Miscibility and Interactions in Blends and Complexes of Poly[2-(dimethylamino)ethyl methacrylate] with Poly(*p*-vinylphenol)

Xu-Dong Huang, S. H. Goh,* S. Y. Lee, Z. D. Zhao, and Ming Wah Wong

Department of Chemistry, National University of Singapore, Singapore 119260

C. H. A. Huan

Department of Physics, National University of Singapore, Singapore 119260

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ABSTRACT: Poly(*p*-vinylphenol) (PVPh) and poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) formed interpolymer complexes in methanol, ethanol, or methyl ethyl ketone. However, only polymer blends were obtained from tetrahydrofuran or dimethylformamide. Each of the complexes and blends showed one composition-dependent glass transition temperature (T_g), indicating its single-phase nature. Positive deviations of T_g values were observed for both complexes and blends, suggesting a strong interaction between the two components. Thermal treatment at 190 °C resulted in an increase in T_g for the blends as well as the complexes. Fourier transform infrared spectroscopy revealed the existence of hydrogen-bonding interactions between the hydroxyl groups of PVPh and the carbonyl groups of PDMAEMA in the blends and complexes. In addition, X-ray photoelectron spectroscopy showed that the nitrogen atoms in PDMAEMA are also involved in hydrogen-bonding interactions as shown by the development of a high-binding-energy N1s peak in each complex or blend. Ab initio calculations on dimers of the saturated monomers revealed that the carbonyl oxygen and the nitrogen are about equally favored as proton-accepting sites.

Introduction

Two dissimilar polymers are likely to form a miscible blend if there are favorable intermolecular interactions between them. For an immiscible polymer blend, it is possible to induce miscibility when one or both polymers are functionalized to contain interacting groups. For example, we have reported that while polysulfone is immiscible with poly(4-vinylpyridine) (P4VPy), miscibility can be achieved when polysulfone is carboxylated.[1] Furthermore, when the degree of carboxylation is sufficiently high, carboxylated polysulfone (CPSf) forms complexes with P4VPy in a form of precipitates upon mixing the dimethylformamide solutions of CPSf and P4VPy. Such a transition from immiscibility to miscibility and from miscibility to complexation through the introduction of interacting groups has been reported for many systems.[2−9]

The formation of polymer complexes depends on the nature of solvent used. For example, the minimum vinylphenol content in poly(styrene-*co*-*p*-vinylphenol) (STVPh) to form complexes with poly(ethyl methacrylate) (PEMA) is 9 mol % in toluene and 22 mol % in 1-nitropropane because of the different abilities of the two solvents to accept protons.[4] Moreover, complete decomplexation of the STVPh/PEMA complexes can be realized by adding a small amount of the tetrahydrofuran. Therefore, when polymer−polymer interaction is strong and outweighs polymer−solvent interaction, the two polymers coprecipitate as highly associated materials called complexes. If the solvent interacts strongly with the polymers and thus prevents precipitation, the resulting materials obtained upon evaporation of the solvent are called blends. Miscible polymer blends and complexes are single-phase materials as shown by the presence of one glass transition temperature (T_g) in each sample. However, because of the more compact nature of complexes, the T_g values of complexes are higher than those of miscible blends of the same system with similar compositions.[10−14] Zhou et al.[15] recently reported a small-angle neutron scattering (SANS) study on the equilibrium structure of hydroxyl-modified polystyrene [PS(OH)]/poly(*n*-butyl methacrylate) (P*n*BMA) blends. Qiu and Jiang[3] have earlier found that [PS(OH)] containing 1 mol % hydroxyl groups is miscible with P*n*BMA and [PS(OH)] containing 18 mol % hydroxyl groups forms complexes with P*n*BMA. The SANS study showed that increasing density of hydrogen bonds greatly suppresses the freedom of polymer chains to fluctuate.

