Miscibility and Interactions in Blends and Complexes of Poly(*N*-methyl-4-piperidinyl methacrylate) with Poly(*p*-vinylphenol)

Xiaofeng Luo, S. H. Goh,* and S. Y. Lee

Department of Chemistry, National University of Singapore, Singapore 119260, Republic of Singapore

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ABSTRACT: Poly(*N*-methyl-4-piperidinyl methacrylate) (PMPMA) was synthesized and characterized. PMPMA formed complexes with poly(*p*-vinylphenol) (PVPh) in ethanol over the entire feed composition range. The yields of complexes were in the range 29−76%, which were lower than those of poly(4-vinylpyridine) (P4VPy)/PVPh complexes obtained in ethanol. Complexation did not occur in *N*,*N*-dimethylformamide (DMF), but the DMF-cast blends were miscible. Fourier-transform infrared spectroscopic studies showed that the hydroxyl groups of PVPh interact with the carbonyl groups of PMPMA, and the intermolecular hydrogen-bonding interactions are weaker than the self-association of PVPh. X-ray photoelectron spectroscopic studies showed that the nitrogen atoms in the piperidine groups are not involved in intermolecular interactions with PVPh, likely a result of steric effects asserted by the *N*-methyl groups. Because of the inaccessibility of the piperidine nitrogen atoms, PMPMA interacts less intensely with PVPh than P4VPy does.

Introduction

Basic polymers such as poly(vinylpyridine)s are miscible with proton-donating polymers through hydrogen-bonding interactions. Poly(4-vinylpyridine) (P4VPy) is miscible with poly(*p*-vinylphenol) (PVPh),[1,2] poly(acrylic acid) (PAA),[3,4] poly(methacrylic acid) (PMAA),[4] poly(monoalkyl itaconate)s,[5−7] and poly(hydroxyether of Bisphenol A).[8] The existence of hydrogen-bonding interactions in these miscible blends is shown by the frequency shifts of the hydroxyl bands of PVPh in various blends.

When polymer−polymer interactions are stronger than polymer−solvent interactions, the two polymers form complexes by coprecipitating from their common solvent, in which both polymers are initially soluble. The complexes usually have glass transition temperatures (T_g's) higher than those calculated from the linear additivity rule. Moreover, the compositions of the complexes are different from the feed compositions of the initial solutions. P4VPy also forms complexes with PVPh, PAA, PMAA, and poly(monoalkyl itaconate)s in some solvents. On the other hand, if the solvent is able to interact strongly with one or both of the polymers, precipitation will not occur upon mixing of the two polymer solutions. Upon evaporation of the "non-complexing" solvent, a polymer blend of predetermined composition is obtained.

The formation of complexes also depends on the number of interacting groups in the two polymers. For the poly(2-vinylpyridine) (P2VPy)/poly(ethylene-*co*-methacrylic acid) (EMAA) system in tetrahydrofuran, complexation occurs when EMAA contains 32 wt % or more of methacrylic acid groups.[9] Similarly, Qiu and Jiang[10,11] have shown that by increasing the amount of hydroxyl groups in modified polystyrene [PS(OH)], transitions from immiscibility to miscibility and then from miscibility to complexation can be achieved in PS(OH)/poly(methyl methacrylate) and PS(OH)/poly(*n*-butyl methacrylate) systems.

However, the miscibility and complexation behavior of polymers containing basic groups other than the pyridinyl type have not been well studied. Van de Grampel *et al.*[12] reported complex formation in template polymerization of 1-vinylimidazole along with PMAA in water. We have recently reported that poly(1-vinylimidazole) (PVI) is miscible with PVPh and the T_g values of the blends are significantly higher than those calculated from the linear additivity rule.[13]

Piperidine (pK_b = 2.88) is a stronger base than imidazole (pK_b = 7.05) and pyridine (pK_b = 8.75). Therefore, polymers containing piperidine groups are likely to be miscible or even to form complexes with proton-donating polymers. We now report the miscibility and complexation behavior between poly(*N*-methy-4-piperidinyl methacrylate) (PMPMA) and PVPh. The use of PMPMA instead of poly(4-piperidinyl methacrylate) (PPMA) is to avoid complications arising from the overlapping of N−H bands of PPMA with hydroxyl bands of PVPh in the Fourier-transform infrared (FTIR) spectroscopic studies.

