Effect of Intermolecular Hydrogen Bonding on Low-Surface-Energy Material of Poly(vinylphenol)

Han-Ching Lin,[†] Chih-Feng Wang,[‡] Shiao-Wei Kuo,[†] Pao-Hsiang Tung,[†] Chih-Feng Huang,[†] Chun-Hung Lin,[§] and Feng-Chih Chang*,[†]

Institute of Applied Chemistry, National Chiao Tung University, 30050 Hsinchu, Department of Materials Science and Engineering, I-Shou University, 84041 Kaohsiung, and National Nano Device Laboratories, 30050 Hsinchu, Taiwan

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We discovered that poly(vinylphenol) (PVPh) possesses an extremely low surface energy (15.7 mJ/m²) after a simple thermal treatment procedure, even lower than that of poly(tetrafluoroethylene) (22.0 mJ/m²) calculated on the basis of the two-liquid geometric method. Infrared analyses indicate that the intermolecular hydrogen bonding of PVPh decreases by converting the hydroxyl group into a free hydroxyl and increasing intramolecular hydrogen bonding after thermal treatment. PVPh results in a lower surface energy because of the decrease of intermolecular hydrogen bonding between hydroxyl groups. In addition, we also compared surface energies of PVPh-*co*-PS (polystyrene) copolymers (random and block) and their corresponding blends. Again, these random copolymers possess a lower fraction of intermolecular hydrogen bonding and surface energy than the corresponding block copolymers or blends after similar thermal treatment. This finding provides a unique and easy method to prepare a low-surface-energy material through a simple thermal treatment procedure without using fluoro polymers or silicones.

Introduction

The performance of polymeric materials is often dictated by surface properties, such as wettability, friction, and adhesion. In particular, hydrophobicity and oleophobicity have attracted tremendous interest due to their wide range of applications.[1–4] Both poly(dimethylsiloxane) (PDMS) and poly(tetrafluoroethylene) (PTFE) are two well-known examples possessing low surface energies.[5–8] PTFE may be regarded as the benchmark lower surface energy material, displaying water repellency[9] in combination with other desirable properties.[10] The small size of the fluorine atom with high electronegativity, low polarizability, and strong fluorine–fluorine repulsion[11] results in weak intermolecular forces of fluorinated polymer chains and thus relatively lower surface energies. However, PTFE and many fluorinated polymers have some application limitations such as high cost and poor processibility. Many efforts have been attempted to search for low-surface-free-energy polymeric materials with low cost, easy processibility, and good film-forming characteristics.[12–14]

The amorphous comblike polymers possessing a flexible linear backbone on the side chain with low intermolecular interaction generally exhibit a low surface energy.[15] We have found that the intermolecular hydrogen bonding between the hydroxyl groups increases their surface energies in the poly-benzoxazine system.[12] Chung et al.[16] have reported that the presence of amide groups in the main-chain-fluorinated liquid-crystalline polymer system tends to induce strong intermolecular hydrogen bonding and results in a higher surface energy and hydrophilicity. The nature of the pendant chain has a most

profound effect in determining the surface energy of the material; therefore, a low-surface-free-energy material can be obtained by decreasing the intermolecular interaction from the comblike polymer with a flexible linear backbone.[17] In this study, the relationships between the hydrogen-bonding strength and the surface energy of poly(vinylphenol) (PVPh) before and after thermal treatment were investigated on the basis of infrared spectroscopy and contact angle measurements. It is well-known that high-temperature thermal treatment tends to disrupt hydrogen bonds and the hydrogen bonds are re-formed in a different distribution (inter- and intramolecular) after fast cooling to ambient temperature relative to that before thermal annealing. Besides, the free hydroxyl content is also changed. To our surprise, we discovered that PVPh, a fluorine- and silicone-free polymer, can possess an extremely low surface energy (15.7 mJ/m²) after a simple thermal treatment procedure which is even lower than that of PTFE (22.0 mJ/m²) calculated on the basis of the two-liquid geometric method. To the best of our knowledge, this is the first reported thermoplastic to achieve a low surface energy by weakening the intermolecular hydrogen-bonding interaction. Furthermore, we use PVPh/PS (polystyrene) random and block copolymers and their respective blends to investigate the importance of the hydrogen-bonding strength in the resulting surface energy.