Poly(*p*-vinylphenol) (PVPh), a proton-donating polymer, can form complexes through hydrogen-bonding interactions with P4VPy,[11,16] poly(*N*-vinyl-2-pyrrolidone),[10] poly(*N*,*N*-dimethylacrylamide),[10] poly(2-ethyl-2-oxazoline),[10] poly(*N*-methyl-4-piperidyl methacrylate) (PMPMA),[12] and poly(*N*-acryloyl-*N*′-methylpiperazine) (PAMP).[13] Poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) is a water-soluble polymer with good film-forming properties. It can form complexes with poly(carboxylic acid) in water, and the membrane produced from the complex has been used in dialysis and untrafiltration.[17] We now report the complexation between PDMAEMA and PVPh. PDMAEMA possesses three possible proton-accepting sites: carbonyl oxygen, ether oxygen, and nitrogen. It is of interest to study if all the sites are involved in hydrogen-bonding interactions with the hydroxyl groups of PVPh. We have recently found that PMPMA interacts with PVPh though the carbonyl groups but not the piperidine nitrogens.[12] However, PAMP interacts with PVPh through its carbonyl groups

* To whom correspondence should be addressed.

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as well as two types of nitrogen.[13] It will be shown that PDMAEMA interacts with PVPh through the carbonyl oxygens and also the nitrogens.

Experimental Section

Materials. 2-(Dimethylamino)ethyl methacrylate was obtained from Fluka and was purified by fractional distillation (57 °C/4 mmHg). PDMAEMA was prepared by solution polymerization in tetrahydrofuran (THF) at 60 °C for 12 h, using 0.005 M azobisisobutyronitrile (AIBN) as initiator. The polymer was recovered by precipitation in excess hexane. The resulting polymer was purified by two dissolution/precipitation cycles using THF as solvent and hexane as nonsolvent, followed by drying in a vacuum oven at 60 °C for several days. The weight-average molecular weight (M_w) and polydispersity of PDMAEMA are 25 800 and 3.0, respectively, as determined by gel permeation chromatography (GPC) using a Waters 600E system containing two mixed bed Phenogel 10 linear columns and a Waters 410 differential refractometer with THF as eluent. The column setting was calibrated using eight monodisperse polystyrene standards.

PVPh (M_w = 20 000) was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI). Methanol, ethanol, THF, methyl ethyl ketone (MEK), and dimethylformamide (DMF) were of analytical pure grade and used as received.

Preparation of Blends and Complexes. PDMAEMA and PVPh were separately dissolved in methanol, ethanol, THF, MEK, or DMF to form 1% (w/v) solutions. Appropriate amounts of PDMAEMA and PVPh solutions were mixed by dropwise adding the PDMAEMA solution to the PVPh solution with vigorous stirring. In the case where precipitation occurred, the solution mixture was stirred continuously for 1 day. The complex in the form of precipitate was isolated by centrifugation, followed by washing with the solvent three times. The complex was then dried *in vacuo* at 60 °C for 3 days. The ratio of the amount of dried complex to the total weight of 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.

In the case where precipitation did not occur, the solution was allowed to evaporate to dryness to give a polymer blend. The blend was also dried *in vacuo* at 60 °C for 3 days.

DSC Measurements. The glass transition temperature (T_g) values of various complexes and blends were measured using a TA Instruments 2920 differential scanning calorimeter. The instrument was calibrated with an indium standard and a nitrogen atmosphere (flow rate = 50 mL/min) was used throughout. T_g values of samples were taken from the second heating scan as the extrapolated onset point of the abrupt increase in heat capacity in DSC curve.

FTIR Characterization. FTIR spectra were acquired using a Bio-Rad 165 FTIR spectrophotometer. Both blend and complex samples were prepared by grinding the dry powders with KBr and compressing the mixture to form disks. The disks were stored in a desiccator to avoid moisture absorption. All spectra were recorded at room temperature. Sixty-four scans were signal-averaged at a resolution of 2 cm^{-1}.

XPS Measurements. X-ray photoelectron spectroscopic (XPS) measurements were made on a VG ESCALAB MkII spectrometer using a Mg Kα X-ray source (1253.6 eV) and a hemispherical energy analyzer. Various complexes were ground to fine powders and then mounted on standard sample studs by means of a double-sided adhesive type. The X-ray source was run at 12 kV and 10 mA, and pass energy of 20 eV was used in the analyzer. The pressure in the analysis chamber was maintained below 10^{-8} mbar during measurements. All spectra were obtained at a takeoff angle of 75° to the sample surface and were curve fitted with the XPSPEAK 3.1 software. To compensate for surface charging effects in the insulating samples, all binding energies were corrected with reference to the saturated hydrocarbon C1s peak at 285.0 eV.