Experimental Section

Materials. *N*-Methyl-4-piperidinol was supplied by Aldrich Chemical Co., Inc. PVPh (M_w =22 000) was supplied by Polysciences, Inc.

Synthesis of *N*-Methyl-4-piperidinyl Methacrylate. *N*-Methyl-4-piperidinyl methacrylate was prepared by ester exchange between methyl methacrylate (MMA) and *N*-methyl-4-piperidinol. The inhibitor in MMA was removed by reduced pressure distillation. MMA and methanol were dried before use over anhydrous calcium chloride and molecular sieves 3 Å respectively. A three-necked round-bottom flask was fitted with a 45 cm Vigreux column, a condenser, and a nitrogen inlet. The setup was thoroughly flame-dried before 0.375 g of magnesium turings and 8 mL of dry methanol were placed into it. A small amount of iodine was introduced, and the mixture was warmed slightly to initiate the formation of magnesium methoxide. After about 2 h, when the magnesium turnings had all dissolved, 29 g (0.16 mol) of *N*-methyl-4-piperidinol, 90 mL (0.85 mol) of MMA, and a small amount of copper turnings were added. The reaction mixture was then heated in an oil bath and methanol distilled at 65 °C. The oil temperature was gradually increased to 125 °C and maintained at that temperature for 15 min to allow the reaction to

* To whom correspondence should be addressed.
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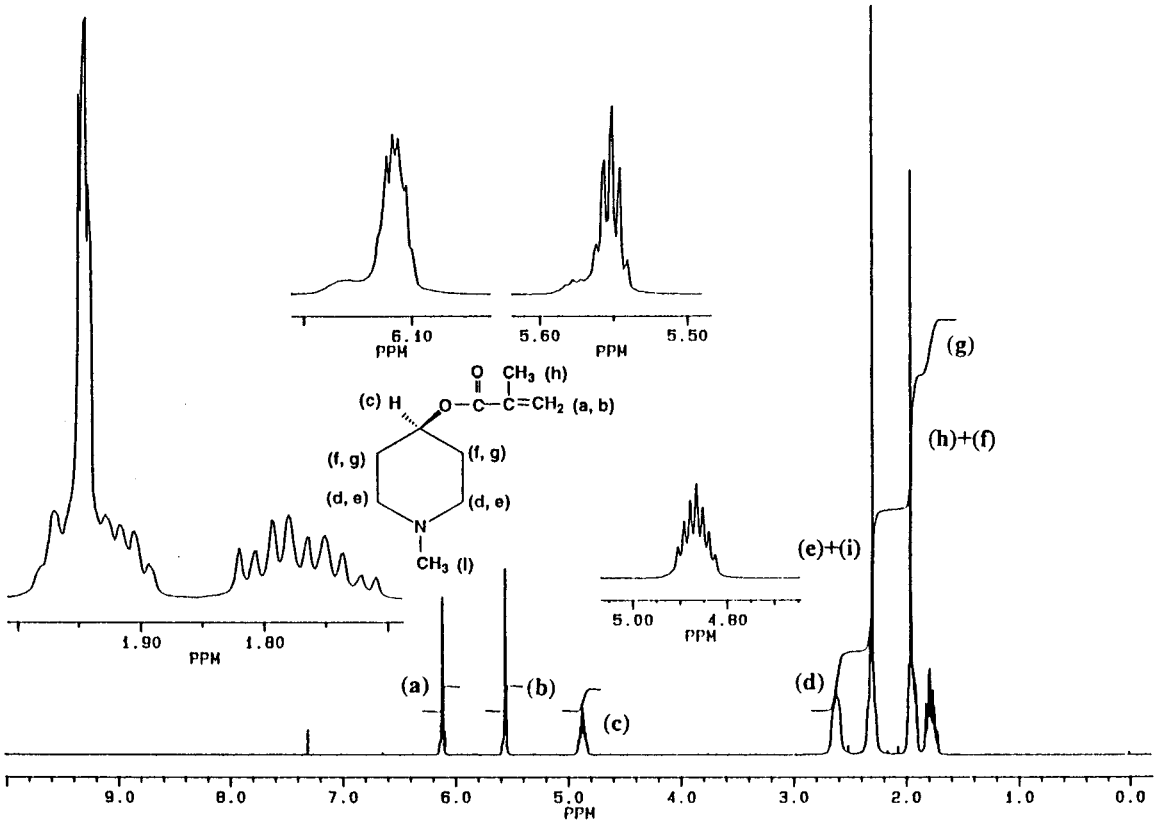

