Complexation and blending of some water-soluble polymers: solid-state nuclear magnetic resonance relaxation studies

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Water-soluble polymers such as poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), poly(ethylene oxide) (PEO) and poly(vinyl pyrrolidone) (PVP) form interpolymer complexes with secondary bonds. These solid amorphous complexes, blends and mechanical mixtures of component polymers have been studied and the results have been compared. The structures have been analysed using differential scanning calorimetry and ^{13}C cross-polarization/magic-angle spinning nuclear magnetic resonance, and the molecular mobility has been studied using ^{1}H relaxation measurements. The interaction between component polymers affects the molecular motion. $T_{1\rho H}$ and T_{1H} show the molecular-level mixing in complexes and partial mixing in blends. The glass transition of the PMAA–PVP complexes indicates the dominant role of PMAA in the complex. This conclusion is supported by T_{1H} and $T_{1\rho H}$ measurements.

(Keywords: polymer complexes; polymer blends; interaction; nuclear magnetic resonance; cross-polarization; magic-angle spinning; relaxation)

INTRODUCTION

Interpolymer complexes are formed through secondary binding forces such as hydrogen bonds, Coulombic forces or hydrophobic interactions in aqueous solution or in organic solvents. Typical synthetic water-soluble complex-forming polymers are poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), poly(ethylene oxide) (PEO) and poly(vinyl pyrrolidone) (PVP). The association of these systems has been very widely studied[1–3]. The interaction in solutions is very sensitive to temperature, concentration, medium and chain length of the component polymers. The high molecular mass of component polymers leads to the precipitation of complexes with a solid-state character between those of the component polymers.

A blend of two polymers may be prepared either by mixing two polymer solutions or by mixing the components in the molten state. Dissolved polymers are usually expanded by the interaction of the solvent with the chains. Mixing of two polymer solutions allows the component polymers to interact better than in the molten state where the level of mixing depends greatly on mixing time and temperature[4]. When blends are prepared in solution, the solid products have regions with varying level of association. The phase morphology varies strongly when different mixing techniques are employed[5]. The intimacy of mixing and the phase structure are important factors, and the understanding of the interactions between polymers in a blend may give some insight into reasons for the physical and chemical properties of blends[6,7].

Differential scanning calorimetry (d.s.c.) has been mostly used to study polymer miscibility. The detection of a single glass transition temperature, T_g, is generally considered as evidence of compatibility[4]. The question is, what size of domains is required to yield one T_g? First, the difference between the glass transition temperatures of component polymers has to be at least 20 K in order to be resolved from each other. Secondly, a single T_g indicates phase sizes about 10–15 nm[6,8]. The glass transition temperatures of miscible systems lay between the T_g values of component polymers, and may go through a maximum as a function of concentration if strong specific interactions occur between polymers[4].

The ^{13}C cross-polarization and magic-angle spinning (c.p./m.a.s.) n.m.r. technique enables one to obtain information on the molecular structure of amorphous polymers. The method is very useful when the phase structure of blends is studied. ^{13}C relaxation measurements can be used to analyse the motion of polymer chain segments and side chains. Interactions between polymers change the molecular motion and these changes are reflected in the relaxation times. Proton relaxation measurements can be used to show the molecular interaction between the component polymers and to show that mixing takes place on a molecular level[9].

EXPERIMENTAL

The polymers were complexed and blended in distilled water. The polymers, presented in *Table 1*, were used without purification or fractionation. The pH of polyacid solutions was adjusted using hydrochloric acid during complexation.

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Table 1 Component polymers used in this study

Name	Acronym	$\bar{M}_w$	Source
Poly(acrylic acid)	PAA	230 000	BDH
Poly(methacrylic acid)	PMAA	50 000	BDH
Poly(vinyl pyrrolidone)	PVP	40 000	Fluka AG
Poly(ethylene oxide)	PEO	20 000	Fluka AG

Table 2 The extent of PMAA–PVP complexation: wt% means weight per cent PMAA in complex and $r = [\mathrm{PMAA}]/[\mathrm{PVP}]$, i.e. the ratio of repeat units in component polymers

