

# Specific Interactions and Phase Behavior of Poly(2-vinylpyridine)/Bisphenol Blends

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**ABSTRACT:** Hydrogen-bonding interaction and miscibility between poly(2-vinylpyridine) (P2VPy) and five bisphenols are studied by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and wide angle X-ray diffraction (WAXD). It is found that the miscibility behavior strongly depends on the flexibility of the

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**Key words:** phase behavior; miscibility; glass transition; infrared spectroscopy; thermal properties

## INTRODUCTION

Blends of polymers and low-molecular-weight compounds have received considerable attention during the past decade. Particular attention has been directed to polymer/surfactant complexes and supramolecular side-chain liquid crystalline polymers.<sup>1-9</sup> Polymers interact with the low-molecular-weight compounds through hydrogen-bonding or ionic interactions, which result in materials with new properties not possessed by either component. Recently, some dihydric phenol/polymer blends were studied. Wu et al.<sup>10-12</sup> reported that a dihydric phenol greatly improved the damping properties of chlorinated polyethylene (CPE) and acted as a compatibilizer for CPE/acrylic rubber blends. He et al. found that the addition of 4,4'-thiodiphenol (TDP) to poly( $\epsilon$ -caprolactone) (PCL) and poly(L-lactic acid) (PLLA) effectively modified the thermal and mechanical properties of PCL and PLLA.<sup>13-15</sup> He et al. also studied blends of TDP with poly(3-hydroxybutyrate) (P3HB) or poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).<sup>16</sup> TDP is effective in modifying the physical properties as well as the biodegradability of P3HB and PHBV. More recently, they reported the thermal and infrared spectroscopic study on the hydrogen-bonding interaction between PCL and a series of dihydric phenols and diamino compounds.<sup>17,18</sup> They concluded that the hydrogen bonds were strongly affected by the polarity of the group linking two hydroxyphenyls and the flexibility of the molecular chain. We have recently reported that two bifunctional low-molecular-weight

compounds, 4-hydroxybenzoic acid (HBA) and bis(4-hydroxyphenyl)methane (BHPM), interacted with poly(2-vinylpyridine) (P2VPy) and poly(N-vinyl-2-pyrrolidone) (PVP) through hydrogen bonding.<sup>19,20</sup> HBA and BHPM interacted with P2VPy and PVP simultaneously in P2VPy/PVP/HBA and P2VPy/PVP/BHPM ternary blends and miscibilized the immiscible P2VPy/PVP blends. Therefore, it is of interest to study the interaction and phase behavior between polymers and multifunctional low-molecular-weight compounds. In the present study, blends of P2VPy with several bisphenols were studied. The thermal and phase behavior of the blends and the underlying interactions are reported.

## EXPERIMENTAL

### Materials

P2VPy [weight-average molecular weight ( $M_w$ ) = 200,000] was supplied by Scientific Polymer Products, Inc. (Ontario, NY). Hydroquinone (HDQ) and 4,4'-(1,4-phenylene-diisopropylidene)-bisphenol (PDIPBP) were supplied by Aldrich Chemical Company, Inc. (Milwaukee, WI). BHPM, 4,4'-biphenol (BP), and bisphenol A (BPA) were supplied by Tokyo Chemical Industry (Tokyo, Japan). All the materials were used as received.

### Preparation of blends

All the P2VPy/bisphenols blends were cast from ethanol solution (2% w/v) after being continuously stirred for 48 h. The solvent was subsequently evaporated at room temperature to obtain solid blends. The blends were further dried *in vacuo* at 60°C for 2 weeks.

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The blends are denoted as (P2VPy)<sub>x</sub>bisphenol, where *x* is the molar ratio of vinylpyridine repeat unit to bisphenol.

#### Fourier transform infrared characterization

FTIR spectra were recorded on a Bio-Rad 165 FTIR spectrophotometer (Bio-Rad, Richmond, CA) at 120°C using a SPECAC high-temperature cell, equipped with an automatic temperature controller, which was mounted in the spectrophotometer. Thirty-two scans were signal-averaged at a resolution of 2 cm<sup>-1</sup>. Blend samples were prepared by dropping the ethanol solutions to KBr powder followed by drying *in vacuo* at 60°C for 2 weeks. The mixtures were then ground and compressed to form disks. The KBr disks were further dried *in vacuo* at 60°C for another two days and then stored in a desiccator.