Figure 1. ^{1}H-NMR spectrum of *N*-methyl-4-piperidinyl methacrylate.

complete. Then 40 mL of deionized water was added. The magnesium hydroxide formed was filtered off and extracted several times with small portions of MMA. The organic layer was washed with deionized water and dried over anhydrous sodium sulfate. Fractional distillation at 74−75 °C/2 mmHg gave pure *N*-methyl-4-piperidinyl methacrylate. Yield: 42%. The product was a colorless liquid. IR, ν (cm^{-1}): 3092 (m, $=CH_2$), 2934 (m, $=CH_2$), 1713 (s, C=O), 1634 (m, C=C), 1175 (s, C−O−C). ^{1}H-NMR ($CDCl_3$), ppm: 6.11 (m, 1H), 5.56 (m, 1H), 4.86 (m, 1H), 2.60 (m, 2H), 2.30 (m, 5H), 1.93 (m, 5H), 1.82−1.71 (m, 1H). Signal assignments are shown in Figure 1. Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.57; H, 9.29; N, 7.65. Found: C, 65.29; H, 9.28; N, 7.42.

Polymerization. Poly(*N*-methyl-4-piperidinyl methacrylate) was prepared by bulk polymerization. A mixture of *N*-methyl-4-piperidinyl methacrylate (31.5 g) and azobis(isobutyronitrile) (AIBN) (0.06 g) was placed in a glass ampule and sealed under nitrogen. Polymerization was allowed to proceed at 65 °C for 40 h. The resulting polymer was purified by precipitation twice with hexane from benzene solution and dried in a vaccum oven at 70−80 °C for 2 days. Yield: 60%. M_w = 6000. T_g: 96 °C. The polymer shows an initial decomposition temperature of 300 °C, as shown by thermogravimetry.

Anal. Calcd for PMPMA: C, 65.57; H, 9.29; N, 7.65. Found: C, 65.35; H, 9.23; N, 7.50 .

Preparation of Blends and Complexes. Polymer complexes were obtained by mixing appropriate amounts of ethanol solutions (1% w/v) of PVPh and PMPMA. After 1 h of continuous stirring, polymer complexes in the form of precipitates were isolated by centrifugation and washed with ethanol. The complexes were then dried *in vacuo* at 90 °C for at least 2 weeks. The ratio of the amount of dried complex to the total amount of the two polymers in the initial solution gives the yield of the complex. The nitrogen contents of various complexes were determined by elemental analysis using a Perkin-Elmer 2400 elemental analyzer.

Polymer blends were obtained by solution casting from *N*,*N*-dimethylformamide (DMF) solutions. Blends were similarly dried *in vacuo* at 90 °C for at least 2 weeks. Since PVPh and PMPMA are hygroscopic, all the dried complexes and blends were stored in a desiccator.

T_g Measurements. The glass transition temperatures (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}. Spectra were recorded at 140 °C using a SPECAC high-temperature cell, equipped with an automatic temperature controller, which was mounted in the spectrophotometer. Blend samples for FTIR analysis were prepared by casting the DMF solutions onto KBr disks followed by drying *in vacuo* at 90 °C for 2 weeks. Complex samples were prepared by grinding the dry complex with KBr and compressing the mixture to form disks.

NMR Measurements. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ACF300 spectrometer at 25 °C with tetramethylsilane as an internal standard.