Composition in preparation		Composition in products	
wt%	r	wt%	r
66	3.00	67	3.15
56	2.00	60	2.36
39	1.00	45	1.24
24	0.50	44	1.20
18	0.33	43	1.15

The complexes were prepared with different molecular ratios ($r = [\mathrm{PMAA}]/[\mathrm{PEO}]$, i.e. the ratio of repeat units) and solid complexes include only polymers precipitated due to association. The blends were prepared by mixing the solutions of polymers and evaporating the solvent. Therefore these blends include regions with high-level association and also regions with weak interactions. To see the effects of molecular interactions, mechanical mixtures were prepared, where molecular-level mixing is not possible. The blends and the mechanical mixtures were prepared with $r = 1/1$.

The chemical composition of the complexes was determined by elemental analysis. The samples were dried under vacuum over night before d.s.c. and n.m.r. measurements.

Thermal measurements were made with a Perkin–Elmer DSC-2. Standard calibration methods were used. Samples were sealed in aluminium pans and a heating rate of 10°C min^{-1} was used.

The solid-state ^{13}C n.m.r. spectra were obtained with a JEOL FX 200 n.m.r. spectrometer equipped with a solid-state probe and a home-built m.a.s. accessory. The samples were packed into ceramic rotors made of Macor and spun at about 3.3 kHz. Chemical shifts of the spectra were obtained with respect to the benzene carbon resonance of solid hexamethylbenzene (132.3 ppm). The 90° pulse was 5 μs. Measurements were done at room temperature with 1 or 1.5 ms contact time and with 1 s pulse delay. ^{1}H spin–lattice relaxation times were determined with the proton inversion–recovery pulse sequence prior to cross-polarization[10]. This method allows the determination of $T_{1\mathrm{H}}$ for each line in the ^{13}C spectrum. ^{1}H relaxation in the rotating frame, $T_{1\rho\mathrm{H}}$, was measured with a delayed contact pulse. The intensity of the ^{1}H field is 50 kHz. Direct ^{1}H determinations are not possible with our n.m.r. equipment.

RESULTS AND DISCUSSION

The extent of complexation was analysed for PMAA–PVP systems. It was calculated from the nitrogen content of the complex. The results are presented in *Table 2*. PMAA has a great affinity for complexing PVP. This is seen in the high ratios r, especially when the complex is prepared from solutions with $r = 0.5$ or 0.33, where the products have r ratios greater than unity.

D.s.c. measurements

D.s.c. measurements show that all complexes are amorphous; even the melting peak of crystalline PEO was not detected in the complexes. The glass transition temperatures have been measured for pure polymers and for their complexes. The T_g for a complex of PAA–PVP with $r = 1$ is 446 K, which is between the T_g values of the component polymers, $T_g^{\mathrm{PAA}} = 360$ K and $T_g^{\mathrm{PVP}} = 451$ K. The calorimetric measurements for the PMAA–PVP complexes were done with five different molecular ratios and the T_g values of the complexes were found between the T_g values of component polymers. When the amount of PMAA in the complexes increases, the T_g decreases. The results of d.s.c. measurements for PMAA–PVP complexes are presented later in *Figure 5* and plotted as in ref. 11. The single glass transition of the complexes means that the diameters of pure polymer domains are smaller than 15 nm. It was not possible to estimate the glass transitions of PMAA–PEO and PAA–PEO complexes with sufficient accuracy to yield information on complex formation.

C.p./m.a.s. n.m.r. studies

The ^{13}C chemical shifts of the component polymers studied are presented in *Table 3*. PEO has a minimum of $T_{1\rho\mathrm{H}}$ at room temperature[12] and because of this the spectrum of pure PEO was not measured.