#### Glass transition temperature measurements

Glass transition temperature (*T<sub>g</sub>*) measurements were conducted on a TA Instruments 2920 differential scanning calorimeter (DSC) (New Castle, DE). The blends were heated to 180°C using a heating rate of 20°C/min. The samples were kept at 180°C for 3 min before being quenched to -20°C. The quenched samples were then rescanned and the midpoints of the transition regions in the DSC curves were taken to be the *T<sub>g</sub>*s. All measurements were conducted under a nitrogen atmosphere with a flow rate of 70 mL/min.

#### Wide-angle X-ray diffraction measurements

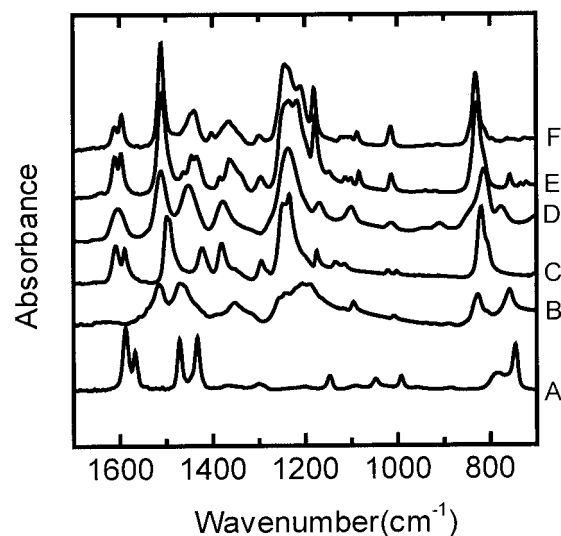
A Siemens D5005 X-ray powder diffractometer (Karlsruhe, Germany) with Cu-Kα (1.54051 Å) radiation (40 kV, 40 mA) was used to record the wide-angle X-ray diffraction (WAXD) patterns of the blends. The measurements were conducted at room temperature.

#### Optical observation

The optical appearance of samples was examined using a Fisher-Johns melting point apparatus (Fisher Scientific, Pittsburgh, PA). A small amount of sample was sandwiched between two microscope cover glasses and heated in the melting point apparatus until the sample softened and formed a film. The optical appearance of the film was observed with a magnifying glass attached to the apparatus over a temperature range from room temperature (~25°C) to 200°C.

#### Thermogravimetric analysis

Thermogravimetric (TG) analysis was carried out on a TA Instruments SDT 2960 thermogravimetric analysis



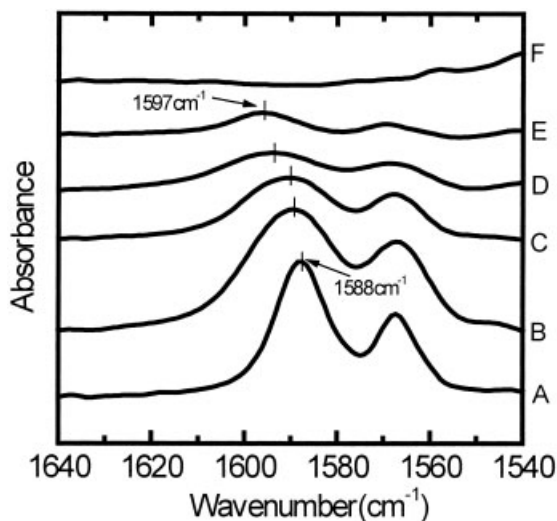
**Figure 1** FTIR spectra, recorded at 120°C, of pure (A) P2VPy, (B) HDQ, (C) BP, (D) BHPM, (E) BPA, and (F) PDIPBP.

instrument (New Castle, DE). The samples were heated at a heating rate of 10°C/min from room temperature to 550°C under a nitrogen atmosphere with a flow rate of 70 mL/min. The peak in the derivative TG curve is taken as *T<sub>max</sub>* and the temperature at 5% weight loss of each component in the blends is taken as the initial decomposition temperature (*T<sub>i</sub>*).

