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Interpolymer complexation between poly(ethylene oxide) and poly(acrylic acid)

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SUMMARY

Solution and solid state properties of the interaction between poly(acrylic acid) and poly(ethylene oxide) have been studied in the presence and absence of $CaSO_4$ in water or in methanol systems. The association in solution has been investigated by viscosity measurements and NMR spectroscopy. The solid state of the systems has been studied using DSC, IR, X-RAY and 13-C-CPMAS-NMR. Complex formation is also clearly indicated.

INTRODUCTION

Macromolecules undergo interactions with each other in solution, resulting in so-called intermolecular complexes. The formation of such associates is due to the secondary binding forces between the polymer chains. The complex-forming ability is related to the structure of the polymers, the chain length of the components, the solvent and the pH (1,2).

The ability to form interpolymer complexes between poly(carboxylic acid) and poly(ethylene oxide) (PEO) has been found to vary with the type of carboxylic acid. This phenomenon appears to be due to differences in the hydrophobic character of the component polymers. Highly hydrophobic polymers are able to participate in the interactions between their hydrophobic groups and the main chain of PEO, as well as participating in hydrogen bonding. Since this is the main interacting force, the cooperativity on complexation is larger and the complexes formed with PEO are more stable. For this reason the complexation of PEO with poly(acrylic acid) (PAA) behaves quite differently to that with poly(methacrylic acid) (PMAA) (1,2).

It has been shown that sequences of a minimum length are required for complex formation in the PAA-PEO system. It appears that even the presence of a low content of carboxylate sites in the PAA chain is sufficient to destroy complexation. Futhermore complexation is prevented at pH>5, where a fairly substantial proportion of the carboxylic groups on PAA are dissociated (3).

We have studied these phenomena, and especially the association between PAA and PEO in solution, and analysed their character in the solid state with different methods. In addition, we have also investigated whether the presence of a salt ($CaSO_4$) in the solution could prevent the association interaction.

EXPERIMENTAL

The polymers used were Fluka AG poly(ethylene glycol) 400, poly(ethylene oxide) 4000, 20000, EGA CHEMIE poly(acrylic acid) 2000,5000 and BDH poly(acrylic acid) 230000.

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The viscosities of the aqueous solutions containing PEO and PAA of three different molecular weight combinations, 400/2000, 4000/5000 and 20000/230000, were measured at 25°C with an Ubbelohde viscometer. In each series of experiments the PAA concentration was kept constant at 0.03, 0.022 and 0.006 unit mol/l for the sample pairs, only the unit molar ratio r = $[PEO]/[PAA]$ varied from 0 to 3. 0.1 M NaOH was used to adjust the pH to 5. The effect of a salt on complexation was measured by using saturated solutions of $CaSO_4*2H_2O$.

The NMR measurements were made on a JEOL FX 200 FT NMR-spectrometer. The observation frequency was 50.1 MHz for ^{13}C. 10 mm $^1H/^{13}C$ dual probe was used in solution measurements. The signal intensity was accumulated approximately 5000 times with 45° pulses, and the data obtained on 16 K data points over the 10 KHz bandwidth.

DSC measurements were made on a Perkin-Elmer DSC-1B in the range -70°-+150°C. The heating rate was 8°C/min. The DSC was calibrated with indium and n-octane.

The infra-red spectra were measured on a Perkin Elmer 457 Spectrophotometer using the KBr-pellet or film technique.

The X-ray diffraction measurements were made with a DRON-UM1 diffractometer using wide-angle X-ray scattering. 2θ was recorded from 10° to 30°.

The solid state ^{13}C-NMR-spectra were made by the CP-MAS technique (4). Spectra were obtained at room temperature using a KELF-rotor, the spinning speed being 2.8-3.0 KHz. The 90° pulse width for protons was 7.0 µs. A contact time of 0.5 ms and repetition period of 2.0 s were used. Chemical shifts of the spectra were obtained with respect to the benzene carbon resonance of solid hexamethylbenzene (132.3 ppm) measured before each run.

RESULTS AND DISCUSSION

Interaction in solution

The results of the viscosity measurements are presented in Figures 1a-1e. Neutralization of poly(acrylic acid) in pure solutions increased the viscosities in all three cases. The highest increase was obtained with the largest molecular chains . This may be due to the straightening of the chains as a result of the electrostatic repulsion of COO^- groups.