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 blends and complexes were ground to fine powders and were then mounted on standard sample studs by means of double-sided adhesive tape. A take-off 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

Complex and Blend Formation. PMPMA formed complexes with PVPh in ethanol solutions over the entire feed composition. The characteristics of complexes are shown in Table 1. The yields of the complexes are in the range 29−76%, which are lower than

Table 1. Characteristics of PMPMA/PVPh Complexes

feed composition		interpolymer complexes			
PMPMA (wt %)	content (mol %)	yield (wt %)	PMPMA content (mol %)	T_g (°C)	ΔC_p[a] [(J/g)/°C)]
20	14	29	34	163	0.378
40	30	75	40	166	0.397
50	39	76	44	169	0.385
60	49	65	47	175	0.332
80	72	31	49	185	0.318

[a] ΔC_p of PMPMA: 0.188 (J/g)/°C; ΔC_p of PVPh: 0.422 (J/g)/°C.

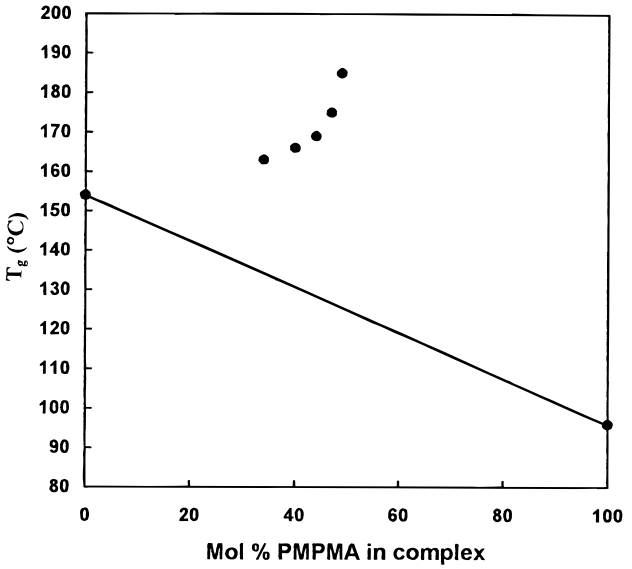

Figure 2. T_g–composition plot for PMPMA/PVPh complexes.

those of P4VPy/PVPh complexes (44–90%).[2] This may be taken as an indication of a stronger interaction between PVPh with P4VPy than with PMPMA.

The T_g values of PMPMA/PVPh complexes are in the range 163–185 °C and are higher than those calculated from a linear additivity rule by 30–55 °C (Figure 2). In comparison, P4VPy/PVPh complexes show larger positive deviations (about 60–70 °C) in their T_g values. Therefore, the T_g values also suggest that PVPh interacts more strongly with P4VPy than with PMPMA.

Similar to P4VPy, PMPMA did not form complexes with PVPh in DMF whose amide carbonyl groups are capable of competing with P4VPy or PMPMA for the hydroxyl groups of PVPh and thus preventing complex formation. All the DMF-cast PMPMA/PVPh blends were transparent and each showed a single T_g, indicating miscibility. As shown in Figure 3, the T_g–composition curve for PMPMA/PVPh blends can be fitted by the Kwei equation:[14,15]

$$T_g(\text{blend}) = [(w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2)] + q w_1 w_2$$

where k and q are fitting constants. The curve in Figure 3 was drawn using k and q values of 5 and 90, respectively. In comparison, DMF-cast P4VPy/PVPh blends also show large positive deviations in their T_g values and the T_g–composition curve can also be fitted by the Kwei equation using k and q values of 1 and 200, respectively.[2] Kwei pointed out that the quadratic term qw_1w_2 is proportional to the number of specific interactions in the blends.[14] Therefore, the larger q value also suggests a stronger interaction between P4VPy and PVPh.

Figure 4 shows the heat capacity changes at T_g (ΔC_p) of various blends and complexes. The ΔC_p values show

