalorimetry and *FT*i.r. spectroscopy is found in *Table 3*, where the peak wavenumber and the observed width at half-height of the C=O band of MIB in mixtures with various chlorinated solvents are given besides the heat of mixing as measured by calorimetry.

From these results we can draw the following conclusions:

(i) A shift to lower frequency (< 1740 cm^{-1}) measured by infra-red spectroscopy corresponds to a negative heat of mixing as expected (a maximum is found for $CHCl_3$, directly followed by CH_2Cl_2).

(ii) A shift to higher frequency (> 1740 cm^{-1}) measured by infra-red spectroscopy corresponds to a positive heat of mixing, with the maximum effect for pentane.

(iii) A shift of the C=O vibration, whether positive or negative, is also accompanied by band broadening at half-height.

In performing studies with low-molar-mass model compounds, we now have an idea of the type of interactions that may occur between the polymers. However, for entropic and steric reasons it can be

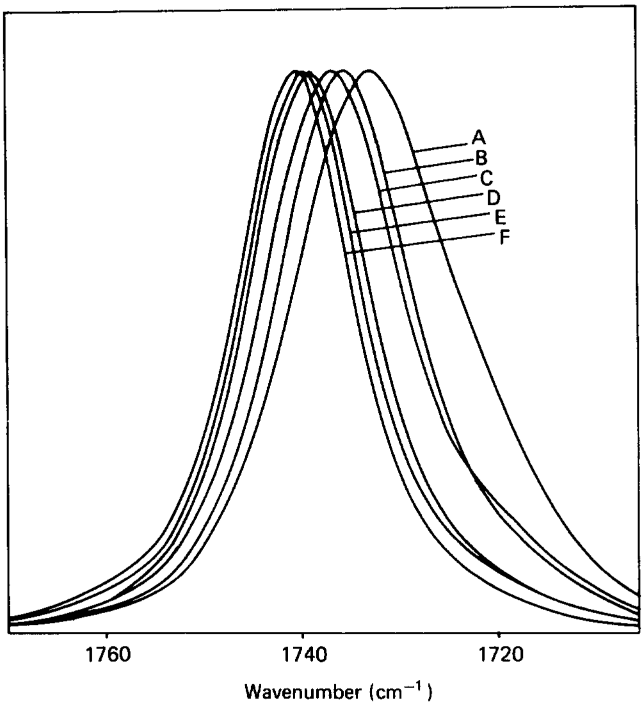

Figure 5 *FT*i.r. spectra in the carbonyl stretching region of solvent mixtures of methyl isobutyrate and (A) 1,2,3-trichloropropane, (B) 1,3-dichloropropane, (C) 1,3-dichlorobutane, (D) 2,2-dichloropropane, (E) *N*-chloropropane, (F) *N*-chlorobutane

Table 3 Data on the carbonyl stretching vibration and the evolved heat of mixing in mixtures of methyl isobutyrate with various chlorinated solvents

MIB mixed with	ν(C=O) (cm^{-1})	Width (C=O) (cm^{-1})	Enthalpy (J g^{-1})
Chloroform	1732	24.9	−14.0
Dichloromethane	1733	20.4	−5.5
1,2,3-Trichloropropane	1733.5	20.75	−5.1
1,2-Dichloroethane	1735	18.0	−2.8
1,3-Dichloropropane	1736.5	16.85	−2.0
1,3-Dichlorobutane	1737.5	17.5	−2.0
2,2-Dichloropropane	1739.5	15.25	−1.6
Tetrachloromethane	1740.7	13.7	−1.05
N-Chloropropane	1741.3	14.85	−0.55
2-Chlorobutane	1741.3	14.7	+0.8
N-Chlorobutane	1741.3	14.25	+0.75
Pentane	1747	15.81	+7.7
Deuterated chloroform	1732	25.0	−16.0

