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# Preparation of Fluorescent Conjugated Polymer Fibrous Membranes for Rapid Recognition of Aromatic Solvents

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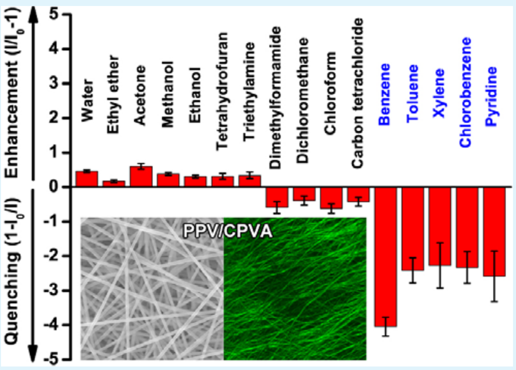
Ⓢ *Supporting Information*

**ABSTRACT:** Fluorescent poly(phenylenevinylene) (PPV)/poly(vinyl alcohol) (PVA) fibrous membrane was prepared via electrospinning of PPV precursor and PVA aqueous solution followed by thermal elimination. Further cross-linking produced the cross-linked membrane PPV/CPVA. Both PPV/PVA and PPV/CPVA membranes were found to have similar morphology and photophysics. These membranes showed a great fluorescence quenching response to aromatic solvents and a much smaller response to other organic solvents. Water also effectively quenched the fluorescence of PPV/PVA but not that of PPV/CPVA. This was attributed to un-cross-linked PVA being able to dissolve in water and the cross-linking improving the resistance of the membrane toward water. The sensing behavior was found to have good reversibility. The contact angle study showed that addition of only about 1% of PPV into the matrix reduced the hydrophilicity of the membrane significantly, suggesting that the PPV chains would be located at the surface of the fibers. X-ray photoelectron spectroscopy (XPS) investigation further confirmed such surface enrichment of PPV in the binary polymer blends. The PPV chain on the surface facilitated the $\pi-\pi$ interaction between the polymer backbones and the aromatic molecules, thus leading to good selectivity and fast response of the two fibrous membranes toward aromatic solvents.



**KEYWORDS:** *poly(phenylenevinylene), aromatic solvent, fluorescence sensing, electrospinning, polymer blend*

## 1. INTRODUCTION

Organic solvents are widely used in the chemical industry and research laboratories. Most organic solvents have more or less toxicity and may cause environmental pollution or direct harm to human health.[1] The fast development of the chemical industry, such as the pharmaceutical industry and the polymer industry, and the related research have resulted in the ever increasing use of organic solvents. However, the harness/recycling of the organic solvents is still not well developed, especially in the developing countries. The systematic treatment of the solvent wastes, the expired solvents, or unlabeled solvents requires the rapid classification/recognition of the organic solvents.

Fluorescence-based sensing is superior to other techniques in many ways (e.g., short response time and easy measurement).[2−7] The integration of the fluorescence sensing technique into the portable and reusable device is very promising for the real-time "in situ" sensing applications. One of the key challenges in fabricating such a device is to design reusable fluorescent solid materials for rapid recognition and signaling of the presence of the specific analytes, such as a class of organic solvents. Conjugated polymers have distinctive advantages for fluorescence sensing including great sensitivity and good processability.[8−12] The incorporation of conjugated polymers into nano/microfibrous membranes via electrospinning has been demonstrated to be very successful in reversible sensing of analytes,[13−17] and these membranes have great potential to be integrated in miniaturized sensing devices.

Here, we present a strategy for preparation of fluorescent fibrous membranes through electrospinning (Figure 1), for sensing the commonly used aromatic solvents in the research lab and chemical industry. The electrospinning technique is employed to fabricate nano/microfibrous membranes with a high surface-to-volume ratio.[13,18−22] The well-studied poly(phenylenevinylene) (PPV)[23−27] without any side groups is selected as the fluorescence emitting species. In addition, $\pi-\pi$ interaction between polymer backbone and aromatic solvent molecule is used for the molecule recognition. The water-soluble flexible PPV polymer precursor (pre-PPV) and poly(vinyl alcohol) (PVA) are dissolved in water to form an aqueous solution, which is used to prepare the pre-PPV/PVA fibrous membrane via electrospinning. The fluorescent PPV/PVA fibrous membrane is obtained after thermal treatment. The cross-linking step for PVA is carried out on the PPV/PVA

