Interpolymer Complexation between Poly(*N*-methyl-4-piperidinyl Methacrylate) and Acidic Polymers

Xiaofeng Luo,[†] S. H. Goh,*[,†] S. Y. Lee,[†] and K. L. Tan[‡]

Departments of Chemistry and Physics, National University of Singapore, Singapore 119260, Republic of Singapore

Received October 28, 1997

ABSTRACT: Polymer complexes of a basic polymer, poly(*N*-methyl-4-piperidinyl methacrylate) (PMPMA), with a weak acidic polymer poly(*p*-vinylphenol) (PVPh), and strong acidic polymers such as poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), poly(styrenesulfonic acid) (PSSA), and poly(vinylphosphonic acid) (PVPA), have been prepared by mixing ethanol/H_2O (1:1) solutions of the respective components. The complexes were examined by Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and differential scanning calorimetry. Both the FTIR and XPS studies showed the existence of piperidinium ions in the complexes of PMPMA with PAA, PMAA, PVPA, and PSSA, indicating that the interactions in these complexes are ionic in nature. However, the *N*-methyl groups prevent the piperidine nitrogen atoms from interaction with PVPh and hence the carbonyl groups of PMPMA interact with the hydroxyl groups of PVPh by hydrogen bonding. From the XPS studies, the number of protonated piperidine atoms was found to correlate with the acid strength of the polyacid.

Introduction

Interpolymer complexation has been the subject of many recent papers.[1−14] When polymer−polymer interactions are stronger than polymer−solvent interactions, the two polymers form precipitates (complexes) upon mixing the two constituent polymer solutions in a common solvent. One common characteristic of the complexes is that their glass transition temperatures (T_g's) are higher than those calculated from a linear additivity rule. Poly(4-vinylpyridine) (P4VPy) and poly(2-vinylpyridine) (P2VPy) are able to form complexes with various acidic polymers through hydrogen-bonding or ionic interactions involving the pyridine nitrogen atoms.

Interpolymer complexation involving basic polymers other than the pyridinyl type has not been well studied. In view of the basicity of piperidine, we have recently studied the complexation between poly(*N*-methyl-4-piperidinyl methacrylate) (PMPMA) and poly(*p*-vinylphenol) (PVPh).[14] PMPMA forms complexes with PVPh in ethanol. However, spectroscopic studies show that PMPMA interacts with PVPh through its carbonyl groups but not the piperidine nitrogen atoms. The result is rather surprising since one would expect the piperidine nitrogen atoms to interact with the hydroxyl groups of PVPh. We suggested that the *N*-methyl groups might have shielded the nitrogen atoms from interaction with the hydroxyl groups of PVPh.

Recently, Kudaibergenov *et al.* [15] reported the complexation between poly[4-(but-3-en-1-ynyl)-1-methylpiperidin-4-ol] (PBMP) with poly(acrylic acid) (PAA) and with poly(methacrylic acid) (PMAA). There was evidence of ionic interactions between PBMP and the two polyacids. It appears that if the polymer is sufficiently acidic, protons may still be transferred to the *N*-methylated nitrogen atoms on the piperidine rings. We have studied the complexation between PMPMA and four acidic polymers, namely, PAA, PMAA, poly(vinylphosphonic acid) (PVPA), and poly(styrenesulfonic acid) (PSSA). It will be shown that PMPMA is indeed able to form complexes with the four acidic polymers through ionic interactions.

Experimental Section

Materials. The synthesis of PMPMA was reported previously.[14] The weight-average molecular weight (M_w) and the glass transition temperature (T_g) of PMPMA are 6000 and 96 °C, respectively. PMAA (viscosity-average molecular weight (M_v) = 400 000, T_g = 153 °C), PSSA (M_n = 22 500) and PVPA (molecular weight information not available, T_g = 165 °C) were obtained from Polysciences, Inc. PAA (M_v = 450 000, T_g = 127 °C) was supplied by Aldrich Chemical Co., Inc. The T_g of PSSA was difficult to detect by DSC.

Preparation of Complexes. Polymer complexes were obtained by mixing stoichiometric amounts of ethanol/water (1:1 volume ratio) solutions (1% w/v) of polyacid and PMPMA. After 1 h of continuous stirring, polymer complexes in a form of precipitates were isolated by centrifugation and washed repeatedly with the mixed solvent. The complexes were then dried in vacuo at 90 °C for at least 2 weeks. The bulk compositions of various complexes were calculated from their nitrogen contents as determined by elemental analysis using a Perkin-Elmer 2400 elemental analyzer. The surface compositions of the complexes were determined by XPS measurements based on the nitrogen/oxygen peak-area ratios after correction with appropriate sensitivity factors.