Experimental Part

Preparation of PVPh/PS Random and Block Copolymers and Blends. The detailed synthesis procedures of PVPh-*r*-PS and PVPh-*b*-PS copolymers have been reported previously.[18,19] Table 1 lists the characterizations of PVPh, PS, and PVPh/PS random and block copolymers. Various binary PVPh/PS blend compositions were prepared by solution-casting. A THF solution containing 5 wt % polymer was stirred for 6–8 h and then cast onto a Teflon dish. The solution was left to evaporate at room

Hydrogen-Bonding Effect on Poly(vinylphenol)

J. Phys. Chem. B, Vol. 111, No. 13, 2007 **3405**

TABLE 1: Formulations and Thermal Properties of PVPh-*co*-PS Copolymers and Corresponding Blends

copolymer	phenol ratio[a] (mol %)	M_n[b]	M_w/M_n[b]	T_g (°C)	T_d (°C)
PS	0	11000	1.21	100	371
PVPh22-*r*-PS78	21.5	24000	2.05	104	368
PVPh36-*r*-PS64	36.0	17400	2.05	118	365
PVPh55-*r*-PS45	55.2	23200	2.10	154	359
PVPh78-*r*-PS22	77.8	24400	2.34	162	353
PVPh24-*b*-PS76	24.2	12400	1.13	101, 172	370
PVPh49-*b*-PS51	49.0	17400	1.09	98, 175	363
PVPh71-*b*-PS29	71.0	30200	1.08	99, 177	356
PVPh80-*b*-PS20	80.7	20900	1.13	99, 176	354
PVPh/PS = 20/80	20.0			98, 178	364
PVPh/PS = 60/40	60.0			101, 180	360
PVPh/PS = 80/20	80.0			99, 182	353
PVPh	100	20000	1.07	175	352

[a] Obtained from ^{1}H NMR measurement. [b] Obtained from GPC analysis.

temperature for 1 day and dried in vacuum at room temperature for 2 days. The thermal treatment was carried out by placing the as-prepared polymer film in a vacuum oven at 120 or 180 °C for 24 h and then quenching to ambient temperature.

Characterizations. ^{1}H NMR spectra were recorded on a Varian Unity Inova 500 FT NMR spectrometer operated at 500 MHz; deuterated chloroform was used as the solvent. Thermal analyses were performed using a DuPont DSC-9000 differential scanning calorimeter operated at a scan rate of 20 °C/min within a temperature range from 30 to 220 °C. Thermal stabilities of the cured samples were investigated using a DuPont 2050 TGA instrument operated at a rate of 10 °C/min from 30 to 700 °C under a nitrogen flow. Infrared spectroscopic measurements were conducted on a Nicolet Avatar 320 FTIR spectrophotometer; 32 scans were collected with a spectral resolution of 1 cm^{-1}. All sample preparations were under continuous nitrogen flow to ensure minimal sample oxidation or degradation. Surface roughness profiles of film structures were acquired using a Digital Instruments DI5000 scanning probe microscope in the tapping mode. The values of root-mean-square (rms) roughness were calculated over scan areas of 5 μm × 5 μm. For contact angle measurements, deionized water and diiodomethane (DIM) were chosen as testing liquids because significant amounts of data are available for these liquids. The advancing contact angle measurement of a polymer sample was determined at 25 °C after injection of a liquid drop (5 μL) onto the surface, and a Krüss GH-100 goniometer interfaced to image-capture software was employed to perform the measurement. A two-liquid geometric method was employed to determine the surface energy.[20] XPS was performed using a VG Microlab 310F spectrometer equipped with an Al Kα X-ray source (1486.6 eV).

Results and Discussion

Formulations and thermal properties of these synthesized copolymers are summarized in Table 1. It is well-known that a high temperature above T_g tends to partially disrupt hydrogen bond formation, and this is why we chose 180 °C as the thermal treatment temperature. Thermal treatment at 120°C was chosen because it is between the T_g values of PS and PVPh. Furthermore, 120 and 180 °C are both far lower than the decomposition temperature (Table 1), and the thermal treatment should not damage the polymer structure. Table 2 lists the surface roughness, advancing contact angles, and surface free energies of all specimens, before and after thermal treatment. The surface roughnesses of all specimens are lower than 20 nm; therefore, the influence of topography on the surface free energy is
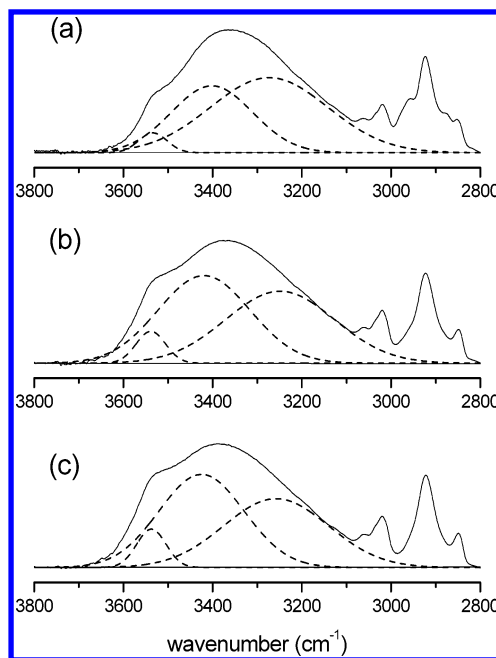

Figure 1. FTIR spectra and curve-fitting result of pure PVPh (a) at room temperature and after (b) 120 °C and (c) 180 °C thermal treatment procedures.