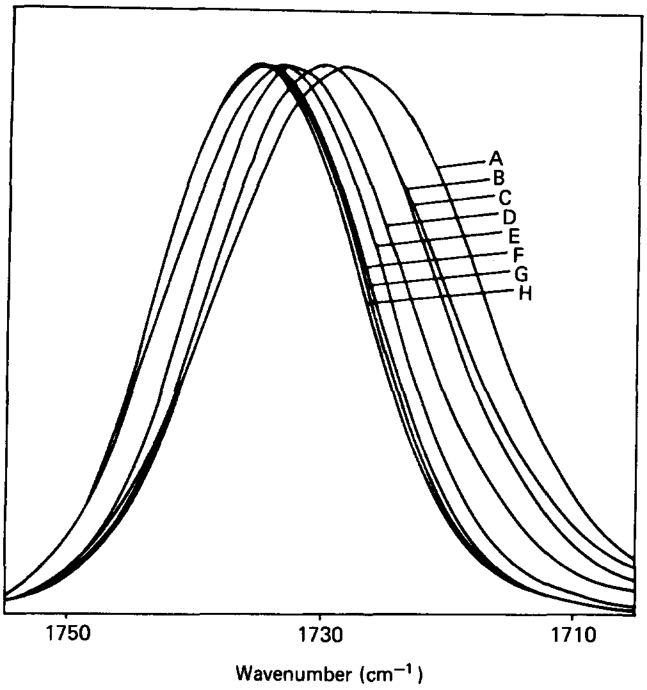

Figure 6 *FT*i.r. spectra in the carbonyl stretching region of PMMA dissolved in (A) chloroform, (B) 1,2,3-trichloropropane, (C) dichloromethane, (D) 1,3-dichloropropane, (E) tetrachloromethane, (F) 2,2-dichloropropane, (G) *N*-chlorobutane, (H) *N*-chloropropane

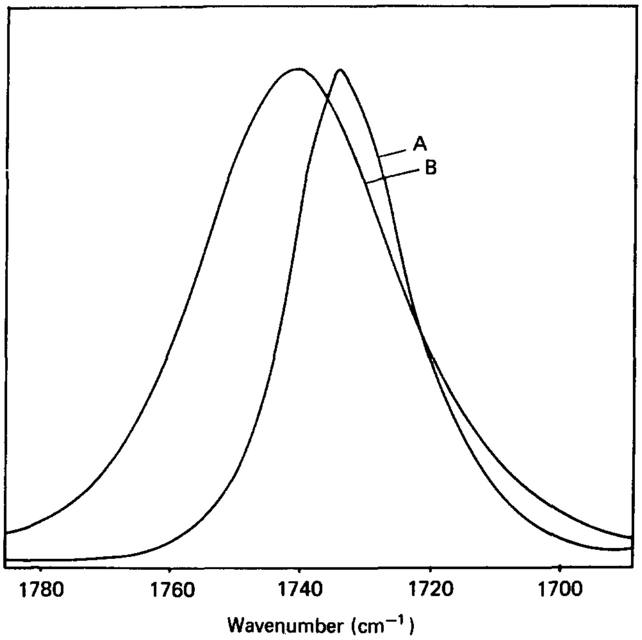

Figure 7 *FT*i.r. spectra in the carbonyl stretching region of (A) traces of methyl isobutyrate in PVC film and (B) methyl isobutyrate

To obtain further information concerning the nature of the intermolecular interaction, we studied the effect of specific solvents on the spectra of our polymers. Based on the model-compound work described above, we used dilute solutions of (C)PVC in MIB and of PMMA in chlorinated solvents to study interaction effects on PVC or PMMA, respectively. Effects on the model compounds themselves were best derived from the spectra of solvent traces in films of PVC or PMMA, made by solution casting from MIB or chlorinated solvent, respectively. *FT*i.r. measurements on solutions of PMMA in the chloroalkanes did show the same trends as the mixtures of MIB with the chloroalkanes, as can be seen from *Figure 6*. Again the largest shift of the C=O vibration is measured in chloroform, followed by 1,2,3-trichloropropane. Solutions of (C)PVCs in MIB did not show any influence of the solvent on the C–Cl vibration band. However, i.r. study on traces of MIB in PVC film did show a red shift of the carbonyl stretching vibration, as can be seen from *Figure 7*, which again clearly confirms the involvement of the carbonyl group. Studying spectra of traces of chlorinated solvents in PMMA film was only successful for 1,2,3-trichloropropane. A clear shift of the C–Cl stretching vibration to lower frequency was detectable, as can be seen from *Figure 8*.