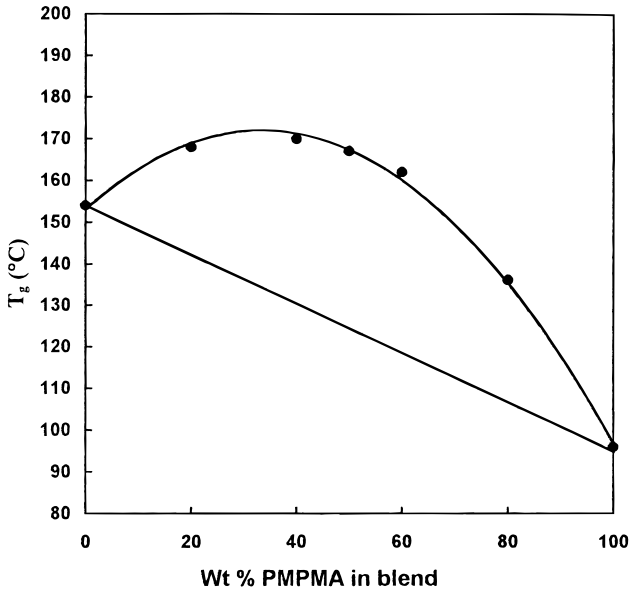

Figure 3. T_g–composition curve of PMPMA/PVPh blends.

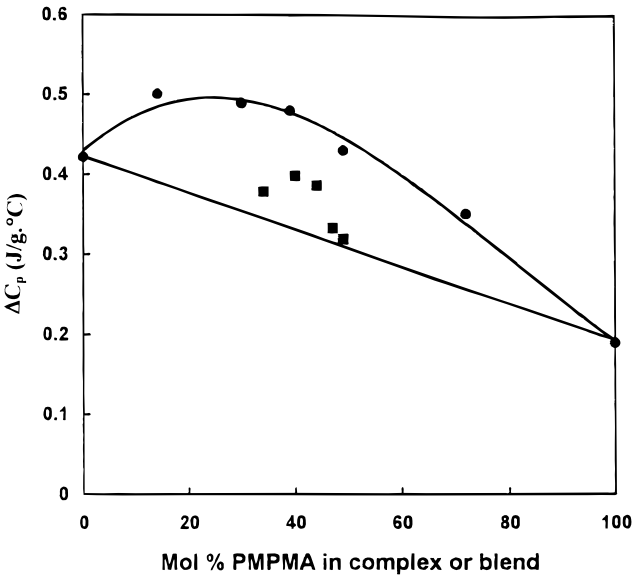

Figure 4. ΔC_p–composition plots of PMPMA/PVPh blends (●) and complexes (■).

positive deviations from the additivity rule. This is consistent with previous studies that miscible blends show positive excess heat capacities.[16,17] It is also of interest to note that the ΔC_p value of a complex is smaller than that of a blend of the same composition. A similar trend has also been observed by Wang *et al.*[18] for blends and complexes involving PVPh, although the ΔC_p values do not show positive deviations.

FTIR Characterization. Figure 5 shows the infrared spectra of the complexes and PVPh in the hydroxyl region at 140 °C. PVPh has a band centered at 3531 cm^{-1} attributed to free hydroxyl groups, and a broad band centered at 3332 cm^{-1}, which represents a broad distribution of self-associated hydroxyl groups. As the PMPMA content in the complex increases, the intensity of the free hydroxyl band at 3531 cm^{-1} decreases, indicating that more free hydroxyl groups are involved in intermolecular association with PMPMA. This peak almost disappears when the PMPMA content reaches 44 mol % in the complex (curve d). In addition, the center of the broad hydrogen-bonded hydroxyl band shifts from 3332 to 3460 cm^{-1}. Figure 6 shows the