Ca^{2+} and SO_4^{2-} ions present in the solution disturb the interaction. At low pH it increases interaction slightly, but at pH = 5 it decreases it. The interaction product precipitates from solution along with high molecular weight components of the polymers if the concentration is large enough, occuring already at 0.006 unit mol/l if a salt is present.

^{13}C-NMR-spectroscopy proved to be a powerful tool in investigating polymer solutions of this sort instead of ^1H-NMR. The molecular weights of the polymers affect the spectra, indicating the chemical shifts of the end groups with low ones as in Figure 2. Interaction between the polymer chains depends on the solvent. MeOH and H_2O solutions were also studied. In MeOH solution the association between the polymers moves the chemical shifts of the component polymers to another magnetic field. It most affects the shift of carboxylic carbons of PAA's and ethylene carbons of PEO's. The effects of varying amounts of PEO 400 at constant PAA 2000 concentrations are presented in Table 1. In all these samples the chemical shift of -COOH carbons moves towards an upper magnetic field, and the chemical shift of $-CH_2-$ carbons moves towards a lower one with decreasing r (r represents the molar ratio of PEO to PAA). In water these changes do not appear.

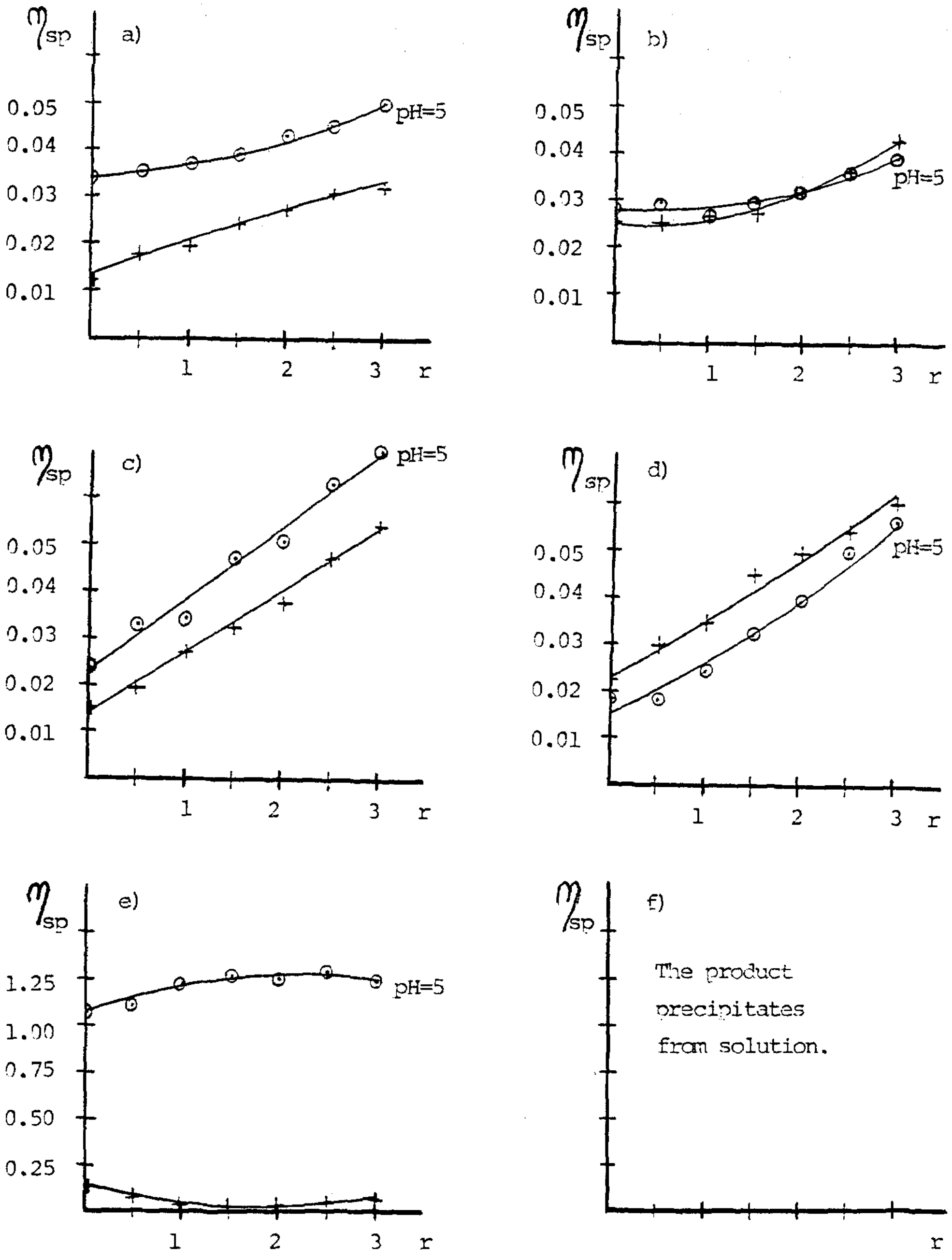

Figure 1. Specific viscosity of PEO/PAA solutions, vs. unit molar ratio, r. a) PEO400/PAA2000, c=0.03, b) PEO400/PAA2000, c=0.03, $CaSO_4$, c) PEO4000/PAA5000, c=0.022, d) PEO4000/PAA5000, c=0.022, $CaSO_4$, e) PEO20000/PAA230000, c=0.006, f) PEO20000/PAA230000, c=0.006, $CaSO_4$.

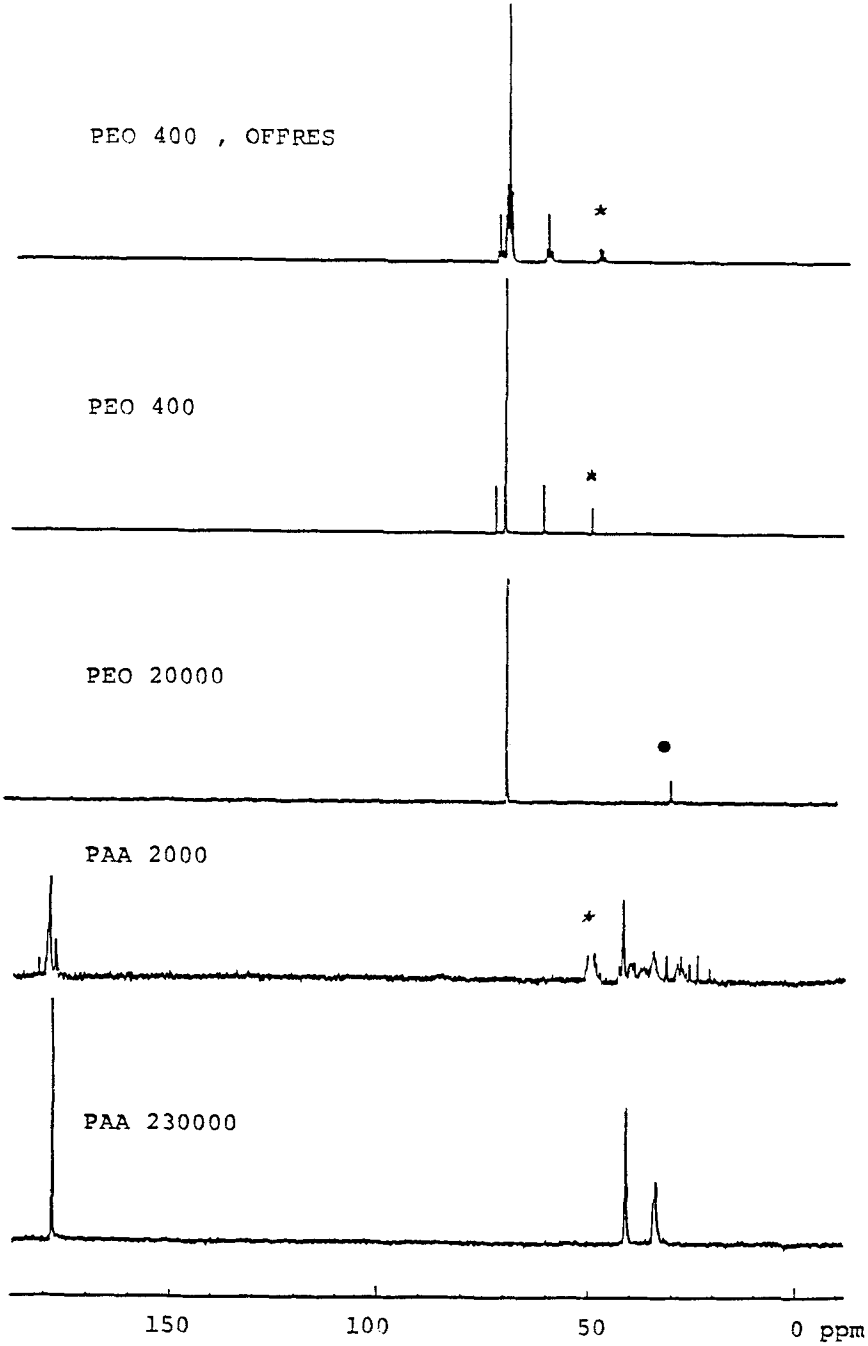

Figure 2. ^{13}C-NMR spectra of PEO and PAA of different molecular weights. (* MeOH/MeOD-d_4, ● acetone).