Table 3 ^{13}C c.p./m.a.s. n.m.r. chemical shift data for the polymers studied

Polymer	δ (ppm)	Assignment
PAA	182	$-\mathrm{COOH}$
	40–30	$-\mathrm{C}(\alpha)\mathrm{H}$ and $-\mathrm{C}(\beta)\mathrm{H}_2-$
PMAA	183	$-\mathrm{COOH}$
	56	$-\mathrm{C}(\beta)\mathrm{H}_2-$
	46	$-\mathrm{C}(\alpha)-$
	17	$-\mathrm{CH}_3$
PVP	176	$-\mathrm{C{=}O}$
	52	$-\mathrm{C}(\alpha)\mathrm{H}-$
	44	$-\mathrm{C}(5)\mathrm{H}_2-$
	38	$-\mathrm{C}(\beta)\mathrm{H}_2-$
	33	$-\mathrm{C}(4)\mathrm{H}_2-$
	20	$-\mathrm{C}(3)\mathrm{H}_2-$
PEO	70[a]	$-\mathrm{CH}_2-$

[a] From ref. 14

The association between PAA and PEO chains leads to the splitting of the carboxylic carbon resonance[13], from the original 182 ppm to 183 and 176 ppm in the complex. A different behaviour was observed for the PAA–PVP complex (*Figure 1*), in which one sharp resonance can be found at 178 ppm. The chemical shift of this resonance is between the carboxylic resonance of PAA and the amide carbonyl of PVP. Both of these resonances can be found in the spectrum of a mechanical mixture of PAA and PVP. One resonance in the spectra of the complex and of the blend indicates molecular interaction between component polymers, i.e. hydrogen bonding between the hydroxyl in PAA and the carbonyl in PVP. The resonance of the C(3) carbon in the pyrrolidone ring at 20 ppm is also well separated from

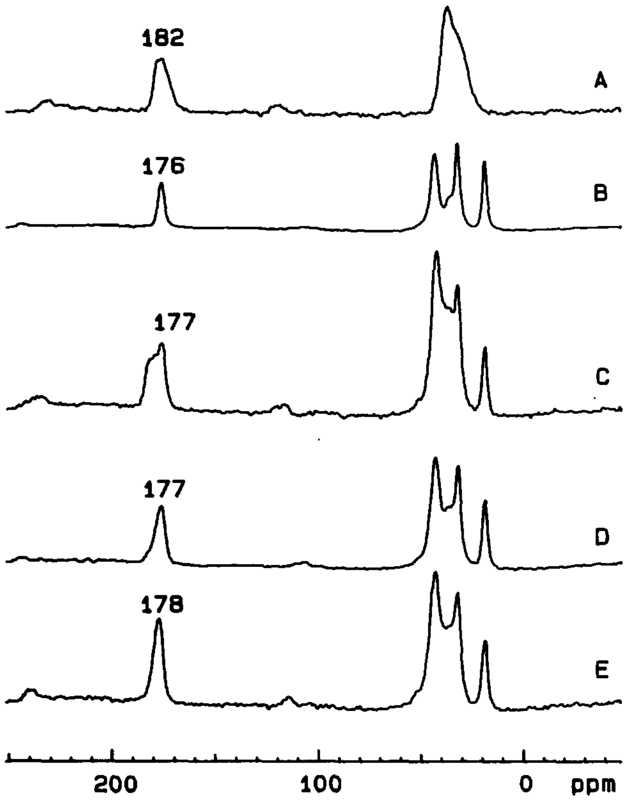

Figure 1 The ^{13}C c.p./m.a.s. n.m.r. spectra of PAA (A), PVP (B), their mechanical mixture (C), blend (D) and association complex prepared with $r = 1/1$ (E)

other resonances, but the chemical shift of this carbon does not vary with complexation. The other resonances of the component polymers are overlapped as can be seen from *Figure 1*.

In the spectra of the complexes as well as the blend of PMAA and PEO all the resonances are well resolved and the complexation can be seen from the shapes of the carboxylic resonances (see *Figure 2*). The resonance of PEO at 70 ppm is not present in the spectrum of the mechanical mixture, and hence PEO behaves as pure polymer in the mixture. Interactions between PEO and PMAA slow down the molecular motion of PEO, which makes it possible to observe the resonance of PEO at 70 ppm at the temperature of the experiment. The chemical shifts between 70 and 17 ppm remain unchanged when the molecular ratio of the prepared complex changes. Only a speculative conclusion could be drawn from the shape of carboxylic resonances in these complexes, since the amounts of component polymers in the complexes are not exactly known. The resonance of PEO is largest in the spectrum of the blend where $r = [PMAA]/[PEO] = 1$ and it is smaller in the spectra of the complexes. It can be seen from the spectra that the interaction between PMAA and PEO also affects the shape of methyl carbon resonances at 17 ppm.