Table 1. Characteristics of PDMAEMA/PVPh Complexes from MEK

feed composition		intermolecular complexes				
PDMAEMA content			PDMAEMA content			
(wt %)	(mol %)	yield (wt %)	(wt %)	(mol %)	T_g (°C)	T_g annealed at 190 °C for 30 min (°C)
20	16	64	30	25	135	149
40	34	93	42	35	124	146
50	43	94	44	38	125	147
60	53	76	47	41	117	129
80	75	38	47	41	113	128

Results and Discussion

Complex Formation. PDMAEMA and PVPh formed complexes in methanol, ethanol, and MEK but not in THF or DMF. As mentioned earlier, one of the important factors governing complexation is the solvent medium in which complexation takes place.[10,14,18−22] This is because solvent molecules can also take part in hydrogen-bonding interactions, either as a donor or as an acceptor, with the component polymers. Methanol and ethanol are protic solvents whereas MEK, THF, and DMF are aprotic solvents. Thus, methanol and ethanol have favorable interactions with the proton-accepting polymer PDMAEMA, whereas the aprotic solvents THF, MEK, and DMF exhibit favorable interactions with the proton-donating polymer PVPh. The formation of complex is governed by the interaction between two polymers and those between the polymers and solvent. If the former interaction is stronger than the latter, an interpolymer complex is formed.

Table 1 shows the characteristics of the complexes formed from MEK. The yields of the complexes are in the range of 38−94%. In general, the composition of interpolymer complex corresponds to a simple ratio of the monomer units of the component polymers. However, it may be dependent on feed ratio in the preparation process. In the present system, the compositions of the complexes can be determined through elemental analysis of nitrogen. A PDMAEMA:PVPh ratio close to 2:3 is observed for all the complexes except the one obtained from the lowest PDMAEMA content in the feed.

Glass Transitions. Many polymer complexes have higher T_g values than those calculated from the weight-average values of the T_g values of the component polymers.[10−14] In several cases, the T_g values of the complexes even exceed that of high-T_g component. The high T_g has been ascribed to interactions between the component polymers which act as physical cross-links, resulting in reduced segment mobility. The T_g values of the complexes are in the range of 113−135 °C and are higher than those calculated from a linear additivity rule by 10−20 °C. The T_g of the complex decreases with increasing PDMAEMA content.

The PDMAEMA/PVPh blends cast from THF were studied in detail. All the blends were transparent and each showed a single T_g, indicating miscibility. As shown in Figure 1, the T_g−composition curve of the blends can be fitted by the Kwei equation:

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

The q value reflects the extent of interaction between the two polymers.[23] The formation and dissociation of hydrogen bonds are reversible with temperature for

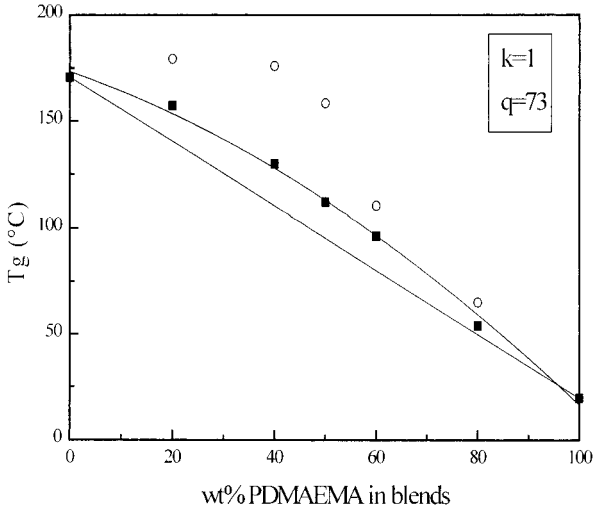

Figure 1. Glass transition temperatures of THF−cast PDMAEMA/PVPh blends: (■) fresh; (○) annealed at 190 °C for 30 min.

small molecules as well as for polymers in the solid state. The number of hydrogen bonds might be increased if a specimen was annealed for a period of time in its rubbery state, at which the increased chain mobility might permit additional interaction groups to approach each other.[10] Therefore, the various samples were subjected to thermal treatment at 190 °C for 30 min. followed by quenching. Indeed the thermal treatment resulted in an increase in T_g for the blends as well as for the complexes (Table 1 and Figure 1). Similar increases in T_g values for hydrogen-bonded blends and complexes upon annealing have also been reported.[10,18] Yang et al.[18] provided spectroscopic evidence to show that the increase in T_g was related to more extensive hydrogen-bonding interactions.