T_g Measurements. The T_g's of various samples were measured with a TA Instruments 2920 differential scanning calorimeter using a heating rate of 20 °C/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible T_g values. The initial onset of the change of slope in the DSC curve is taken to be the T_g.

FTIR Characterization. FTIR spectra were recorded on a Bio-Rad 165 FTIR spectrophotometer. Sixty-four scans were signal-averaged at a resolution of 2 cm^{-1}. To eliminate moisture absorption, spectra were recorded at 140 °C using a SPECAC high-temperature cell, equipped with an automatic temperature controller, which was mounted in the spectrophotometer. Complex samples were prepared by grinding the dry complex with KBr and compressing the mixture to form disks.

---

* To whom correspondence should be addressed.

[†] Department of Chemistry.

[‡] Department of Physics.

S0024-9297(97)01583-0 CCC: $15.00

Table 1. Characteristics of PMPMA Complexes

	PVPh	PSSA	PAA	PMAA	PVPA
T_g (°C)	175	nil	nil	187	nil
bulk composition[a]	0.47	0.61	0.41	0.26	0.28
surface composition[a]	0.42	0.69	0.44	0.38	0.39
fraction of high-BE peak	0.00	0.44	0.58	0.36	0.67

[a] Mole fraction of PMPMA.

XPS Measurements. X-ray photoelectron spectroscopic (XPS) measurements were made on a VG ESCALAB MKII spectrometer with a Mg Kα X-ray source (1253.6 eV photons). Various complexes were ground to fine powders and then mounted on standard sample studs by means of a double-sided adhesive tape. A takeoff angle of 75° was used in all XPS runs. The X-ray source was run at 12 kV and 10 mA. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during measurements. To compensate for surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 284.6 eV.

Results and Discussion

General Characteristics of Complexes. PMPMA forms complexes with PVPh, PSSA, PVPA, PAA, and PMAA. The characteristics of the complexes are shown in Table 1. In our previous study, the PMPMA/PVPh complex was prepared from ethanol.[13] In the present study, PMPMA/PVPh and the other four complexes were all prepared from ethanol/water (1:1) solution. The T_g value and the composition of the PMPMA/PVPh complex obtained in the present study are in good agreement with those obtained from pure ethanol.[14]

The T_g values of the PMPMA/PVPh and PMPMA/PMAA complexes are higher than those of the component polymers. As mentioned earlier, such a positive deviation of T_g values has been commonly observed for complexes. No distinct T_g's could be detected for the PMPMA/PSSA, PMPMA/PVPA, and PMPMA/PAA complexes. The inability to detect the T_g of PSSA and the small heat capacity change upon glass transition of PVPA render the detection of the glass transitions difficult for the PMPMA/PSSA and PMPMA/PVPA complexes. The inability to detect the glass transition of the PMPMA/PAA complex could be due to the strong intermolecular interactions in the complexes which raise the T_g value beyond the degradation temperature. We were also unable to detect the glass transitions of PVPA/P4VPy, PVPA/P2VPy, PSSA/P4VPy, and PSSA/P4VPy complexes.[14,16] A similar problem in detecting the glass transitions of complexes has been reported for other complex systems.[8,17]

Although all the complexes were prepared by mixing stoichiometric amounts of PMPMA and the acidic polymers, the compositions of the complexes vary significantly. In addition, the surface composition of the complex is different from the bulk composition. Except for the PMPMA/PVPh complex, the surface regions of all the other complexes show an enrichment of PMPMA.