The study of the PMAA-PVP system is also difficult from ^{13}C chemical shifts, because of overlapping of resonances. The chemical shift of the carboxylic carbon for PMAA is at 183.0 ppm and for PVP at 175.8 ppm. In the spectra of the complexes one broad line is observed and the chemical shift is between the carboxylic resonance of PMAA and the amide carbonyl of PVP. Furthermore, the resonance is shifted towards higher field as the molecular ratio $r = [PMAA]/[PVP]$ decreases. The shapes of these resonances are seen in *Figure 3*.

T_{1H} *and* $T_{1\rho H}$ *of the polymer systems*

Many investigations have been done to study the interactions between the components in polymer blends with proton relaxation measurements in a laboratory frame (T_{1H}) and in a rotating frame ($T_{1\rho H}$). In a homogeneous system one spin temperature is established among the abundant spins, but in heterogeneous systems domains of different components have different proton relaxation times[14]. For T_{1H} the spin energy, magnetization, diffuses over a length of some tens of nanometres and for $T_{1\rho H}$ over some nanometres[15]. Some proton relaxation studies ($T_{1\rho H}$) have been done to illustrate minimum domain dimensions (2 nm). This means that domains of component polymers are smaller than this minimum size and good thermal contact between domains is demanded to average the proton relaxation. N.m.r. criteria for miscibility are that all protons in the sample have the same $T_{1\rho H}$ value and that relaxation decays are single exponentials[16].

The proton relaxation times in this study have been calculated separately for all lines in the spectra and the average of all are used. The results are presented in *Tables 4* and *5* with standard deviations.

When T_{1H} of PAA (1.17 s) and PMAA (0.30 s) are compared, it seems that the fast relaxation of PMAA is due to the methyl groups in the α-position, which are

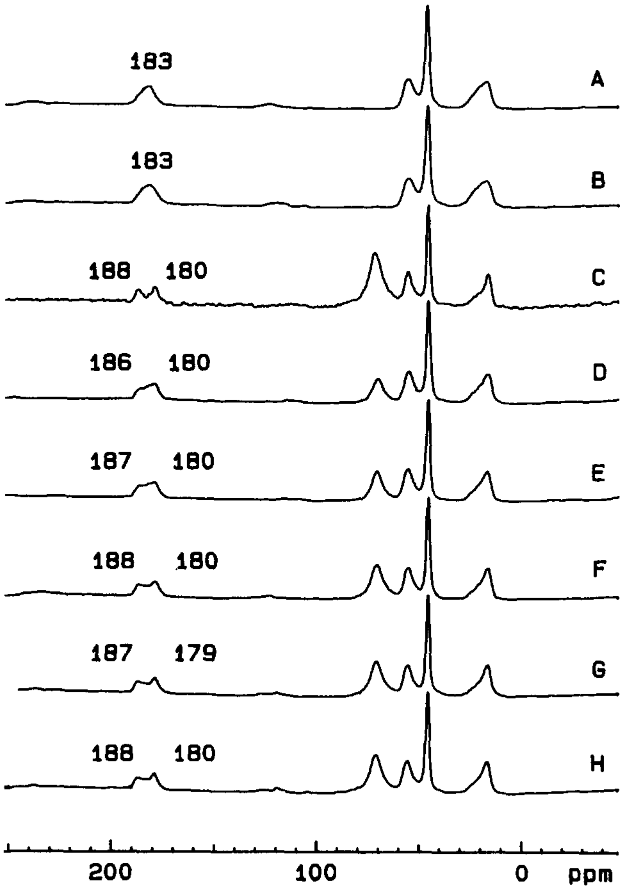

Figure 2 The ^{13}C c.p./m.a.s. n.m.r. spectra of PMAA (A), the mechanical mixture of PMAA and PEO (B), their blend (C) and their association complexes prepared with $r = [PMAA]/[PEO] = 3/1$ (D), 2/1 (E), 1/1 (F), 1/2 (G), 1/3 (H)