negligible. The advancing contact angle is relatively less sensitive to surface roughness and heterogeneity than the receding angle; thus, the advancing contact angle data are commonly used to calculate the components of surface and interfacial tension.[21,22] In the pure PVPh system, the advancing contact angles of water and diiodomethane increase substantially after thermal treatment, resulting in a significant decrease in surface free energy (from 41.8 to 15.7 mJ/m^2). Compared with the surface free energy of PTFE (22.0 mJ/m^2) by using the same testing liquids and calculated method,[23] surprisingly, the surface free energy of this fluorine- and silicone-free PVPh (15.7 mJ/m^2) is significantly lower than that of the pure PTFE after the simple thermal treatment procedure.

It has been reported that increasing the intermolecular hydrogen bonding of a polymeric material tends to increase its surface energy.[12,16] We speculate that the decrease of surface energy in the present case is due to the decrease of the intermolecular hydrogen-bonding interaction. Figure 1 shows the FTIR spectra and the curve-fitting result of the pure PVPh at room temperature and after 120 and 180 °C thermal treatment for 1 day. For clarity, the spectra only display the hydroxyl stretching region between 2800 and 3800 cm^{-1}. According to a recent study,[24] the −OH band can be fitted by three Gaussian functions: a narrower shoulder band at 3525 cm^{-1} represents the free hydroxyl group, the peak at $\nu \doteqdot 3280$ cm^{-1} corresponds to the hydroxyl groups involved in intermolecular hydrogen bonding, and the peak at $\nu \doteqdot 3420$ cm^{-1} corresponds to the hydroxyl groups involved in intramolecular hydrogen bonding. Scheme 1 displays the schematic representation of free hydroxyl and inter- and intramolecular hydrogen bonding in poly-(vinylphenol). During the process of fast cooling, it is more favorable to re-form hydrogen bonds from neighboring hydroxyl groups or those in the vicinity (most likely from the same chain, defined as an intramolecular hydrogen bond). This is probably the reason for the decrease in the number of intermolecular hydrogen bond (longer distance between hydroxyls, mostly from different chains) content. Table 3 lists results of curve-fitting data for PVPh before and after the thermal treatment. Combining our analyses of the FTIR spectra and the corresponding curve-

TABLE 2: Root-Mean-Square Surface Roughness, Advancing Contact Angle for Water and Diiodomethane, Surface Free Energy, and XPS Analysis of PVPh/PS Copolymers (Standard Deviations in the Range 0.3−2.4)

| | before 180 °C thermal treatment | | | | after 180 °C thermal treatment | | | | XPS: oxygen content (mol %) | |
| | | contact angle (deg) | | | | contact angle (deg) | | | | |
polymer	roughness (nm)	H_2O	DIM	γ (mJ/m^2)	roughness (nm)	H_2O	DIM	γ (mJ/m^2)	before thermal treatment	after thermal treatment
PVPh	7.8	70.5	42.1	41.8	5.1	105.5	84.1	15.7	13.5	17.3
PVPh22-r-PS78	8.2	100.0	53.1	33.1	3.8	105.5	75.6	19.8		
PVPh36-r-PS64	4.3	101.5	56.4	31.2	5.4	107.3	75.2	20.1		
PVPh55-r-PS45	7.1	97.7	53.6	32.5	4.7	105.8	76.3	19.4		
PVPh78-r-PS22	5.6	88.9	49.1	34.8	5.2	108.5	79.8	17.4	12.4	16.9
PVPh24-b-PS76	6.3	92.0	44.2	37.5	7.2	105.7	43.6	41.0		
PVPh49-b-PS51	4.7	102.5	47.9	37.0	3.6	103.9	42.6	41.0		
PVPh71-b-PS29	8.4	95.4	43.9	38.1	6.4	103.3	59.5	29.4		
PVPh80-b-PS20	5.9	100.6	47.8	36.6	5.8	103.5	75.6	19.8	10.4	14.9
PVPh/PS = 20/80	14.2	100.4	44.0	40.1	11.3	101.2	41.2	41.1		
PVPh/PS = 40/60	17.6	98.6	42.1	40.8	9.7	101.8	43.5	40.8		
PVPh/PS = 60/40	19.8	90.1	41.0	40.2	14.6	100.5	44.7	40.2		
PVPh/PS = 80/20	13.7	76.7	43.3	40.4	10.5	100.9	52.6	33.6	12.5	12.0
PS	3.2	100.6	41.3	40.9						