To find out which sites of the groups are responsible for the interaction, we used deuterated chloroform as a model in *FT*i.r. studies on mixtures with MIB or PMMA. As can be seen from *Figure 9a*, there is an influence of the other component on the C–D stretching vibration. We observe a shift in mixtures with MIB or PMMA of 3 cm^{-1} to higher wavenumber compared to mixtures with chloroform. In studying blends of PCL with PVC, Coleman *et al.*[15] observed a similar result in a mixture of methyl acetate and $CDCl_3$. They came to the conclusion that the shift of the C–D stretching vibration is still a shift to lower frequency when compared with the wavenumber of $CDCl_3$ in the vapour phase ($\nu_s = 2260\,cm^{-1}$)[21]. The expected that the interactions and their measurable effects are less pronounced. In studying the infra-red spectra of blends of PMMA with (C)PVC, no influence of mixing on the spectra of the two components was detectable at all. This is in contradiction with the similar miscible system, PCL/PVC[15], which shows a shift of the carbonyl stretching vibration, together with a shift of the C–D stretching mode in blends with α-deuterated PVC. From the lack of any interaction effect on the i.r. spectra in our systems, we must conclude that the interactions between the polymers are only minor in strength or number.

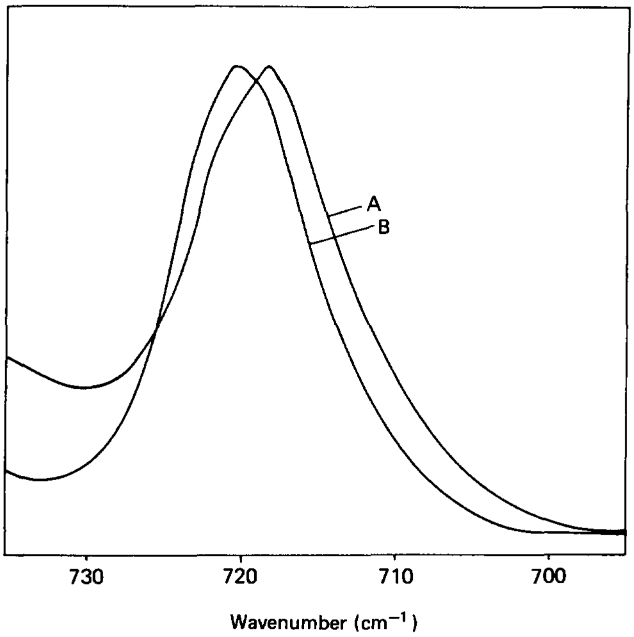

Figure 8 *FT*i.r. spectra in the C–Cl stretching region of (A) traces of 1,2,3-trichloropropane in PMMA film and (B) 1,2,3-trichloropropane