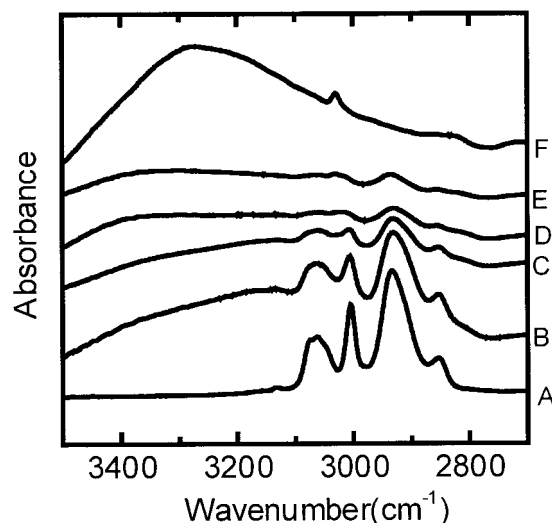
## RESULTS AND DISCUSSION

#### FTIR characterization

The skeletal vibration bands of pyridine ring of P2VPy at 1588 and 992 cm<sup>-1</sup> have been widely studied in P2VPy/proton-donating polymer blends.<sup>21,22</sup> Figure 1 shows the FTIR spectra of all the pure materials in the range from 700 to 1800 cm<sup>-1</sup>. Except for HDQ, the absorption bands of bisphenols overlap to a large extent with those of P2VPy in that region. Another characteristic vibration band of P2VPy at 1048 cm<sup>-1</sup>, the in-plane deformation of C—H in the pyridine ring, is examined instead because it does not overlap with the vibration bands of the bisphenols. However, the peak at 1588 cm<sup>-1</sup> in P2VPy/HDQ blends can be used first as an example to demonstrate the interaction between P2VPy and HDQ, as shown in Figure 2. The peak at 1588 cm<sup>-1</sup> shifts to a higher frequency, demonstrating that pyridine ring is involved in a hydrogen-bonding interaction.<sup>21,22</sup> The largest shift is to 1597 cm<sup>-1</sup> when *x* is equal to 1. Figure 3 shows that the peak of P2VPy at 1048 cm<sup>-1</sup> shifts to 1055 cm<sup>-1</sup>. Figure 4 shows the FTIR spectra in the hydroxyl region of P2VPy/HDQ blends. HDQ has a peak centering at 3271 cm<sup>-1</sup>, which is attributed to self-associated hydroxyl groups of HDQ. This peak shifts to a higher frequency and its intensity is weakened when HDQ is



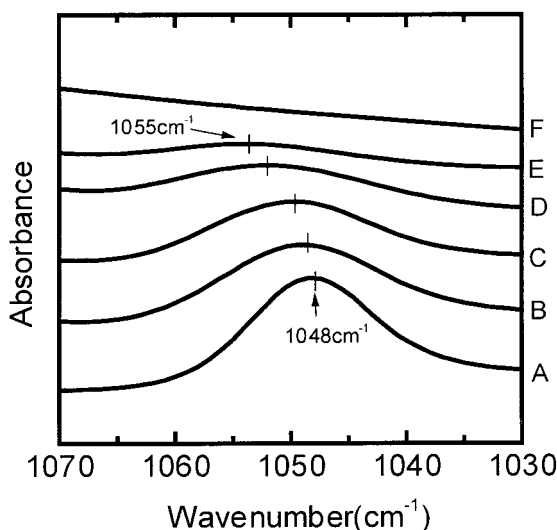
**Figure 2** FTIR spectra, recorded at 120°C, of the pyridine region of (A) P2VPy, (B) (P2VPy)<sub>10</sub>HDQ, (C) (P2VPy)<sub>4</sub>HDQ, (D) (P2VPy)<sub>2</sub>HDQ, (E) (P2VPy)<sub>1</sub>HDQ, and (F) HDQ.