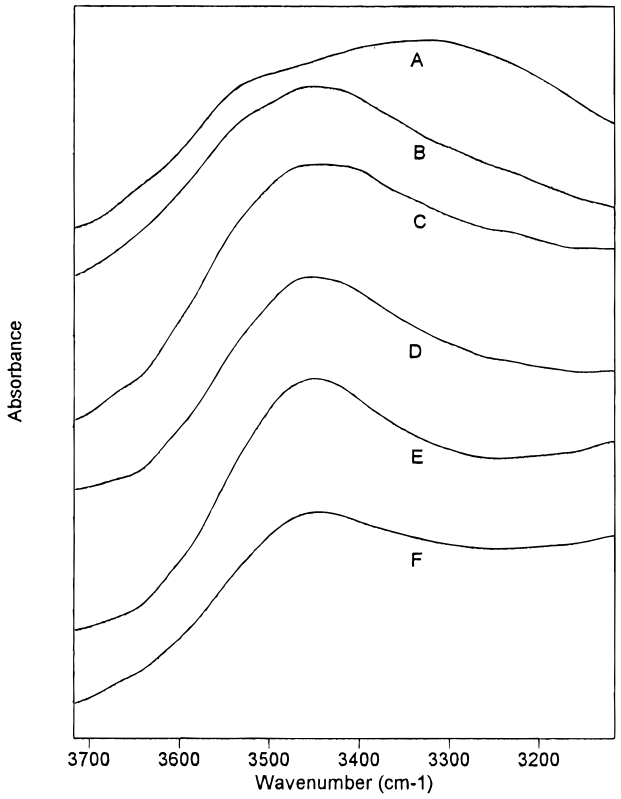

Figure 5. FTIR spectra, recorded at 140 °C, of the hydroxyl region of PMPMA/PVPh complexes: (A) 0, (B) 34, (C) 40, (D) 44, (E) 47, and (F) 49 mol % PMPMA.

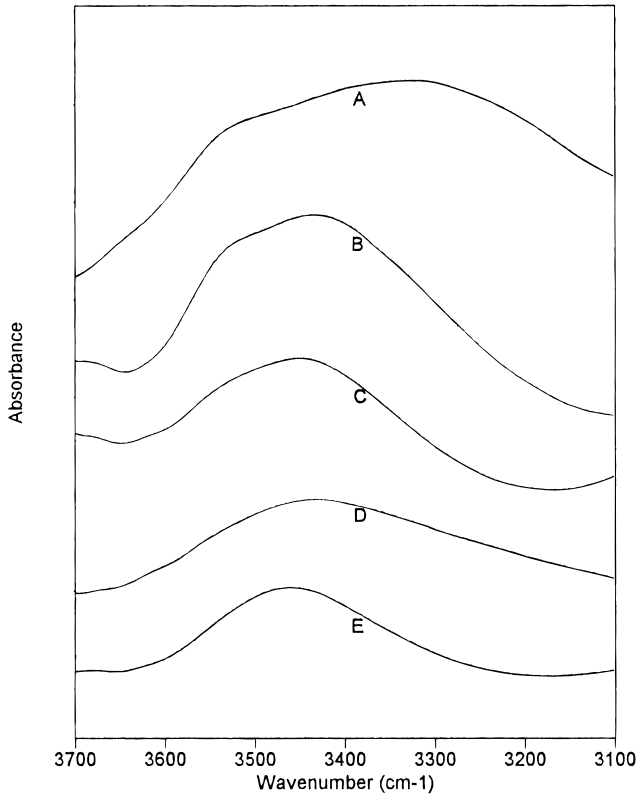

Figure 6. FTIR spectra, recorded at 140 °C, of the hydroxyl region of PMPMA/PVPh miscible blends: (A) 0, (B) 20, (C) 40, (D) 50, and (E) 60 wt % PMPMA.

hydroxyl region of DMF-cast PVPh/PMPMA blends. Similar high-frequency shifts of the hydroxyl bands in various blends are also observed. Such a high-frequency shift indicates that the self-association of PVPh is