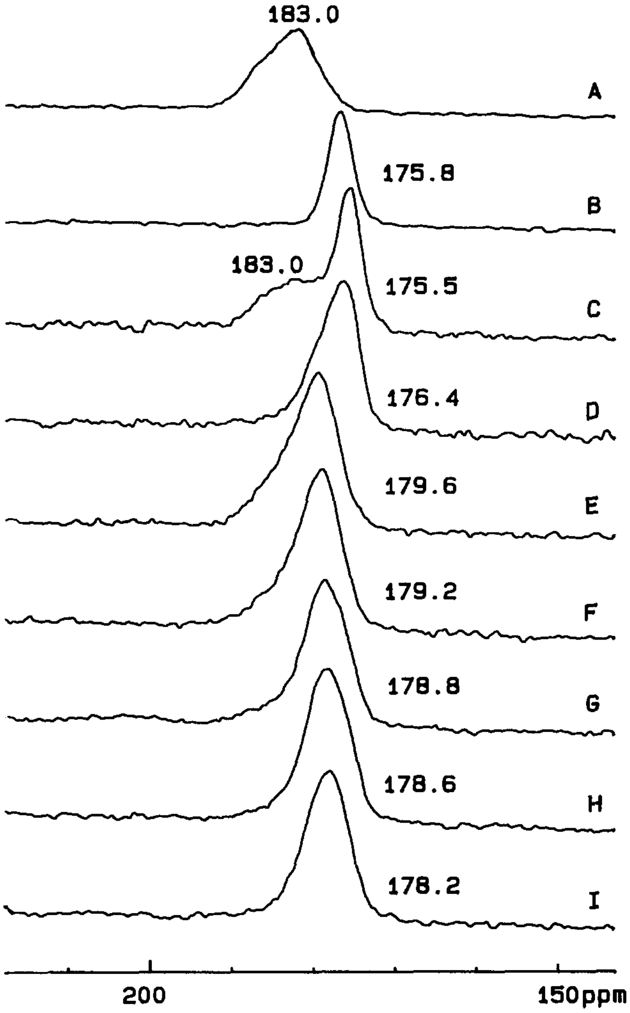

Figure 3 The carboxylic resonance of PMAA (A), the amide carbonyl resonance of PVP (B), their mechanical mixture (C), blend (D) and complexes prepared with $r = [\mathrm{PMAA}]/[\mathrm{PVP}] = 3/1$ (E), 2/1 (F), 1/1 (G), 1/2 (H), 1/3 (I)

acting as relaxation sinks. Such a difference was not seen between $T_{1\rho H}$ of PAA (4.39 ms) and PMAA (4.50 ms).

The differences in T_{1H} are obvious between PMAA (0.30 s) and PVP (1.23 s) and also in $T_{1\rho H}$ between PMAA (4.50 ms) and PVP (15.79 ms). Because of this it is possible to study spin energy averaging due to the interaction between component polymers. The differences in other systems, PAA–PEO, PAA–PVP and PMAA–PEO, are not so clear, as seen in *Tables 4* and *5*.

Because of small standard deviations of T_{1H} calculated for PMAA–PVP complexes with different molecular ratios compared to the standard deviation of T_{1H} for a mechanical mixture, it is possible to say that mixing takes place on a molecular level. This is a good way to show the mixing between component polymers in complexes and blends of PMAA and PVP. The method is efficient when measuring domains with dimensions of some tens of nanometres. The T_{1H} increases in PMAA–PVP complexes when the molecular ratio (r) decreases, i.e. when there are more PVP units than PMAA units in the complex.

The intimacy of molecular mixing is seen by $T_{1\rho H}$ measurements for PAA–PVP and PMAA–PVP. The average distance between the component polymers can be estimated from the diffusive path length (L) by[14,16]:

$$L = (6DT_{1\rho H})^{1/2}$$

where D is the spin-diffusion coefficient ($10^{-12}\ \mathrm{cm^2\ s^{-1}}$). The distances are 2.5 nm for PAA–PVP and 2.2–2.3 nm for PMAA–PVP, which shows that association occurs between the component polymers.