Table 1. ^{13}C chemical shifts of PEO400-PAA2000 association in methanol solution. Molar ratio r=[PEO]/[PAA].

r	-COOH	$-CH_2CH_2OH$	$-CH_2-$	$-CH_2OH$
0/∞	178.65	-	-	-
1/3	178.56	72.54	70.32	61.18
1/1	178.54	72.61	70.41	61.21
3/1	178.33	72.69	70.50	61.27
∞/0	-	72.69	70,50	61.27

Interaction in the solid state

The association product is insoluble in most organic solvents when the molecular weights of component polymers increase. The complex formed between PEO 20000 and PAA 230000 has been precipitated, firstly from pure water and secondly from water saturated with $CaSO_4$, at different unit molar ratios (r).

Some solid state studies were carried out to confirm the association phenomenon between the component polymer chains. Thermodynamic studies on the formation of complexes of this type have been carried out by several authors (5-7). The DSC measurements described before indicated a melting peak for PEO at about 67.5°C. In water-precipitated complexes with PAA at different r values this peak was not found at all, thus indicating that no pure PEO species are present in the samples.

The IR spectrum of the complex is similar to that of the sum spectrum of the component polymers, differing only in details. The C-O-C absorbance band of the complex is strong. Shifting of any sort can't be observed in this case when compared to pure PEO spectrum, as elsewhere (8). Distinct shifts can be seen in the absorbances in the CH_2 region. The bending of PEO:s at 1470 cm^{-1} moves to 1450 cm^{-1}, the doublet at 1340-1360 cm^{-1} forms a singlet at 1350 cm^{-1} and the rocking absorbance at 960 cm^{-1} moves to 945 cm^{-1} compared to the spectrum of the complex. The spectra of the complex have been measured on films. The presence of ions in the solutions did not affect the differences in the absorbances.

The wide-angle diffraction patterns of high molecular component polymers of PEO and PAA and of the solid complex between polymers were measured. The X-ray diffractogram of PEO had maxima at $2\theta = 18.98°$ and $23.12°$, as reported in the literature (9). PAA 230000 was amorphous in character and the pattern has no maxima at any angle value. The situation is the same with the complex, there is no pattern from the pure PEO and the presence of salt does not increase the crystallinity of the complex. PEO forms crystalline complexes with inorganic salts that have different diffraction patterns (10), but the complex of PEO and PAA has no intensity maxima.

The solid state NMR spectra were measured at ambient temperature. It is difficult under such conditions to obtain spectra of PEO (11). After about 20000 scans the signal-to-noise ratio is still small, and the shift of the PEO carbons is at 70 ppm. In the spectrum of PAA the line at about 40-30 ppm is assigned to the methylene and the methine carbons of the polymer, which do not differ from each other. The chemical shift of carboxylic carbon is 181 ppm. The CP-MAS-NMR spectra of the complexes were measured and compared to the spectra of component polymers. Solid state NMR measurements show the complexation as a splitting of the carboxylic carbon resonance, as can be seen in Figure 3. The larger the degree of complexation, the bigger is the righthand part of this resonance peak. Furthermore the presence of Ca^{2+} and SO_4^{2-} in the solution increases the complexation.