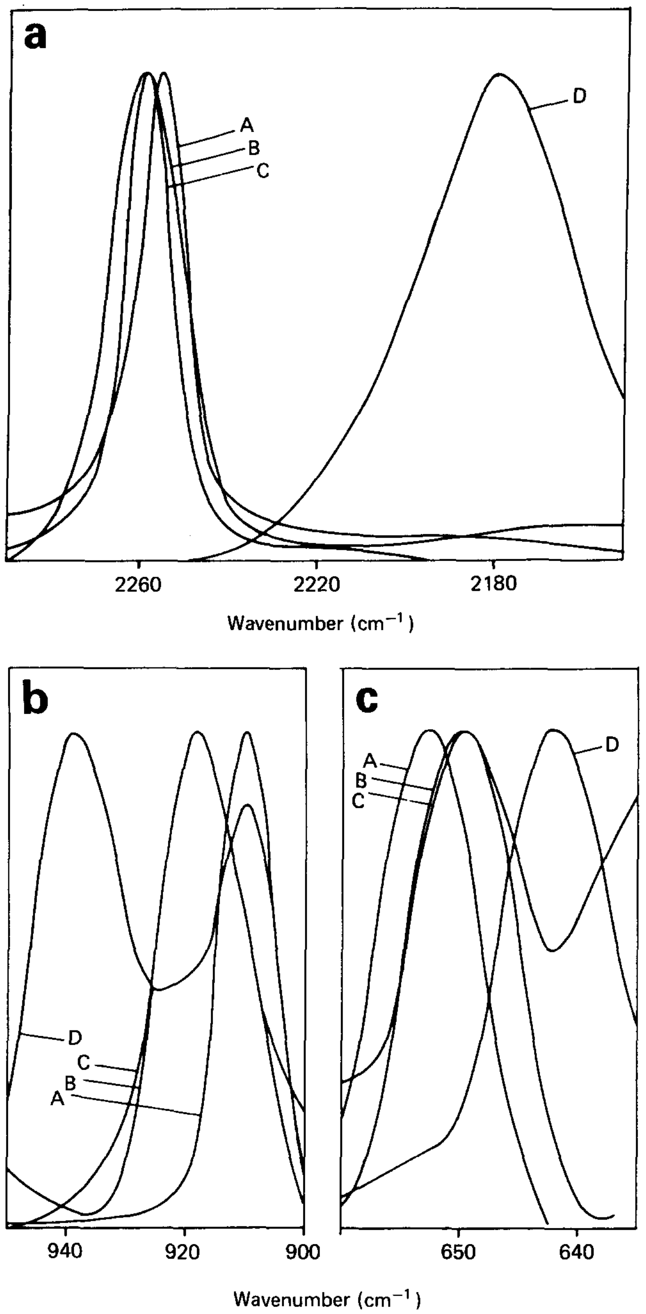

Figure 9 *FT*i.r. spectra in the (a) C–D stretching region, (b) C–D bending region and (c) C–Cl stretching region of CDCl$_3$ mixtures with (A) chloroform, (B) PMMA, (C) methyl isobutyrate and (D) triethylamine

stronger shift of the C–D stretching vibration in CHCl$_3$ is caused by strong self-association, which is present in liquid CDCl$_3$ (or CHCl$_3$). In *Figures 9b* and *9c* the infra-red regions from 950 to 900 cm^{-1} and 660 to 635 cm^{-1} are plotted with bands corresponding to the C–D bending and C–Cl symmetrical stretching vibration modes, respectively. In the presence of MIB or PMMA, a shift to higher frequency is again observed for the C–D bending band but a shift to lower frequencies for the C–Cl stretching vibration.

DISCUSSION

From the results in the previous section we may conclude that the involvement of the carbonyl group in the specific interaction between PMMA and (C)PVC is beyond question. Just as in other miscible systems, like blends of PCL with PVC[4,5], poly(hydroxy ether of bisphenol A)[11] or polyvinylphenol[2], or EVA/VA copolymers with polyvinylphenol[14], a shift of the carbonyl stretching vibration to lower frequency and a subsequent broadening of this band is always found. The types of chemical functionalities acting in the complementary polymeric compounds are less certain. In the literature, miscibility in systems like ours is mostly attributed to the formation of a hydrogen bridge C…H…O=C, yet the presence of a dipole–dipole interaction between C=O and CH–Cl is also mentioned by other authors[7,13]. We believe that a hydrogen bridge, in the normal way involving a shift of a proton, is not present between the carbonyl oxygen and the carbon of the CH–Cl group in our present system. Such a bridge would be strongly influenced by substitution of the α-hydrogen by deuterium. However, measurements of the enthalpy of mixing show nearly no difference in evolved heat of mixing when methyl isobutyrate is mixed with CDCl$_3$ instead of with CHCl$_3$ (*Table 3*). For clarity the effects of added triethylamine (TEA) on the C–D bands and C–Cl band of CDCl$_3$ are also given in *Figures 9a–c*. Comparing the shifts of these bands with those for mixtures with MIB or PMMA, we see that the effects are much more pronounced in mixtures with TEA. This is in line with the expectation that the more strongly electronegative nitrogen of TEA will more easily accept a hydrogen bridge from the CHCl group than the carbon oxygen does.

In our opinion a more reasonable approach to the interactions that occur was described by Fowkes *et al.*[22] using Lewis acid–base interactions. In this explanation, the carbonyl oxygen of the ester is considered to be a Lewis base (electron donor), which can form acid–base 'bonds' with the electron-accepting sites of acidic molecules like PVC. Fowkes showed in his paper that poly(vinyl fluoride) (PVF) interacts more strongly with carbonyl than poly(vinylidene fluoride) (PVDF), which in his opinion indicates that the acidic site of PVF has to be the hydrogen atom on the CHF group. Considering (C)PVC, it seems logical that the differences in interaction of CHCl and CCl$_2$ groups with carbonyl groups are of the same origin and the strongest interactions are of the type C=O…HC–Cl.