The logarithm of the intensity of the resonance of C(3) of PVP in PMAA–PVP complexes and blend *versus*

Table 4 The mean of proton relaxation time, $\bar{T}_{1H}$, calculated from the decay of each resonance and the standard deviations, $\sigma(T_{1H})$

Polymer pair	Sample	$\bar{T}_{1H}$ (s)	$\sigma(T_{1H})$ (s)
PAA–PEO	PAA	1.17	0.02
	PEO	–	–
	Complex 1/1	0.91	0.03
	1/3	1.19	0.02
PAA–PVP	PAA	1.17	0.02
	PVP	1.23	0.01
	Complex 1/1	1.25	0.02
	Blend	1.21	0.03
	Mechanical mixture	1.15	0.04
PMAA–PEO	PMAA	0.30	0.04
	PEO	–	–
	Complex 3/1	0.37	0.02
	2/1	0.33	0.04
	1/1	0.38	0.01
	1/2	0.36	0.01
	1/3	0.38	0.03
	Blend	0.49	0.13
	Mechanical mixture	0.26	0.03
PMAA–PVP	PMAA	0.30	0.04
	PVP	1.23	0.01
	Complex 3/1	0.33	0.01
	2/1	0.37	0.02
	1/1	0.38	0.01
	1/2	0.41	0.02
	1/3	0.42	0.01
	Blend	0.58	0.03
	Mechanical mixture	0.94	0.38

Table 5 The mean of proton relaxation time in the rotating frame, $\bar{T}_{1\rho H}$, for polymer samples calculated from the decay of each resonance and the standard deviations, $\sigma(T_{1\rho H})$

Polymer pair	Sample	$\bar{T}_{1\rho H}$ (ms)	$\sigma(T_{1\rho H})$ (ms)
PAA–PEO	PAA	4.39	0.22
	PEO	–	–
	Complex 1/1	1.75	0.18
	1/3	2.83	0.37
PAA–PVP	PAA	4.39	0.22
	PVP	15.79	0.56
	Complex 1/1	10.50	0.35
	Blend	9.55	0.80
	Mechanical mixture	11.08	3.22
PMAA–PEO	PMAA	4.50	0.23
	PEO	–	–
	Complex 3/1	3.03	0.35
	2/1	3.44	0.61
	1/1	2.65	0.41
	1/2	2.41	0.42
	1/3	2.61	0.25
	Blend	1.83	0.39
	Mechanical mixture	6.00	0.79
PMAA–PVP	PMAA	4.50	0.23
	PVP	15.79	0.56
	Complex 3/1	7.73	0.77
	2/1	8.08	0.30
	1/1	9.17	0.46
	1/2	8.60	0.54
	1/3	9.01	0.73
	Blend	11.12	0.73
	Mechanical mixture	11.19	3.42

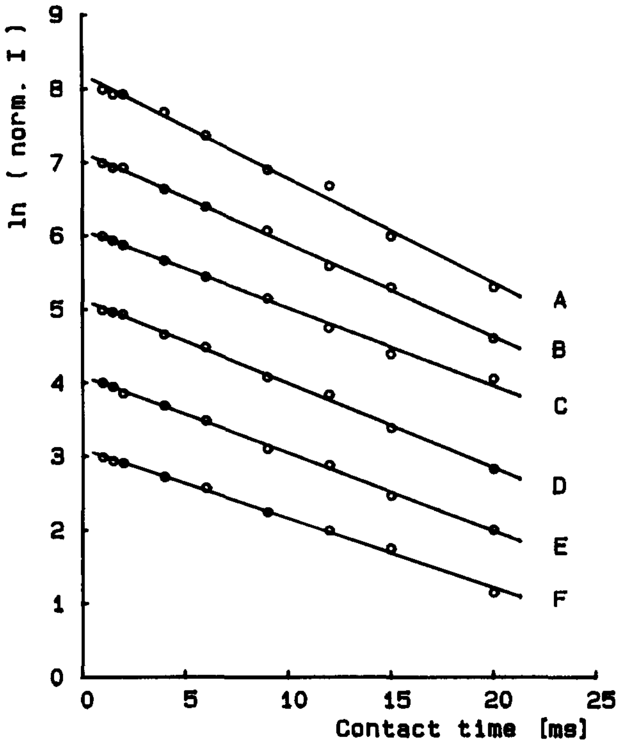

Figure 4 The decay of the normalized intensities of C(3) carbon resonance in pyrrolidone ring for the PMAA–PVP complexes with $r = 3/1$ (A), 2/1 (B), 1/1 (C), 1/2 (D), 1/3 (E) and for their blend (F)