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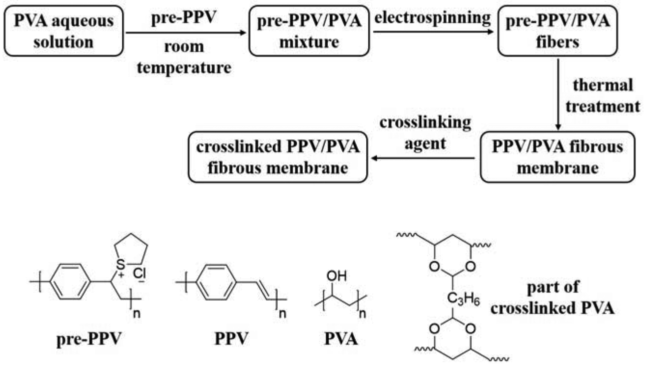

**Figure 1.** Schematic diagram for preparing PPV/PVA and PPV/CPVA fibrous membranes and the chemical structures of the polymers involved. The thermal treatment was carried out at 80 °C in vacuum for 1 h; the cross-linking process was accomplished by placing the fibrous membrane in a (glutaraldehyde + HCl)/acetone solution for 24 h at room temperature.

membrane to improve the stability. The strategy has several merits. First, water is used as the carrier solvent for electrospinning, which is environmentally friendly compared to the commonly used organic solvents. In general, polar organic solvents with high dielectric constant, such as DMF, DMSO, and chloroform, are required for electrospinning.[28−31] Second, most conjugated polymers are rigid macromolecules,[9,18,32] and thus, it is very difficult to coelectrospin them with flexible polymer matrix. For example, PPV without any side group is usually not soluble in any solvent. Here, we circumvent this problem by using the flexible and soluble polymer precursor pre-PPV for electrospinning. Third, a small amount of PPV is dispersed in the general polymer matrix, which may lower the overall cost of the membrane. More importantly, the intermolecular $\pi-\pi$ interaction among PPV chains themselves can be greatly weakened in the PPV/PVA membrane, which not only reduces the fluorescence self-quenching of PPV but also makes the recognition of aromatic solvent through $\pi-\pi$ interaction possible. Fourth, the nano/microfibrous structure provides the membranes the capabilities of fast response and facile regeneration, since the aromatic solvent can diffuse into or out of the membrane readily for effective "$\pi-\pi$ interaction".

In this paper, we present the preparation and characterization of fibrous membranes with fluorescent PPV in the cross-linked PVA (CPVA) or noncrosslinked PVA matrix. The sensing behavior toward solvents commonly used in the research lab and chemical industry was tested, and the different responses were classified. The differences between the cross-linked and noncrosslinked membranes were also investigated. The distribution of PPV in PPV/PVA and PPV/CPVA membranes was characterized by contact angle and X-ray photoelectron spectroscopy (XPS) measurement. Understanding of the structure−property relationship in the conjugated polymer/polymer matrix blends may provide insights for future design of such materials. Aromatic solvents are well-known for many adverse effects.[1] They may cause brain malfunction/damage or liver/kidney/nerve damage or destroy bone marrow and lead to loss of blood cells and so on. The PPV/PVA and PPV/CPVA membranes make the fast recognition of this class of solvents possible and, therefore, may facilitate the reduction of the exposure of these solvents to the environment/humans.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Tetrahydrothiophene and $\alpha,\alpha'$-dichloro-*p*-xylene were purchased from J&K Co., Ltd. Poly(vinyl alcohol) (PVA, $\bar{M}_n$ = 80 000 g/mol, 88% hydrolyzed) was purchased from Beijing Eastern Petrochemical Co., Ltd. Organic solvents were obtained from Chinasun Specialty Products Co., Ltd. All materials were used as received unless otherwise noted. Methanol used for the synthesis of the monomer was dried over molecular sieves.

**2.2. Synthesis of Pre-PPV.** The precursor of PPV was synthesized according to the method we reported previously[33,34] with a slight modification. 1.0 g of *p*-phenylenebis(tetrahydrothiophenium) dichloride and 16.0 mL of deionized water were placed into a two-necked round-bottom flask, which was deoxygenated three times by vacuum-argon cycling before use. The whole flask was placed in an ice−water bath to ensure the reaction took place at 0 °C. Then, the ice-cold, Ar-purged aqueous NaOH (2 mL, 1.4 M) was added dropwise into the reaction flask. The mixture was stirred in an ice−water bath and under an argon atmosphere for 1 h. Afterward, 5 mL of HCl (2 M) aqueous solution was added into the flask to terminate the polymerization. The resulting mixture was dialyzed against water for 24 h, using a dialysis tubing made of a cellulose membrane with a molecular mass cutoff of 3500 Da. Water was changed every 2 h during the daytime, and the water was changed after 12 h overnight. The total volume of the dialysis system was maintained at about 600 mL each time. The precursor solution inside the dialysis tube was then quickly transferred into a glass container and stored in the fridge for further use. The mass percentage of pre-PPV in the aqueous solution was found to be about 0.6% (see Supporting Information for the detailed calculation). With such a preparative method, the number-average of molecular weight of the resulting pre-PPV was about $1.33 \times 10^4$. The method for the molecular weight measurement was described in detail in ref 34 and its Supporting Information.[34]