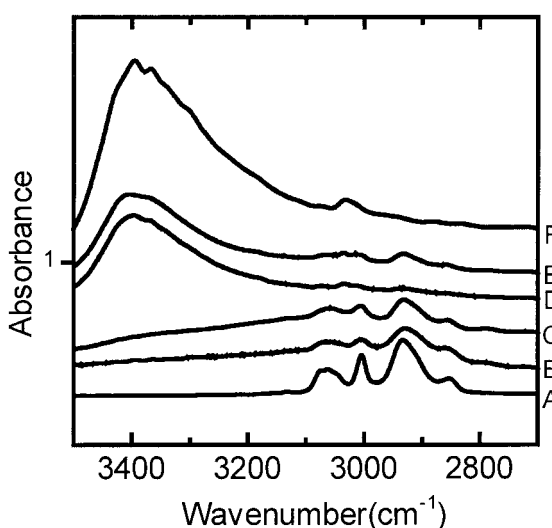
**Figure 4** FTIR spectra, recorded at 120°C, of the hydroxyl region of (A) P2VPy, (B) (P2VPy)<sub>10</sub>HDQ, (C) (P2VPy)<sub>4</sub>HDQ, (D) (P2VPy)<sub>2</sub>HDQ, (E) (P2VPy)<sub>1</sub>HDQ, and (F) HDQ.

blended with P2VPy. This implies that the hydrogen-bonding interaction between HDQ and P2VPy is not as strong as the self-association of hydroxyl groups of HDQ. The pyridine ring band of P2VPy at 1048 cm<sup>-1</sup> also shifted to 1052, 1054, 1056, and 1054 cm<sup>-1</sup> when P2VPy was blended with BP, BHPM, BPA, and PDIPBP, respectively, in a 1:1 ratio. For brevity, the spectra of these blends are not shown. Based on the frequency shift of the 1048 cm<sup>-1</sup> band, the interaction strength between bisphenol and P2VPy is approximately in the order BP < PDIPBP ~ BHPM < HDQ < BPA. Figure 5 shows the FTIR spectra in the hydroxyl region of blends of P2VPy with BP. The peaks in this region shift to higher frequencies and become

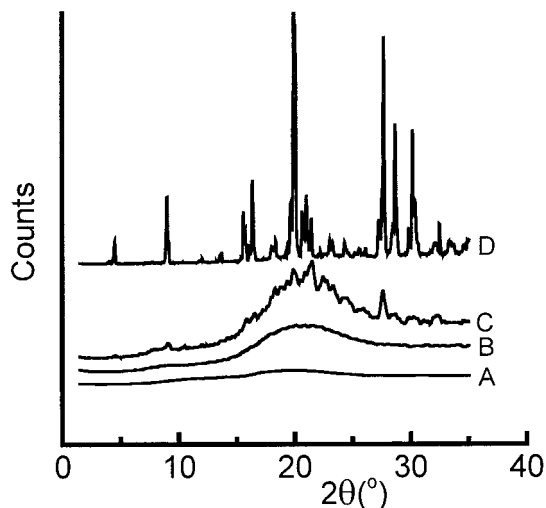
weaker as  $x$  increases. The sharp peaks disappear when  $x$  reaches 4. However, in the blends of P2VPy with BHPM, PDIPBP, and BPA, the sharp peaks disappear when  $x$  is 2. These results indicate that the bisphenol molecules interact with P2VPy through hydrogen bonding and disperse uniformly in the blends to form miscible blends with P2VPy below a certain critical content. As the bisphenol content increases, it tends to aggregate. Some of the bisphenol molecules interact with P2VPy to form a P2VPy-rich phase and the rest aggregate to form self-associated phase. The weaker the hydrogen-bonding interaction, the stronger is the tendency of the bisphenol molecules to self-associate. This explains the difference of the FTIR



**Figure 3** FTIR spectra, recorded at 120°C, of the pyridine region of (A) P2VPy, (B) (P2VPy)<sub>10</sub>HDQ, (C) (P2VPy)<sub>4</sub>HDQ, (D) (P2VPy)<sub>2</sub>HDQ, (E) (P2VPy)<sub>1</sub>HDQ, and (F) HDQ.



**Figure 5** FTIR spectra, recorded at 120°C, of the hydroxyl region of (A) P2VPy, (B) (P2VPy)<sub>10</sub>BP, (C) (P2VPy)<sub>4</sub>BP, (D) (P2VPy)<sub>2</sub>BP, (E) (P2VPy)<sub>1</sub>BP, and (F) BP.