FTIR Characterization. The FTIR spectra of PMPMA and the five complexes in the 2710−2830 cm^{-1} region are presented in Figure 1. In the spectrum of PMPMA (curve C), a peak at 2786 cm^{-1}, the so-called "Bohlmann" band, is related to the interaction between the free axial electron lone pairs of the nitrogen atom and the axial C−H bonds in the α-position in relation to the nitrogen atom of the heterocycle.[15,18] Kudaibergenov *et al.*[15] have previously reported that the Bohlmann band of PBMP in PBMP/PAA complex disappears but a new band appears at 2720 cm^{-1}, corresponding to protonated tertiary amine groups. The IR spectrum of the PMPMA/PVPh complex (curve F) shows that the Bohlmann band is shifted to 2796 cm^{-1}. Such a shift reflects a change in the steric environment of the C−H bond in the α-position to the nitrogen atom when PMPMA is mixed with PVPh. However, there is no new band developed in the 2720 cm^{-1} region, and therefore the piperidine nitrogens are not protonated. In contrast, in the IR spectra of the PMPMA/PVPA, PMPMA/PMAA, PMPMA/PSSA, and PMPMA/PAA complexes (curves A, B, D, and E, respectively), a new band near 2730 cm^{-1} is observed, showing that some of the piperidine nitrogen atoms have been protonated in the four complexes. The Bohlmann bands of the four complexes do not disappear completely, showing that not all the piperidine nitrogen atoms have been protonated. The Bohlmann band also shows a shift in frequency.

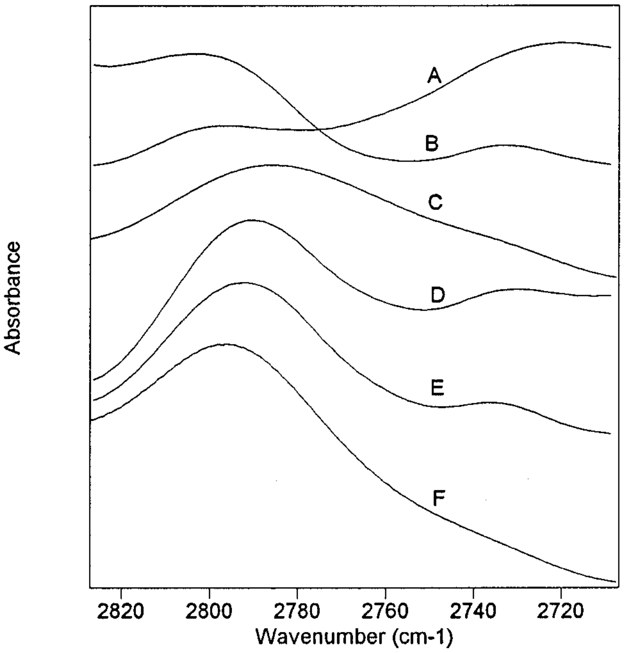

Figure 1. FTIR spectra recorded at 140 °C, of the Bohlmann band region of PMPMA and complexes: (A) PMPMA/PVPA, (B) PMPMA/PMAA, (C) PMPMA, (D) PMPMA/PSSA, (E) PMPMA/PAA, and (F) PMPMA/PVPh.

The transfer of protons from the carboxylic groups of PAA and PMAA to the nitrogen atoms of PMPMA also leads to the appearance of asymmetric vibration signals of carboxylate anions which are situated at 1585 cm^{-1} (Figure 2 curve C) and 1578 cm^{-1} (Figure 3 curve C), respectively.

XPS Characterization. Figure 4 shows the N1s spectra of PMPMA and the five complexes. The N1s spectrum of the PMPMA/PVPh complex cannot be deconvoluted into two different nitrogen environments. This result shows that the nitrogen in the piperidine ring is not involved in interaction. The conclusion is in agreement with the absence of $-NH^+$ band as shown by the FTIR study.

In contrast, two different nitrogen environments can be discerned in the spectra of the other four complexes. The low-BE component is characteristic of neutral nitrogen of piperidine; the high-BE component is located at around 401 eV. Our recent studies[13,16,19,20] on complexes of poly(vinylpyridine) have shown that a high-BE N1s component located at around 400 eV is