SCHEME 1: Schematic Representation of Inter- and Intramolecular Hydrogen Bonding and Free Hydroxyl in Poly(vinylphenol)
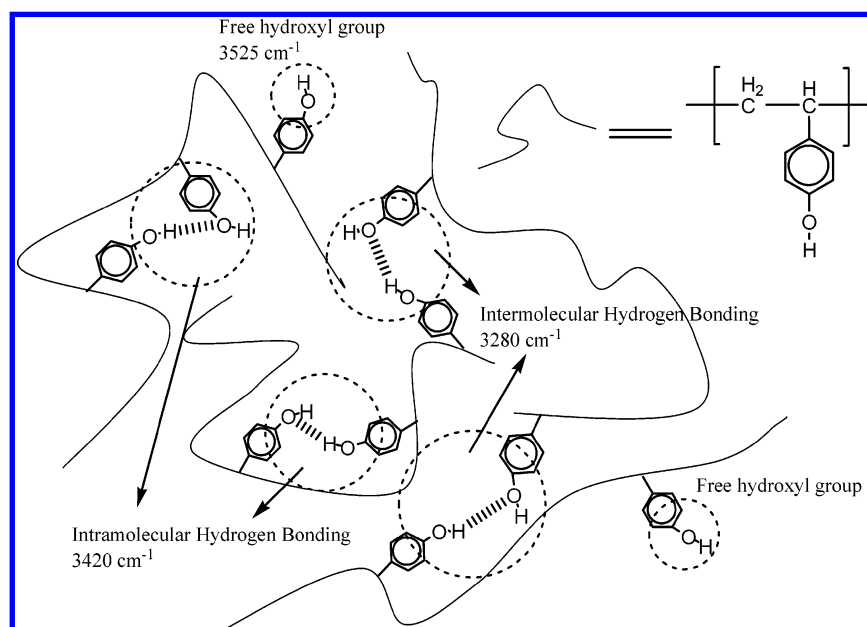
TABLE 3: Results of Curve-Fitting the Data for PVPh, PVPh-*co*-PS, and PVPh/PS Blends before and after the Thermal Treatment

| | before 180 °C thermal treatment | | | | | | after 180 °C thermal treatment | | | | | |
| | intermolecular O−H | | intramolecular O−H | | free O−H | | intermolecular O−H | | intramolecular O−H | | free O−H | |
polymer	ν (cm^{-1})	A_b (%)	ν (cm^{-1})	A_b (%)	ν (cm^{-1})	A_b (%)	ν (cm^{-1})	A_b (%)	ν (cm^{-1})	A_b (%)	ν (cm^{-1})	A_b (%)
PVPh	3276	62	3400	35	3534	3	3279	48	3421	44	3538	8
PVPh22-r-PS78	3289	53	3422	36	3546	11	3308	30	3445	49	3547	21
PVPh36-r-PS64	3280	55	3414	39	3545	6	3303	37	3442	47	3545	16
PVPh55-r-PS45	3279	56	3409	39	3541	5	3290	41	3438	46	3542	13
PVPh78-r-PS22	3278	56	3404	39	3541	5	3282	46	3433	45	3538	9
PVPh24-b-PS76	3280	59	3412	35	3435	6	3285	55	3415	35	3536	10
PVPh71-b-PS29	3280	58	3416	37	3536	5	3284	50	3416	41	3535	9
PVPh80-b-PS20	3285	57	3418	38	3539	5	3285	49	3417	43	3535	8
PVPh/PS = 20/80	3282	58	3413	36	3534	6	3285	56	3416	34	3437	10
PVPh/PS = 60/40	3283	59	3415	36	3535	5	3286	55	3418	37	3435	8
PVPh/PS = 80/20	3281	59	3416	37	3536	4	3285	52	3419	40	3434	8