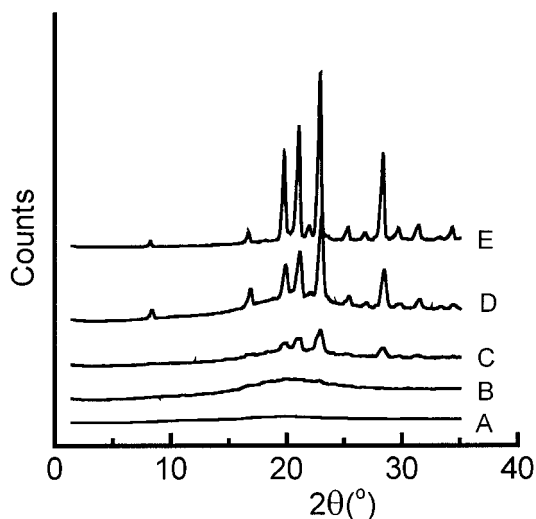


**Figure 6** WAXD patterns of (A) P2VPy, (B) (P2VPy)<sub>2</sub>HDQ, (C) (P2VPy)<sub>1</sub>HDQ, and (D) HDQ.

spectra in the hydroxyl region of the P2VPy/BP blend and those of the other P2VPy/bisphenols blends. The difference also supports the conclusion drawn earlier that BP has the weakest interaction with P2VPy among all the bisphenols studied in this work.

#### WAXD characterization

The WAXD patterns of various P2VPy/bisphenols blends show the presence of crystalline phases of bisphenols in (P2VPy)<sub>1</sub>HDQ, (P2VPy)<sub>1</sub>BHPM, (P2VPy)<sub>1</sub>BPA, and (P2VPy)<sub>1</sub>PDIPBP blends, and the blends are amorphous at lower bisphenol contents. The WAXD patterns of (P2VPy)<sub>1</sub>HDQ and (P2VPy)<sub>2</sub>HDQ are shown in Figure 6 as examples. The crystalline phase in P2VPy/BP blends, which is attributed to self-associated BP, does not disappear until  $x$  is as high as 2 (Fig. 7). This means that



**Figure 7** WAXD patterns of (A) P2VPy, (B) (P2VPy)<sub>4</sub>BP, (C) (P2VPy)<sub>2</sub>BP, (D) (P2VPy)<sub>1</sub>BP, and (E) BP.

**TABLE I**  
Optical Appearance of P2VPy/Bisphenols Blends

$x$	HDQ	BP	BPA	BHPM	PDIPBP
1	Clear	Cloudy	Clear	Cloudy	Cloudy
2	Clear	Cloudy	Clear	Clear	Clear
4	Clear	Clear	Clear	Clear	Clear
10	Clear	Clear	Clear	Clear	Clear

Note: Pure P2VPy film is amorphous and clear.

BP could self-associate at a lower bisphenol content in P2VPy/BP blends than in the other P2VPy/bisphenol blends. The optical observation results are tabulated in Table I. All P2VPy/BPA and P2VPy/HDQ blends are clear—even the WAXD results show the presence of weak diffraction peaks in (P2VPy)<sub>1</sub>BPA and (P2VPy)<sub>1</sub>HDQ blends. Blends of P2VPy with BHPM and PDIPBP have the same optical appearance. When  $x$  is equal to 1, the blends are cloudy but they are clear as  $x$  increases. P2VPy/BP blends show a different behavior. P2VPy(BP)<sub>1</sub> and P2VPy(BP)<sub>2</sub> are cloudy, and the blend becomes clear only when  $x$  is equal to 4. These results demonstrate that P2VPy has a better miscibility with HDQ, BHPM, BPA, and PDIPBP than with BP.