Lower critical solution temperature (LCST) behavior in polymer blends is shown to be the result of compressible nature of the system, the directional-specific character of the intermolecular interaction, or a combination of both.[24] Since hydrogen bonding is of a highly directionally dependent nature, it is of interest to study if the blends and complexes show LCST behavior. However, all the samples remained clear until reaching the decomposition temperature. This result indicates that there exists a strong interaction between two polymers.

FTIR Characterization. PVPh has an excellent potential for hydrogen-bonding as a proton donor because of its phenolic hydroxyl groups. FTIR studies have shown the existence of hydrogen-bonding interactions involving the PVPh hydroxyl groups and either the carbonyl or the ether oxygen moieties of other polymers.[25] Figure 2 shows the IR spectra in the 2900−3800 cm^{-1} region (OH stretching) of PVPh, PDMAEMA, and their blends cast from THF, all recorded at room temperature. The hydroxyl band of pure PVPh consists of two components: a broad band centered at 3383 cm^{-1}, attributed to hydrogen-bonded hydroxyl groups (self-association), and a relatively narrow band at 3510 cm^{-1}, assigned to free (nonassociated) hydroxyl groups. Upon mixing with PDMAEMA, the broad hydrogen-bonded hydroxyl band of PVPh is observed to shift to higher frequencies as a function of increasing PDMAEMA concentration, indicating that there are hydrogen-bonding interactions between the hydroxyl groups of PVPh and PDMAEMA. Such a high-frequency shift

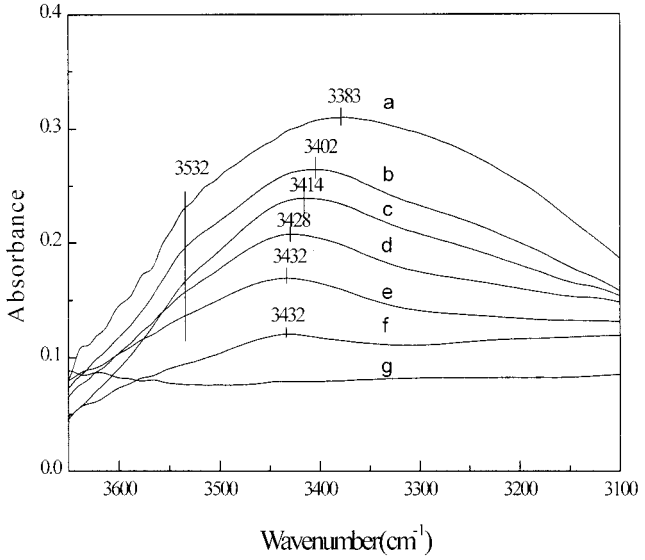

Figure 2. FTIR spectra of the hydroxyl stretching region of PVPh/PDMAEMA blends containing (a) 0, (b) 20, (c) 40, (d) 50, (e) 60, (f) 80, and (g) 100% PDMAEMA at room temperature.

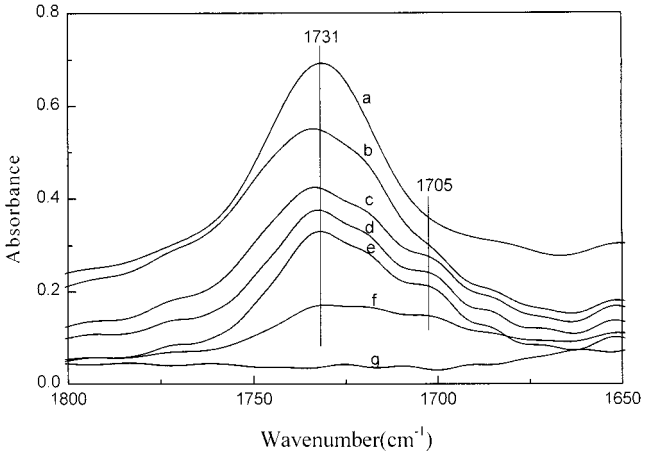

Figure 3. FIIR spectra of the carbonyl stretching region of PVPh/PDMAEMA blends containing (a) 0, (b) 20, (c) 40, (d) 50, (e) 60, (f) 80, and (g) 100% PVPh at room temperature.

indicates that the self-association of PVPh is stronger than the intermolecular hydrogen-bonding interaction between PVPh and PDMAEMA. Miscible blends of PVPh with PMPMP,[12] poly(methyl methacrylate),[26] poly(vinyl acetate),[27] and poly(dialkyl itaconate)s[28] also show similar high-frequency shifts of the hydroxyl bands. As the PDMAEMA content in the blend 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 PDMAEMA.