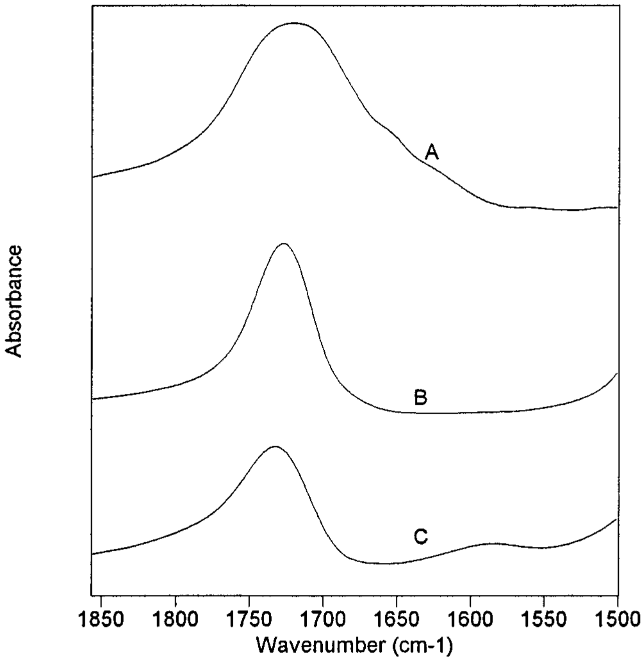

Figure 2. FTIR spectra recorded at 140 °C, of the carbonyl region of (A) PAA, (B) PMPMA, and (C) PMPMA/PAA.

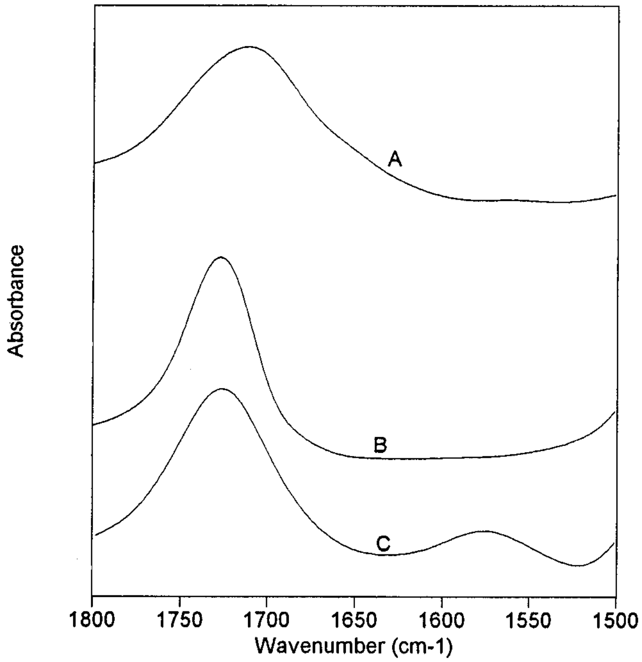

Figure 3. FTIR spectra recorded at 140 °C, of the carbonyl group of (A) PMAA, (B) PMPMA, and (C) PMPMA/PMAA.

developed for complexes involving hydrogen-bonding interactions while a peak located at around 401 eV appears for complexes involving ionic interactions.

It is of interest to note that PMAA interacts with P4VPy and P2VPy through hydrogen-bonding[19] but it interacts with PMPMA through ionic attraction. It is reasonable to infer from the present results that PMPMA is more basic than P4VPy and P2VPy and thereby facilitates the proton transfer from PMAA to PMPMA. In fact, the pH values of 0.1 M ethanol/water (1:1) solutions of PMPMA, P4VPy, and P2VPy are 8.65, 8.25, and 7.84, respectively.

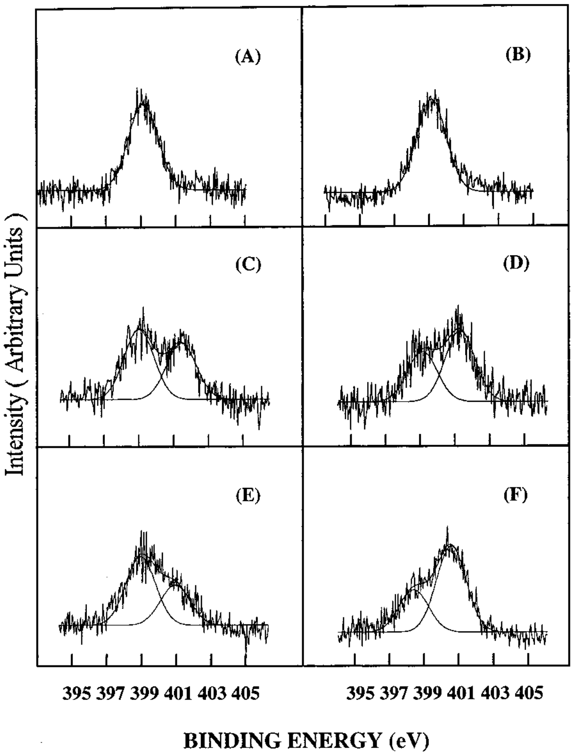

Figure 4. XPS N1s core-level spectra of PMPMA and complexes: (A) PMPMA, (B) PMPMA/PVPh, (C) PMPMA/PSAA, (D) PMPMA/PAA, (E) PMPMA/PMAA, and (F) PMPMA/PVPA.