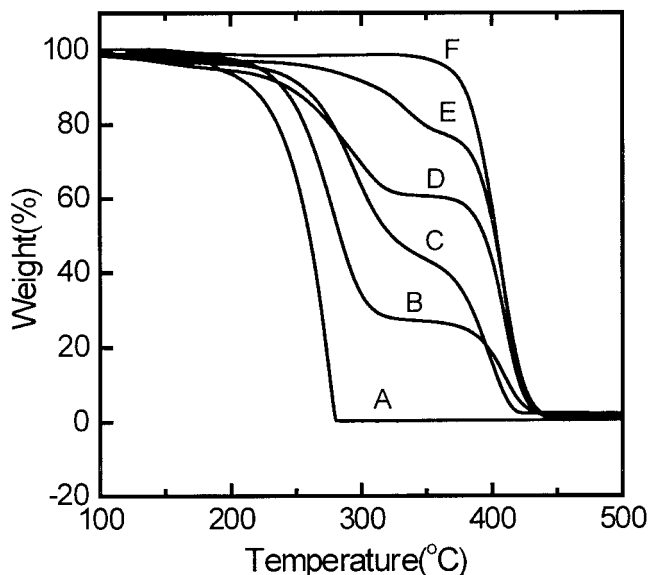
#### DSC characterization

Tables I and II show the glass transition temperatures and the optical appearance of various P2VPy/bisphenol blends. The  $T_g$  values decrease in the blends of P2VPy with HDQ, BHPM, BPA, and PDIPBP with increasing bisphenol content. However, the  $T_g$  values of P2VPy/BP blends do not change significantly. Basically, the influence of low-molecular-weight compound on the  $T_g$  values of polymers depends on the nature of polymers and the additives, and the interaction strength between them. When the interaction between the small molecule and the polymer is strong enough, the  $T_g$  of the polymer increases because the small molecules that interact with the polymer chains reduce the mobility of polymer chains.<sup>13,16,23–25</sup> However, when the interaction between them is not strong enough, the small molecule acts as a plasticizer and thus the  $T_g$  of the polymer decreases. In the blends of P2VPy with HDQ, BHPM, BPA, and PDIPBP, the FTIR and WAXD results have shown that these bisphenols could disperse in P2VPy to form miscible amorphous

**TABLE II**  
 $T_g$  (°C) of P2VPy/Bisphenols Blends

$x$	HDQ	BP	BPA	BHPM	PDIPBP
1	59	106	52	53	73
2	80	106	76	77	89
4	89	106	93	87	99
10	94	103	98	96	103

Note:  $T_g$  of P2VPy: 105°C.



**Figure 8** TG curves of (A) BPA, (B) (P2VPy)<sub>1</sub>BPA, (C) (P2VPy)<sub>2</sub>BPA, (D) (P2VPy)<sub>4</sub>BPA, and (E) (P2VPy)<sub>10</sub>BPA.

blends when  $x$  is as low as 1. This means that hydrogen bonding between P2VPy and bisphenols is the driving force to facilitate the dispersion of bisphenols in P2VPy and expand the space between P2VPy macromolecular chains. The expanding effect results in the plasticization of P2VPy and hence a decrease in  $T_g$ . On the other hand, the hydrogen-bonding interactions between them are not strong enough to increase the rigidity of P2VPy chains. Thus the expanding effect of bisphenols in P2VPy is predominant in these blends and the  $T_g$  of P2VPy decreases upon the addition of these bisphenols. However in P2VPy/BP blends, the miscibility of P2VPy with BP is quite poor, and BP tends to aggregate and crystallize instead of dispersing into the P2VPy phase. As a result, the  $T_g$  of P2VPy is not affected significantly.

### Thermal behavior

The TG curves of P2VPy, BPA, and P2VPy/BPA blends are shown in Figure 8. For brevity, the TG curves of other blends are not shown. From Figure 8, it is obvious that the decomposition temperature of BPA increases after blending with P2VPy, demonstrating an improvement in thermal stability. As shown in Tables III and IV, the  $T_{max}$  and  $T_i$  values of P2VPy in various blends do not change much upon the addition of bisphenols. However, the  $T_{max}$  and  $T_i$  values of the bisphenols change upon blending with P2VPy. The  $T_{max}$  values of most bisphenols increase on blending with P2VPy, implying that P2VPy improves their thermal stability since they disperse well in P2VPy phase and interact with P2VPy. The  $T_i$  values of BPA, BHPM, and PDIPBP in their blends with P2VPy increase significantly while those of BP in its blends with P2VPy

**TABLE III**  
 $T_{max}$  (°C) of P2VPy and Bisphenols in Their Blends<sup>a</sup>

$x$	HDQ	BP	BPA	BHPM	PDIPBP
0	204	288	275	284	365
1	218, 396	281, 394	278, 409	284, 392	333, 409
2	205, 404	294, 409	294, 399	295, 405	358, 399
4	218, 405	292, 409	297, 410	289, 407	380, 408
10	212, 385	294, 409	332, 409	285, 406	402, <sup>b</sup>

Note:  $T_{max}$  of P2VPy: 409°C.