fitting results (Figure 1 and Table 3) and the variations in the surface energies (Table 2), it is clear that decreasing the fraction of intermolecular hydrogen bonding leads to a decrease in the surface free energy. This observation is in good agreement with the result of our previous study on the surface-free-energy effect.[12]
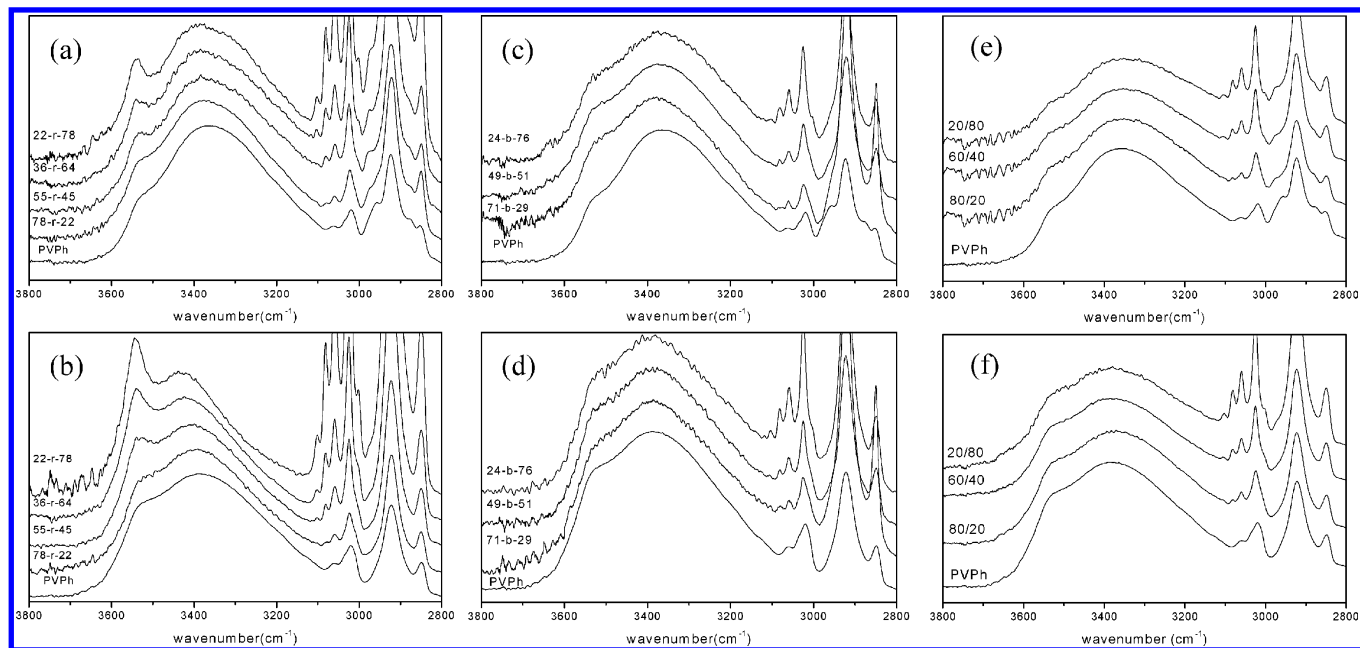
Figure 2. FTIR spectra of PVPh/PS random and block copolymers and blends (a, c, e) before and (b, d, f) after the thermal treatment.
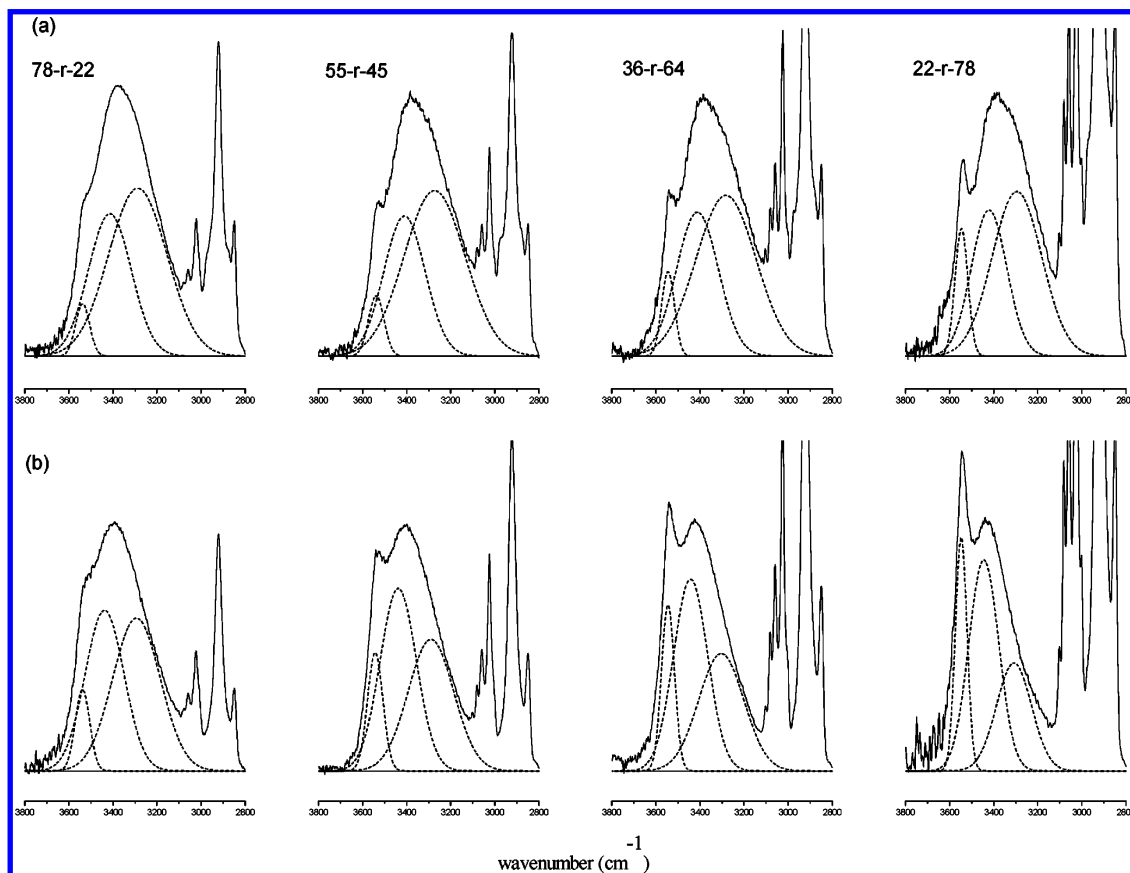

Figure 3. FTIR spectra and curve-fitting result of PVPh-*r*-PS copolymers (a) at room temperature and (b) after the 180 °C thermal treatment procedure.