Figure 3 shows the spectra in the carbonyl region at room temperature of PDMAEMA, PVPh, and their blends cast from THF. The carbonyl band of PDMAEMA is centered at 1731 cm^{-1}. Upon mixing with PVPh, a shoulder at 1705 cm^{-1} gradually developed, indicating that some of the carbonyl groups of PDMAEMA are involved in hydrogen-bonding interactions with the hydroxyl groups of PVPh. The FTIR spectra of the complexes also show similar features as those of the blends and their spectra are not shown.

XPS Characterization. Although FTIR studies have shown the existence of hydrogen-bonding interactions

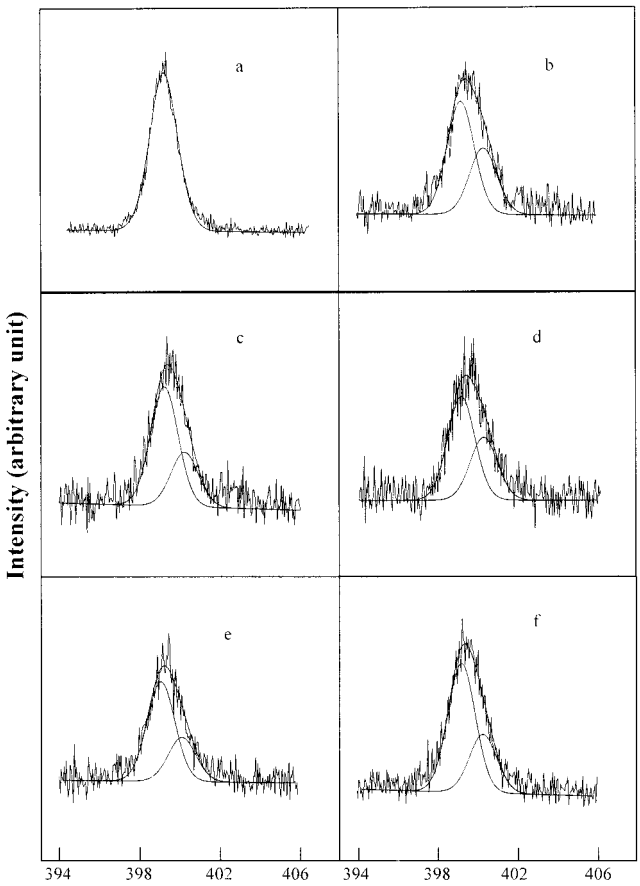

Figure 4. XPS Nls core level spectra of PDMAEMA (a); PDMAEMA/PVPh complexes containing (b) 44 wt % and (c) 47 wt % PDMAEMA; and PDMAEMA/PVPh blends containing (d) 40 wt %, (e) 50 wt %, and (f) 60 wt % PDMAEMA.

between the carbonyl groups of PDMAEMA and the hydroxyl groups of PVPh, there is a possibility that the nitrogen atoms in PDMAEMA may also participate in hydrogen-bonding interactions. We have recently used X-ray photoelectron spectroscopy (XPS) to study intermolecular interactions in polymer blends and complexes.[29−34] 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 molecule. Figure 4 shows the N1s spectra of PDMAEMA and some PVPh/PDMAEMA complexes and blends. The N1s spectrum of PDMAEMA features a symmetrical peak at 399.2 eV with a full width at half-maximum (fwhm) of 1.6 eV. However, the N1s peaks of both complexes and blends are broader and asymmetric. Two different nitrogen environments can be discerned using the curve-fitting software with the fwhms of both peaks fixed at 1.6 eV. The low-BE component at 399.2 eV is characteristic of neutral nitrogen in pure PDMAEMA, and a high-BE component at around 400.2 eV is developed in the complexes and blends. Our recent studies on complexes of poly(vinylpyridine)s have shown a shift of 1 eV for the N1s peaks for complexes involving hydrogen-bonding and a shift of about 2 eV for complexes involving ionic interaction.[32−34] Therefore, the XPS results demonstrate that the nitrogen atoms in PDMAEMA also participate in hydrogen-bonding interaction with PVPh. The BE values of the high-BE N1s peaks are the same for both the complexes and the blends, showing that the strength of hydrogen-bonding