<sup>a</sup> Smaller values are  $T_{max}$  of bisphenols and larger values are  $T_{max}$  of P2VPy in all cells.

<sup>b</sup> Difficult to determine.

decrease. These results indicate that BPA, BHPM, and PDIPBP mix more intimately with P2VPy than BP does, and so the thermal behavior of BP is different from those of BPA, BHPM, and PDIPBP.

All the present results show that P2VPy interacts more strongly with HDQ, BHPM, BPA, and PDIPBP than with BP. The intensity of the hydrogen-bonding interaction is likely to be affected by the acidity and the accessibility of the hydroxyl group of the bisphenol. A more acidic bisphenol will interact more intensely with P2VPy. For polymer/polymer blends, information on the atomic charge distributions in the polymer segments enables a better understanding on the miscibility behavior.<sup>26–29</sup> The structures of various bisphenols were optimized by Gaussian 98 with the HF/6-31G basis.<sup>30</sup> Their atomic charge distributions were then obtained. As shown in Figure 9, the atomic charges of phenolic hydrogen of various bisphenols are almost the same (0.413–0.415), and thus the weaker interaction between BP and P2VPy does not arise from the acidity effect. On the other hand, hydrogen bonding is extremely directional specific. In other words, the two interacting groups must be in the right spatial position to form hydrogen bond.<sup>31</sup> Among all the bisphenols, BP molecule is the most rigid since the two phenyl rings are linked directly without a connecting group. To achieve hydrogen-bonding interactions with P2VPy, the hydroxyl groups need to adjust their direction to meet the spatial requirement in order to interact with pyridine

**TABLE IV**  
 $T_i$  (°C) of P2VPy and Bisphenols in Their Blends<sup>a</sup>

$x$	HDQ	BP	BPA	BHPM	PDIPBP
0	161	240	190	212	278
1	156, 348	233, 354	222, 371	223, 342	267, 376
2	161, 362	247, 374	216, 377	222, 368	290, 386
4	159, 357	227, 376	218, 381	220, 369	277, 380
10	159, 343	216, 374	250, 380	220, 367	338, <sup>b</sup>

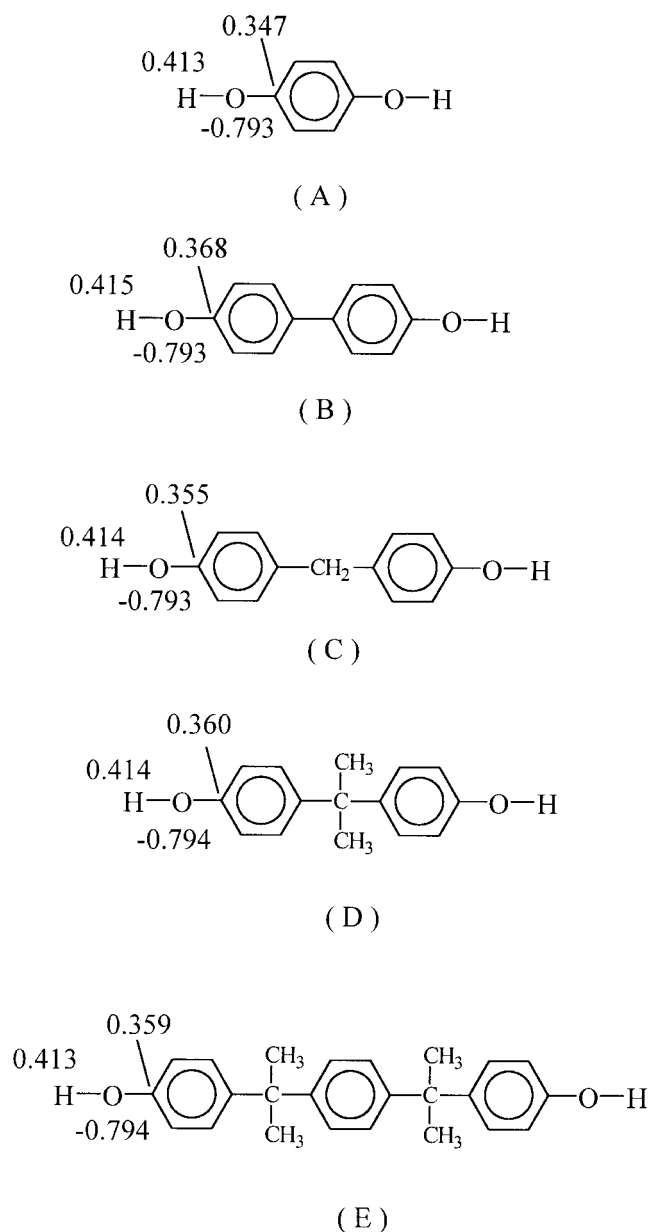
$T_i$  of P2VPy: 382°C.