To further investigate the importance of decreasing the fraction of intermolecular hydrogen bonding or increasing the fraction of free hydroxyl groups in lowering the surface free energy, a series of PVPh/PS random and block copolymers and their corresponding blends were prepared. Their surface energies were measured through the same method as that for the pure PVPh, and the results are summarized in Table 2. Clearly, the contact angles and resulting γ of PVPh/PS blends show no significant change before or after 180 °C thermal treatment. The

PVPh-*r*-PS copolymers possess the most drastic reduction in surface energy after the thermal treatment in comparison with corresponding block copolymers and blends under comparable compositions. Figure 2 summarizes FTIR data at the hydroxyl stretching region of PVPh/PS random and block copolymers and blends before and after 180 °C thermal treatment for 1 day. Figures 3−5 display their respective FTIR spectra and curve-fitting results before and after the thermal treatment. Table 3 also lists results of curve-fitting data for PVPh-*co*-PS and PVPh/
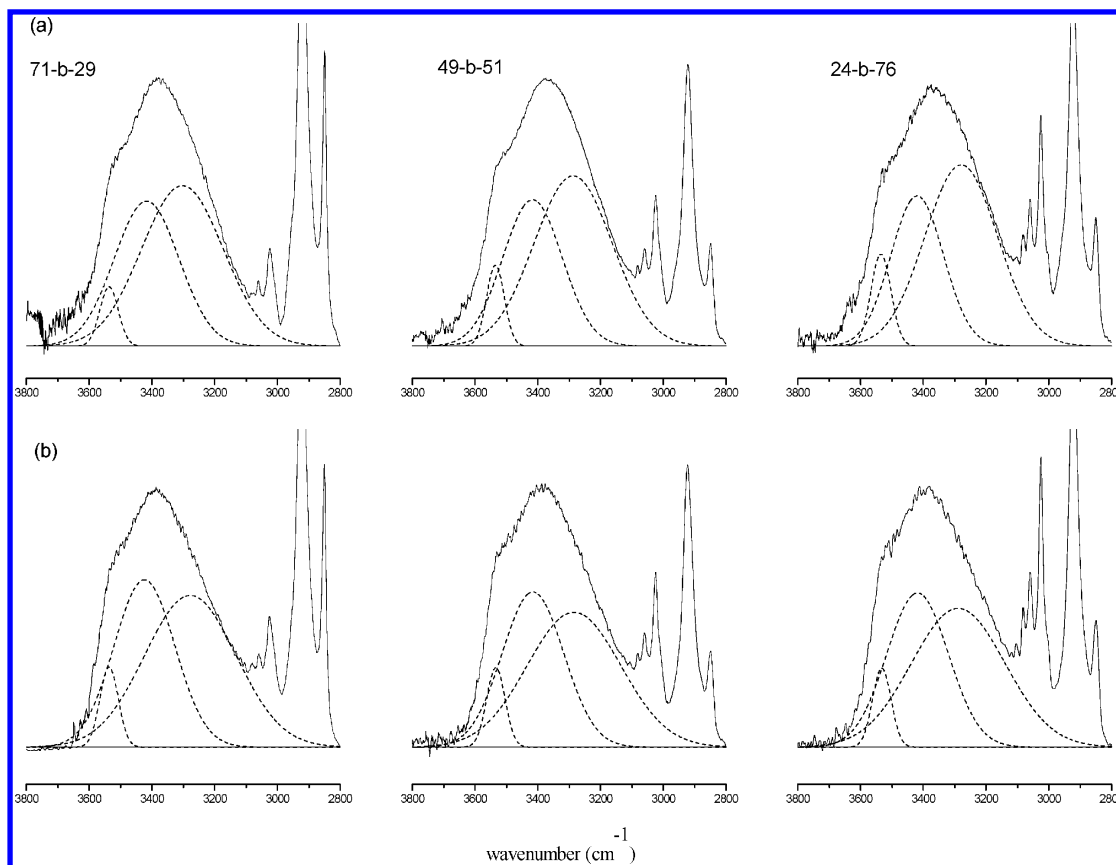
Figure 4. FTIR spectra and curve-fitting result of PVPh-*b*-PS copolymers (a) at room temperature and (b) after the 180 °C thermal treatment procedure.
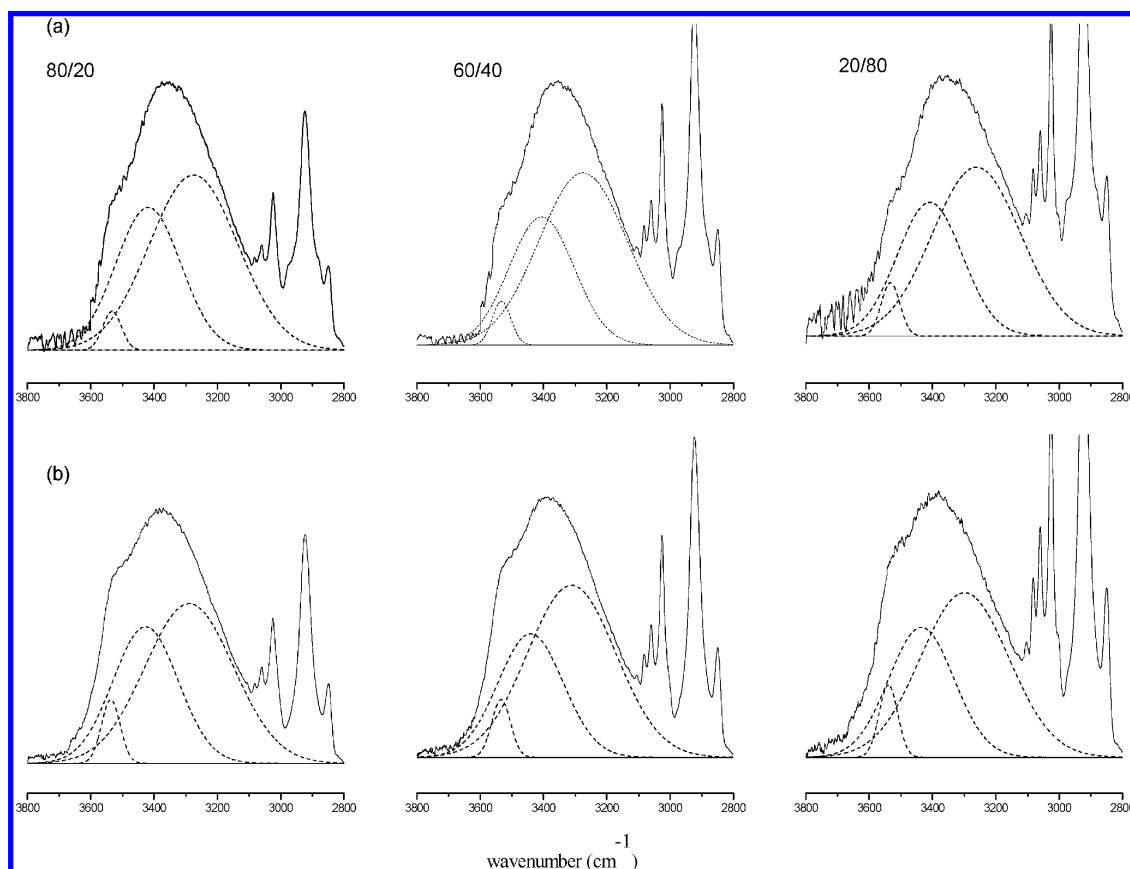