contact time is plotted in *Figure 4*. The plots are linear, which indicates that relaxation in different regions is completely averaged, meaning that the complex forms a continuous phase.

The positive deviation from the additivity line for glass transition temperatures of blends can be correlated with the existence of interaction between component polymers[4,11]. The glass transitions, T_g, of the PMAA–PVP complexes are plotted against complex composition in *Figure 5*. The deviation is negative in these complexes. It is seen that the T_g of the complex remains at the level of PMAA. This is taken as an indication that the PMAA retains its mobility in the complex. T_{1H} and $T_{1\rho H}$ are also plotted against complex composition in *Figure 5*. The behaviour is the same for T_{1H} as for T_g of these complexes and the deviation from linearity of $T_{1\rho H}$ can also be seen in this figure. The relaxation behaviour of the complexes confirms the conclusion that the properties of PMAA dominate in the complex, and that the structure of PVP is broken up. The association between PMAA and PVP in solutions will be analysed further in solutions with n.m.r. and light scattering to obtain more information on the interactions between them.

CONCLUSIONS

The association between component polymers in polymer complexes can usually be seen by the shape of the resonances of the interacting groups in ^{13}C n.m.r. spectra. Complexation also changes the relaxation behaviour of polymer chains. If the component polymers have different relaxation rates, the molecular-level mixing can be analysed with T_{1H} and $T_{1\rho H}$ measurements. The relaxation time averages to some intermediate value between the relaxation times of the pure component polymers. The glass transition of PMAA–PVP indicates the dominant role of PMAA in the complex. This conclusion is supported by T_{1H} and $T_{1\rho H}$ measurements.

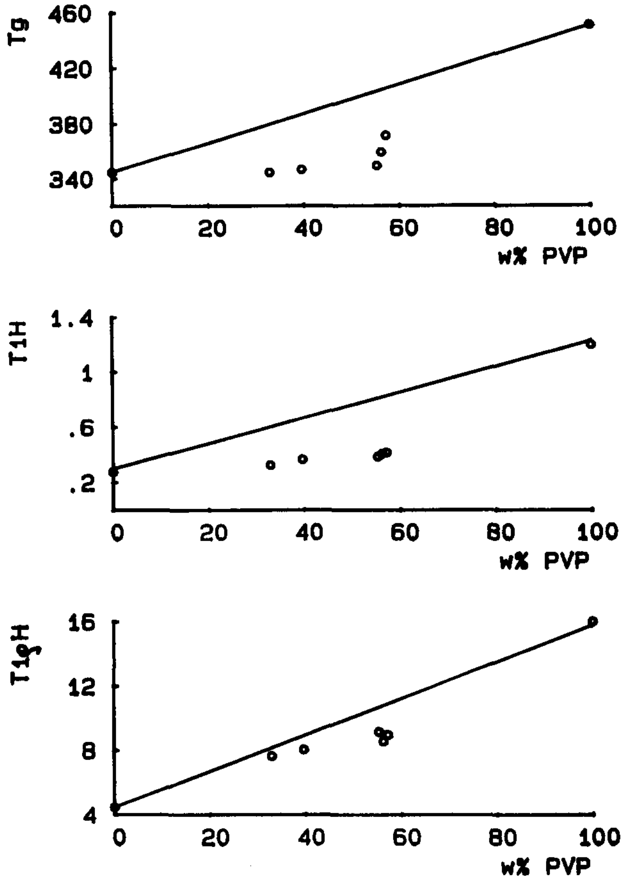

Figure 5 The behaviour of T_g, T_{1H} and $T_{1\rho H}$ of PMAA–PVP complexes as a function of composition (wt% PVP in complexes)

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