<sup>a</sup> Smaller values are  $T_i$  of bisphenols and larger values are  $T_i$  of P2VPy in all cells.

<sup>b</sup> Difficult to determine.

nitrogen atoms. Since BP molecule is more rigid, it is reasonable that it has the weakest interaction with P2VPy among all these bisphenols.

Except for BP, the bisphenols have rather similar miscibility behavior with P2VPy. When the molar ratio of P2VPy repeat unit to bisphenol reaches 1 or higher, the blend contains crystalline phase of the bisphenol. When  $x$  is above 1, the blends are miscible and clear. Therefore the miscibility behavior of P2VPy/bisphenol blends depends on the molar ratio of the 2VPy unit to bisphenol instead of on the weight ratio because these bisphenols have quite different molecular weights. The weight ratio of the 2VPy unit to bisphenol calculated according to their molar ratio



**Figure 9** Calculated atomic charge of (A) HDQ, (B) BP, (C) BHPM, (D) BPA, and (E) PDIPBP.

**TABLE V**  
Weight Ratio of P2VPy Repeat Unit Against Bisphenols

$x$	HDQ	BP	BPA	BHPM	PDIPBP
1	0.96	0.57	0.46	0.53	0.29
2	1.93	1.14	0.93	1.06	0.58
4	3.85	2.28	1.86	2.12	1.15
10	9.64	5.69	4.64	5.29	2.89

is tabulated in Table V. It is clear that the miscibility behavior depends on the molar ratio but not the weight ratio. PDIPBP has almost the same miscibility behavior as HDQ with P2VPy even the weight ratio of the former is much higher than that of the latter. Since hydrogen bonding has a precise stoichiometry, it is evident that the hydrogen-bonding interaction plays a key role in the promotion of miscibility between P2VPy and the bisphenols. When the molar ratio of 2VPy repeat unit to bisphenol is more than 2, the number of 2VPy units is more than that of hydroxyl groups. Therefore all the bisphenol molecules have the possibility to participate in hydrogen bonding with P2VPy even though the hydroxyl groups may have difficulty to adjust their conformation to form the hydrogen bonds. However, when the number of 2VPy repeat units is less than that of hydroxyl groups, i.e., the molar ratio of 2VPy repeat unit to bisphenol is below 2, there are excess hydroxyl groups that cannot form hydrogen bonding with P2VPy, and they tend to self-associate to form the crystalline phase.

## CONCLUSIONS

FTIR study shows that P2VPy interacts with HDQ, BP, BPA, BHPM, and PDIPBP in the order of BP < PDIPBP ~ BHPM < HDQ < BPA in terms of interaction strength. BP tends to aggregate and crystallize in P2VPy more easily than the other bisphenols do. It is concluded that P2VPy mixes more intimately with BPA, HDQ, BHPM, and PDIPBP than with BP. The miscibility behavior strongly depends on the flexibility of the bisphenol molecules and on the molar ratio of the 2VPy repeat unit to bisphenol.

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