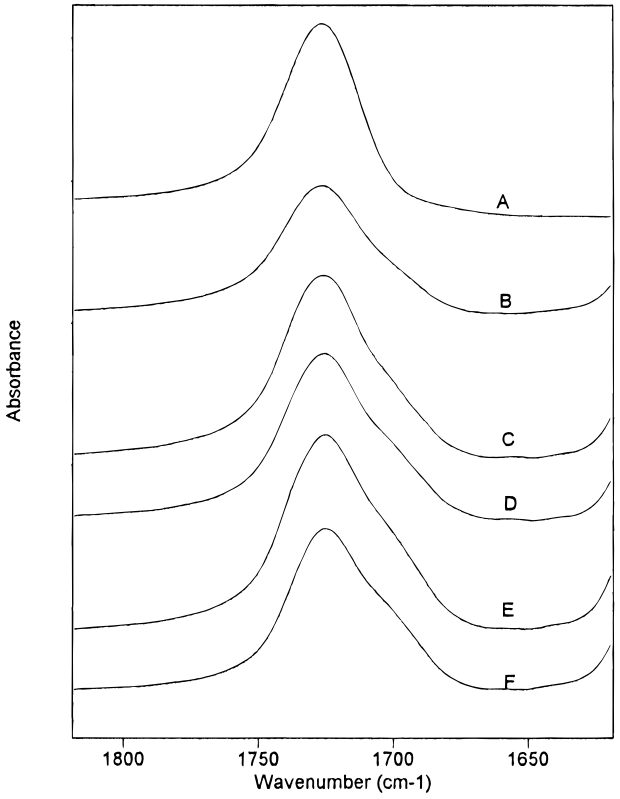

Figure 7. FTIR spectra, recorded at 140 °C, of the carbonyl region of PMPMA and PMPMA/PVPh complexes: (A) 100, (B) 49, (C) 47, (D) 44, (E) 40, and (F) 34 mol % PMPMA.

stronger than the intermolecular hydrogen-bonding interaction between PVPh and PMPMA. Miscible blends of PVPh with poly(methyl methacrylate) (PMMA),[19,20] poly(vinyl acetate),[21] and poly(dialkyl itaconate)s[22] also show similar high-frequency shifts of the hydroxyl bands.

On the other hand, DMF-cast PVPh/P4VPy blends show large low-frequency shifts of the hydroxyl bands, indicating that interactions between PVPh and P4VPy are stronger than the self-association of PVPh.[2] Spectroscopic studies have clearly shown that PVPh interacts more strongly with P4VPy than with PMPMA.

Figure 7 shows the spectra in the carbonyl region at 140 °C of PMPMA and PMPMA/PVPh complexes. The carbonyl band of PMPMA is centered at 1726 cm^{-1}. Upon mixing with PVPh, a shoulder at 1703 cm^{-1} gradually developed, indicating that some of the carbonyl groups of PMPMA are involved in hydrogen-bonding interactions with the hydroxyl groups of PVPh. This observation is similar to that reported by Li and Brisson[20] on PVPh/PMMA blends.

XPS Characterization. We have recently used XPS to study intermolecular interactions in polymer blends and complexes.[23,24] Since the binding energy (BE) of a core-level electron depends on its chemical environment within the molecule, the XPS spectrum provides information on the type and number of different species of a given atom in the molecules. For P4VPy/PVPh blends and complexes, each N1s peak can be deconvoluted into two component peaks: one at 399.0 eV and the other at around 400.0 eV.[24] The high-BE peak arises from pyridine nitrogen atoms that are involved in hydrogen-bonding interactions with PVPh.

Figure 8 shows the N1s spectra of PMPMA and a PMPMA/PVPh complex containing 47 mol % of PMPMA. PMPMA shows a single nitrogen environment at

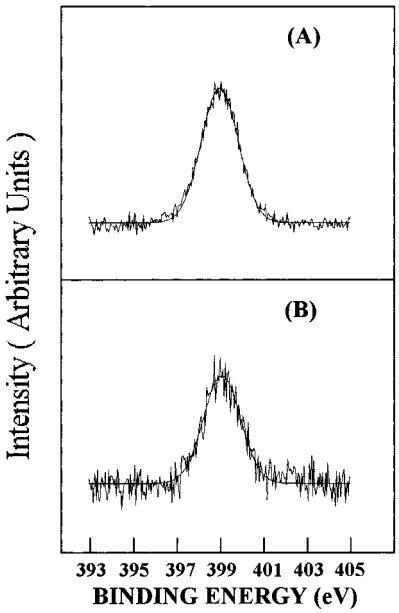

Figure 8. XPS N1s core-level spectra of (A) PMPMA and (B) PMPMA/PVPh complex (47 mol % PMPMA).

399.0 eV. The complex also shows a single N1s peak at 399.0 eV with the same peak width as PMPMA. The other complexes and blends also show a single nitrogen environment. Therefore, XPS studies show that piperidine nitrogen atoms are not involved in hydrogen-bonding interactions with PVPh.

Intermolecular Interactions. The present study has shown that PMPMA interacts less strongly with PVPh as compared to P4VPy. The result is rather surprising in view of the strong basicity of the piperidine group. However, XPS studies show the absence of interaction involving the piperidine nitrogen atoms. It is conceivable that the *N*-methyl groups may have shielded the nitrogen atoms from hydrogen-bonding interactions with the hydroxyl groups of PVPh. Therefore, PMPMA interacts with PVPh through its carbonyl groups and such interactions are weaker than the self-association of PVPh.