The extent of protonation of the piperidine units which are estimated from the deconvoluted piperidinium nitrogen peaks in the four complexes are listed in Table 1. It is of interest to see whether the extent of protonation of the piperidine units is related to the acid strength of the polymer. The pH values of 0.1 M ethanol/water (1:1) solutions of PSSA, PVPA, PAA, PMAA, and PVPh are 1.36, 2.33, 3.04, 3.57, and 6.68, respectively. It appears that the fraction of protonated piperidine units in the complex does not correlate with the acid strength. However, when the surface stoichiometry of the complex is taken into consideration, the number of interacting piperidine groups does correlate with the acid strength. The product of the fraction of PMPMA in the surface region and the fraction of protonated piperidine groups is proportional to the number of protonated piperidine groups. The products are 0.3036, 0.2613, 0.2552, and 0.1368 for the complexes of PMPMA with PSSA, PVPA, PAA, and PMAA, respectively. Thus the stronger the acid, the larger is the number of protonated piperidine groups.

Conclusions

PMPMA forms complexes with PVPh, PSSA, PVPA, PAA, and PMAA in ethanol/water (1:1) solutions. The nature of interpolymer interaction depends on the acidic strength of the polymer as shown by FTIR and XPS studies. The weak acidic polymer PVPh interacts with PMPMA by hydrogen bonding interaction while the other four stronger acidic polymers interact with PMPMA by ionic interactions. XPS studies also show that the stronger the acidity of the polymer, the larger is the number the protonated piperidine groups.

Acknowledgment. The authors thank the National University of Singapore for its financial support of this research.

References and Notes

(1) Zhang, Y.; Xiang, M.; Jiang, M.; Wu, C. *Macromolecules* **1997**, *30*, 2035.
(2) Xiang, M.; Jiang, M.; Zhang, Y.; Wu, C.; Feng, L. *Macromolecules* **1997**, *30*, 2313.
(3) Jiang, M.; Liu, W.; Wu, C.; Woo, K. F. *Polymer* **1997**, *38*, 405.
(4) Huang, J.; Li, X.; Guo, Q. *Eur. Polym. J*. **1997**, *33*, 659.
(5) Doseva, V.; Shenkov, S.; Baranovsky, V. Yu. *Polymer* **1997**, *38*, 1339.
(6) Garay, M. T.; Llamas, M. C.; Iglesias, E. *Polymer* **1997**, *38*, 5091.
(7) Webster, L.; Huglin, M. B.; Robb, I. D. *Polymer* **1997**, *38*, 1373.
(8) Huglin, M. B.; Webster, L.; Robb, I. D. *Polymer* **1996**, *37*, 1211.
(9) Inai, Y.; Kato, S.; Hirabayashi, T.; Yokota, K. *J. Polym. Sci., Part A: Polym. Chem*. **1996**, *34*, 2341.
(10) Velada, J. L.; Cesteros, L. C.; Katime, I. *Macromol. Chem. Phys*. **1996**, *197*, 2247.
(11) Meaurio, E.; Velada, J. L.; Katime, I. *Macromolecules* **1996**, *29*, 4598.
(12) Zhong, Z.; Guo, Q. *Polym. Int*. **1996**, *41*, 315.
(13) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Polymer* **1997**, *38*, 5333.
(14) Luo, X.; Goh, S. H.; Lee, S. Y. *Macromolecules* **1997**, *30*, 4934.
(15) Kudaibergenov, S. E.; Nurkeeva, Z. S.; Sigitov, V. B.; Akimbekova, K. Zh.; Ushanov, V. Zh. *Macromol. Chem. Phys*. **1997**, *198*, 183.
(16) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Appl. Surf. Sci*., in press.
(17) Gargallo, L.; Gatica, N.; Radic, D. *Int. J. Polym. Mater*. **1994**, *27*, 107.
(18) Bohlmann, F. *Angew. Chem*. **1957**, *69*, 641.
(19) Zhou, X.; Goh, S. H.; Lee. S. Y.; Tan, K. L. *Polymer*, in press.
(20) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Appl. Surf. Sci*. **1997**, *119*, 60.

MA9715839