Recently, Shiomi *et al.*[23] ascribed the miscibility in a similar system, viz. EVA/VA copolymer with (C)PVC, to intramolecular repulsion between the monomer units. Considering (C)PVC as a random copolymer of the different chlorinated moieties, they were able to derive the occurrence of a 'miscibility window' using calculated, positive segmental interaction parameters X_{ij}. Just as in our blends of PMMA/(C)PVC they found an improvement of the miscibility when moderately chlorinated PVC was used. The miscibility decreased again at higher degrees of chlorination. It seems logical to apply this approach also to (C)PVC/PMMA, but from the enthalpy of mixing and the infra-red spectral shifts in our model-compound studies, we get a strong indication that the interactions between (C)PVC and PMMA are always attractive, i.e. with negative interaction parameters. Thus the positive influence of any intramolecular repulsion on the miscibility should be expected to be of minor importance only.

Finally, we must realize that the infra-red spectroscopy measurements on mixtures of PMMA and (C)PVC did not reflect any influence of the specific interaction. So, interactions between the polymers in the blends are probably only few in number, which means that the X_{ij} in the polymer blend is close to zero. The reason for this small number of interactions is probably steric hindrance, which prevents a close packing of the polymer chains in the blend. Consequently the possibilities for specific interaction are restricted and only a small number of interactions are realized. This idea is in line with the local inhomogeneities with sizes up to 12 nm found by Albert *et al.*[24] in miscible blends of high-molar-mass s-PMMA and PVC, using a so-called non-radiative energy transfer technique. Moreover, this type of texture confirms the view of Kwei *et al.*[20] that restricted mobility of the chains gives rise to enhanced T_g values as shown in *Figure 3*.

REFERENCES

1 Vorenkamp, E. J., ten Brinke, G., Meyer, J. G., Jager, H. and Challa, G. *Polymer* 1985, **26**, 1725

2 Moskala, E. J., Varnell, D. F. and Coleman, M. M. *Polymer* 1985, **26**, 228

3 Woo, E. W., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1985, **30**, 4243

4 Varnell, D. F. and Coleman, M. M. *Polymer* 1981, **22**, 1324

5 Coleman, M. M. and Zarian, J. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 837

6 McMaster, L. P. *Macromolecules* 1973, **6**, 760

7 Garton, A., Aubin, M. and Prud'homme, R. E. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 45

8 Varnell, D. F., Runt, J. P. and Coleman, M. M. *Polymer* 1983, **24**, 37

9 Woo, E. M., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1986, **32**, 3889

10 Varnell, D. F., Runt, J. P. and Coleman, M. M. *Macromolecules* 1981, **14**, 1350

11 Coleman, M. M. and Moskala, E. J. *Polymer* 1983, **24**, 251

12 Iskander, M., Tran, C., Robeson, L. M. and McGrath, J. E. *Polym. Eng. Sci.* 1983, **23**, 682

13 Coleman, M. M., Moskala, E. J., Painter, P. C., Walsh, D. J. and Rostami, S. *Polymer* 1983, **24**, 1411

14 Moskala, E. J., Howe, S. E., Painter, P. C. and Coleman, M. M. *Macromolecules* 1984, **17**, 1671

15 Varnell, D. F., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Polym. Eng. Sci.* 1983, **23**, 658

16 Jager, H., Vorenkamp, E. J. and Challa, G. *Polym. Commun.* 1983, **24**, 290

17 Sikorski, R. T. and Czerwinska, E. *Eur. Polym. J.* 1986, **22**, 179

18 Lehr, M. H. *Polym. Eng. Sci.* 1985, **25**, 1056

19 Walsh, D. J. and Cheng, G. L. *Polymer* 1984, **25**, 495

20 Min, B. Y., Pearce, E. M. and Kwei, T. K. *Polym. Prepr.* 1983, **24**, 441

21 Green, R. D., 'Hydrogen Bonding by C–H Groups', Wiley, New York, 1974

22 Fowkes, F. M., Tischler, D. O., Wolfe, J. A., Lannigan, L. A., Ademu-John, C. M. and Halliwell, M. J. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 547

23 Shiomi, T., Karasz, F. E. and McKnight, W. J. *Macromolecules* 1986, **19**, 2644

24 Albert, R., Jerome, R., Teyssié, P. and Baeyens-Volant, D. *J. Polym. Sci., Polym. Chem. Edn.* 1986, **24**, 2577