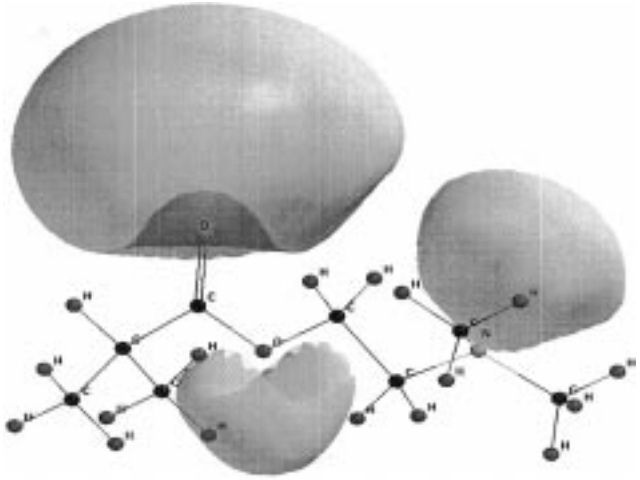

Figure 5. Calculated (HF/3-21G) electrostatic potential isosurface of DMAEMA.

interactions is about the same in all the samples. We have earlier found that the strength of hydrogen-bonding interactions in poly(4-vinylpyridine) (P4VPy)/PVPh complexes obtained from ethanol solutions is the same as that in P4VPy/PVPh blends cast from DMF.[32]

Theoretical Calculation. To provide some insight into the hydrogen-bonding interaction in the PDMAEMA/PVPh complex, we examined various possible hydrogen-bonded dimers between DMAEMA and VPh (the saturated monomers representing the repeating units in PDMAEMA and PVPh, respectively). The OH group of VPh can act as a proton donor for a hydrogen bond. For DMAEMA, there are three plausible sites of proton acceptor: the carbonyl oxygen, the ether oxygen, and the nitrogen. The three acceptor sites, corresponding to the electron lone pairs of DMAEMA, are readily depicted in the calculated electrostatic potential isosurface (Figure 5). Since hydrogen bonding is dominated by electrostatic interaction,[35] atoms with large electrostatic potential are indicators of favorable acceptor sites for hydrogen bonding. We have considered all three possible DMAEMA/VPh hydrogen-bonded dimers, namely C═O···H dimer (**A**), (ether)O···H dimer (**B**) and N···H dimer (**C**). Full geometry optimization [36] were carried at the HF/3-21G level.[37] Higher-level relative energies were obtained at the B3-LYP/6-31G* level, together with zero-point vibration correction (at the PM3 level). For water dimer, the calculated dimerization energy at this level of theory is 21 kJ mol^{-1}, in excellent agreement with the experimental value of 22 kJ mol^{-1}.[38] The calculated hydrogen bond lengths (i.e. O···H or N···H) for **A**, **B**, and **C** are rather short compared to those in CH_2═O···H_2O, H_2O···H_2O, and H_3N···H_2O dimers. The calculated dimerization energies for **A** and **C** are 34 and 37 kJ mol^{-1}, respectively, significantly larger than those of CH_2═O···H_2O (18 kJ mol^{-1}) and H_3N···H_2O (27 kJ mol^{-1}) dimers. For dimer **B**, the calculated dimerization energy (18 kJ mol^{-1}) is significantly smaller than those of **A** and **C**. The results suggest that the carbonyl oxygen and the nitrogen are about equally favored as proton-accepting sites, and the ether oxygen is unlikely to be involved in hydrogen-bonding in the PDMAEMA/PVPh complex. It is important to note that our calculated dimerization energies only provide an indicator of the relative strength of hydrogen bonds in the complex. In PDMAEMA or PVPh polymer chain, which has a rather

rigid structure, the hydrogen bonds will be reduced significantly due to strong steric repulsion.

Conclusion

PDMAEMA forms complexes with PVPh in methanol, ethanol, and MEK. THF-cast blends are miscible. FTIR studies show the existence of hydrogen bonding interactions between the carbonyl groups of PDMAEMA and the hydroxyl groups of PVPh. XPS studies demonstrate that the nitrogen atoms in PDMAEMA also participate in hydrogen-bonding interactions with the hydroxyl groups. Theoretical calculation suggests that the carbonyl oxygen atom and the nitrogen atom in PDMAEMA are about equally favored as proton-accepting sites for the hydroxyl groups of PVPh.

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