Figure 5. FTIR spectra and curve-fitting result of PVPh/PS blends (a) at room temperature and (b) after the 180 °C thermal treatment procedure.

PS blends before and after the thermal treatment. The fractions of free and inter- and intramolecularly hydrogen-bonded hy-

droxyl bands do not show a significant change before and after thermal treatment in the block copolymer, which is similar to
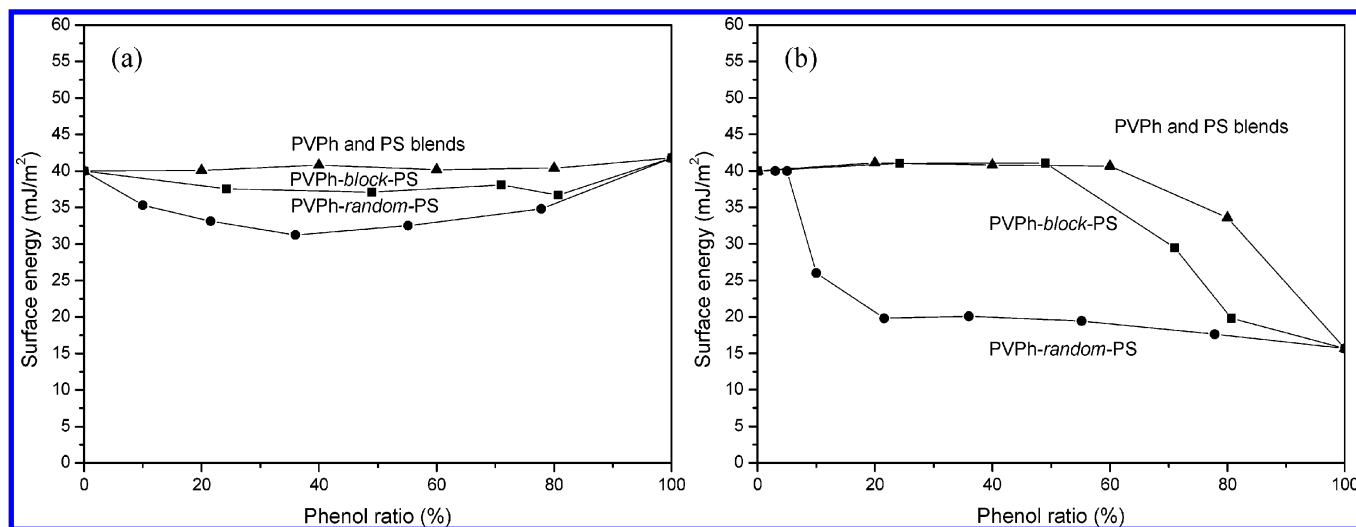
Hydrogen-Bonding Effect on Poly(vinylphenol)