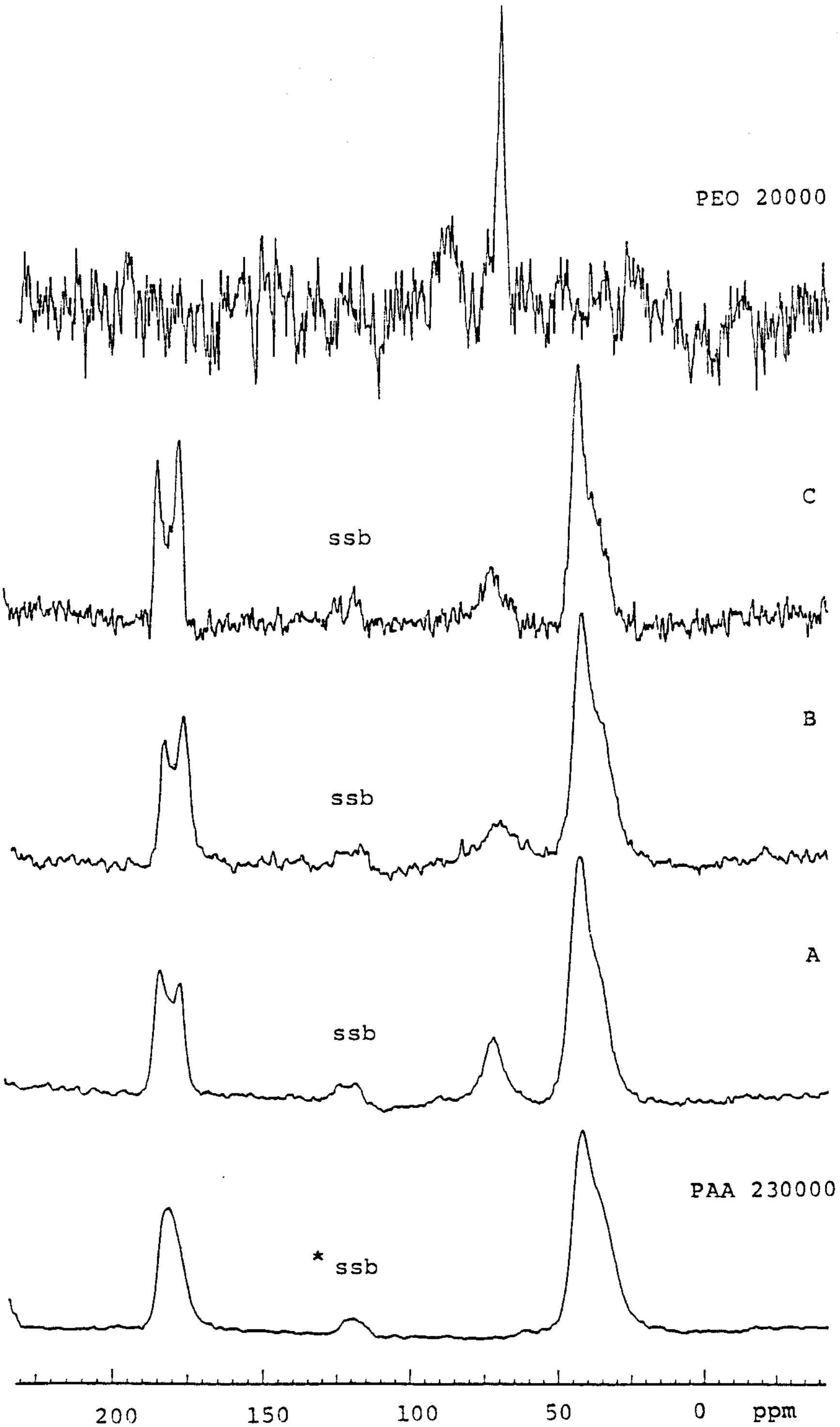

Figure 3. ^{13}C-NMR spectra in solid state of PAA, PEO and those complexes. A) r=[PEO]/[PAA]=1/3, B) r=1, C) r=1 and $CaSO_4$ in solution, * ssb = spinning side bands.

CONCLUSION

The purpose of this work was to determine which methods are best suited for studying interactions in PAA-PEO complexes. Macromolecules with complementary binding sites associate in solution to form the intermacromolecular complex. Viscosity measurements are suitable for low molecular weight component polymers, but with high molecular weight polymers the complex precipitates even at very low concentrations. The interaction occurs between PAA's carboxyl and PEO's oxygen, and the changes can be seen with ^{13}C-NMR in methanol solution but not in water. The use of X-ray and IR is limited in the study of solid PAA-PEO complexes because the addition of polyacid eliminates the PEO's crystalline character, leaving only a single amorphous phase. The absence of pure PEO in the complex can be seen from DSC measurements, the melting peak of PEO disappearing on complexation. The CP/MAS-NMR technique gives more structural information about the amorphous solid complex. It would be important to study the T_1-relaxation processes in both liquid and solid state with NMR spectroscopy.

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