It is noted that the high-frequency shifts of the hydroxyl bands in the blends and complexes are of similar magnitude, indicating that there are no significant differences in the strength of intermolecular interactions. A similar observation was also noted in our study on PVPh/poly(vinylpyridine) complexes and blends.[24] However, complexes formed by coprecipitation are in a more compact state than blends cast from solution, leading to higher T_g values of the complexes. Qiu and Jiang[11] have described that a miscible blend is in a ramdomly mixed state while a complex is in a close proximity state.

Accessibility of functional groups is important in achieving miscibility.[25] Factors such as chain connectivity and steric shielding tend to limit the number of interpolymer contacts. The influence of steric shielding is exemplified by the better ability of P4VPy to interact with hydroxyl-containing polymers than of poly(2-vinylpyridine).[2,6,26] In view of this effect, it will be of interest to study the miscibility and interactions in blends of poly(4-piperidinyl methacrylate) in our future study.

Conclusions

PMPMA forms complexes with PVPh in ethanol, and the DMF-cast blends are miscible. FTIR studies show the existence of weak hydrogen-bonding interactions between the carbonyl groups of PMPMA and the hydroxyl groups of PVPh. As compared to P4VPy, PMPMA interacts less strongly with PVPh.

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References and Notes

(1) Vivas de Meftahi, M.; Frechet, J. M. J. *Polymer* **1988**, *29*, 477.
(2) Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polym. J.* **1994**, *26*, 905.
(3) Oyama, H. T.; Nakajima, T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2987.
(4) Fujimori, K.; Costigan, M. J.; Trainor, G. T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2479.
(5) Velada, J. L.; Cesteros, L. C.; Meaurio, E.; Katime, I. *Polymer* **1995**, *36*, 2765.
(6) Cesteros, L. L.; Velada, J. L.; Katime, I. *Polymer* **1995**, *36*, 3183.
(7) Gargallo, L.; Gatica, N.; Radic, D. *Int. J. Polym. Mater.* **1994**, *27*, 107.
(8) de Ilarduya, A. M.; Eguiburi, J. L.; Espi, E.; Iruin, J. J.; Fernandez-Berridi, M. J. *Makromol. Chem.* **1993**, *194*, 501.
(9) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(10) Qiu, X.; Jiang, M. *Polymer* **1994**, *35*, 5084.
(11) Qiu, X.; Jiang, M. *Polymer* **1995**, *36*, 3601.
(12) Van de Grampel, H. T.; Tan, Y. Y.; Challa, G. *Macromolecules* **1992**, *25*, 1041.
(13) Goh, S. H.; Lee, S. Y.; Tan, L. I. T. *Polym. Bull.* **1996**, *37*, 253.
(14) Kwei, T. K. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 307.
(15) Pennachia, J. R.; Pearce, E. M.; Kwei, T. K.; Bulkin, B. J.; Chen, J. P. *Macromolecules* **1986**, *19*, 973.
(16) Barnum, R. S.; Goh, S. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 395.
(17) ten Brinke, G.; Karasz, F. E. *Macromolecules* **1984**, *17*, 815.
(18) Wang, L. F.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 619.
(19) Landry, C. J. T.; Teegarden, D. M. *Macromolecules* **1991**, *24*, 4310.
(20) Li, D.; Brisson, J. *Macromolecules* **1996**, *29*, 868.
(21) Moskala, E. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1984**, *17*, 1671.
(22) Hong, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polymer* **1995**, *36*, 143.
(23) Goh, S. H.; Lee, S. Y.; Dai, J.; Tan, K. L. *Polymer* **1996**, *37*, 5305.
(24) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Appl. Surf. Sci.*, in press.
(25) Coleman, M. M.; Pehlert, G. J.; Painter, P. C. *Macromolecules* **1996**, *29*, 6820.
(26) Velada, J. L.; Cesteros, L. C.; Katime, I. *Appl. Spectrosc.* **1996**, *50*, 893.

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