J. Phys. Chem. B, Vol. 111, No. 13, 2007 **3409**

Figure 6. Surface energy of PVPh/PS random and block copolymers and their blends (a) before (b) after the thermal treatment process.

the blend system in surface energy. On the contrary, the fraction of the free hydroxyl absorption (3525 cm^{-1}) increases significantly. The peak position of the intermolecular hydroxyl band shifts to higher wavenumber, and its peak area decreases in pure PVPh and PVPh-*r*-PS copolymers after thermal treatment, implying a decrease of the intermolecular hydrogen-bonding fraction. The styrene moiety can act as an "inert" (non-hydrogen-bonding) diluent to space the vinylphenol segment. In our previous work,[18] we have studied the effect of an inert diluent segment on the miscibility behavior of PVPh-*r*-PS copolymers and found that the incorporation of a styrene moiety into the PVPh polymer chain can dilute and decrease the strong self-association in the PVPh component. The spacing of these vinylphenol groups tends to decrease the average hydroxyl– hydroxyl distance and increase the fraction of free hydroxyl in PVPh/PS random copolymers and provides a positive effect to lower the surface energy of the polymer. On the other hand, the interference of the styrene segment tends to prevent the vinylphenol segment from migrating to the surface, which can be regarded as a negative effect, i.e., an increase in the surface energy of the material.

Previous studies[25,26] suggested that the surface energy of a random copolymer usually follows the linear relation $\gamma = x_1\gamma_1 + x_2\gamma_2$. This behavior was observed by Rastogi et al.[27] in random copolymers of ethylene oxide and propylene oxide. It is well-known that backbone lengths of each component have to be taken into account when dealing with copolymers. A greater length in block copolymers or polymer blends is more favorable to induce micro- or macrophase separation and enhances migration of the lower surface free energy component to the surface. When the backbone length of the block is decreased and randomly distributed, as in random copolymers, the preferential accumulation of the low-energy segments at the surface decreases due to conformational restrictions of the polymer chains.

It is interesting to note that, before and after thermal treatment, the above relationship between sequential distribution and surface energy does not exist in the PVPh/PS copolymer system. Figure 6 summarizes the surface energies of PVPh/PS random and block copolymers and blends before and after thermal treatment. After thermal treatment, the surface energies of the random copolymers decrease to 19.8 mJ/m^2; even the PVPh content is only 22 mol %. The surface energy of block copolymers starts to decrease at a relatively higher PVPh content (>50 mol %), while the surface energies of blends do not change

significantly over the whole composition range. For both block copolymers and blends, the intermolecular hydrogen-bonding fractions do not decrease by incorporation of an inert diluent component (polystyrene) because of phase separation, on the basis of DSC results. In addition, the aggregation of the homopolymer segment tends to prevent the vinylphenol segment from migrating to the surface. XPS results (Table 2) show that the atomic fraction of oxygen, an indication of the vinylphenol segment content on the surface, increases drastically after thermal treatment, except for the PVPh/PS blend, which is in good agreement with the measured surface energy in this system. As a result, the combination of infrared spectra, contact angle measurements, and XPS results indicates that the decrease of intermolecular hydrogen-bonding interaction or increase of the fraction of free hydroxyl groups tends to lower the surface free energy of the polymer.

Conclusions

The decrease of the intermolecular hydrogen-bonding fraction between hydroxyl groups of PVPh through a simple thermal treatment procedure tends to decrease the surface energy. The lowest surface energy after thermal treatment for the pure PVPh is 15.7 mJ/m^2, even lower than that of PTFE (22.0 mJ/m^2). The sequence distribution of the vinylphenol group in PVPh-*co*-PS copolymers plays an important role in dictating the final surface energy after thermal treatment. This finding provides a possibility to prepare a new class of low-surface-energy materials through simple thermal treatment by decreasing the intermolecular interaction of polymers.

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