**2.3. Electrospinning and Post-Treatment.** The electrospinning solution was prepared on the basis of the following mass ratios: PVA/$H_2O$ = 1:10 and pre-PPV/PVA = 1:100. 0.6 g of PVA was first added into 4.4 g of deionized water. The mixture was stirred at 50 °C overnight to guarantee the complete dissolution of PVA. After the mixture was cooled to room temperature, 1.0 g of pre-PPV solution (with about 0.006 g of pre-PPV solute in it) was added into the PVA solution. The mixture was stirred for another 5 h before use.

In a typical electrospinning process, about 2.5 mL of pre-PPV/PVA aqueous solution in a 10 mL syringe was pumped through an injection pump with a flow rate of 0.3 mL/h. A grounded stainless steel mesh was used as the collector, and the distance between the mesh and the tip of the syringe needle was 10 cm. The voltage was set at 10 kV, and the electrospinning time was set for 4 h. The resulting fibrous membrane was peeled off the mesh and then dried under ambient conditions. The thermal elimination was carried out at 80 °C under vacuum for 1 h. After being cooled to room temperature, the fluorescent PPV/PVA fibrous membrane was ready for further use. The cross-linking experiment was carried out with a route modified from the literature.[35] The above fibrous membrane was placed in 100 mL of glutaraldehyde (GA)/HCl acetone solution (0.01 M HCl, HCl/GA = 1:10 in molar ratio) for 24 h to give the cross-linked fluorescent PPV/CPVA fibrous membrane. Afterward, the membrane was rinsed with acetone and then dried under vacuum overnight.

**2.4. Instruments and Methods.** The typical electrospinning process was carried out with a variable high voltage power supply (DW-P303-1ACFO, Tianjin Dongwen High Voltage Power Supply Co., Ltd.) and an injection pump (TJ-3A/W0109-1B, Baoding Longer Precision Pump Co., Ltd.). The morphology study was carried out on a scanning electron microscope (SEM, S-4700, Hitachi, Japan) with an operating voltage of 15 kV. The fibrous membrane for SEM observation was directly adhered onto the stage via double-sided adhesive carbon conductive tape. The laser confocal microscopy images were obtained on a Leica TCS SP5 with excitation at 405 nm. Contact angle was measured on a contact angle meter (JC2000D6) with about 5 $\mu$L of water to form the droplet. Digital photos of the fibrous membrane under ambient light or 365 nm UV light were taken with a Nikon D5100 camera (35 mm, 1:1.8G). X-ray photoelectron spectroscopy (XPS) measurement was carried on a multifunction digital X-ray photoelectron spectrometer (ESCALAB 250XI, Thermo Fisher Scientific). TGA data were obtained from a thermogravimetric differential thermal analyzer (TG/DTA 6300). DSC data were obtained from a differential scanning calorimeter (Q200, TA Instruments-Waters LLC).

The excitation spectra were measured on an Edinburgh FLS920 spectrofluorometer, with a fixed emission at 485 nm. The emission spectra were measured on a Horiba FluoroMax-4 spectrofluorometer, with excitation at 395 nm. For the fluorescence study, the fibrous membranes were cut into pieces (about 22 × 7 mm$^2$). One piece of the membrane was pasted onto a quartz slide on the top, using double-sided adhesive tape. The quartz slide with the membrane was placed into a quartz cuvette, at 45° to the incident (exciting) light. For the sensing experiment, the emission spectrum of the initial membrane was recorded. Afterward, 3 mL of solvent was added into the cuvette carefully to avoid moving the membrane from the position, and the emission spectrum was then recorded again immediately. The whole process was accompolished within 10 s. The emission intensities at the peak were collected to give the response data. For the reversibility study, the spectra were recorded repeatedly, when the solvent was totally removed or right after the solvent was refilled into the cuvette. To accelerate the removal of toluene, the membranes were rinsed with ethanol first before getting dried naturally under ambient conditions.

## 3. RESULTS AND DISCUSSION

**3.1. Preparation and Characterization.** The electrospinning was carried out following a routine procedure. All the solutes were well dissolved in water. The temperature and humidity for electrospinning were well-controlled, since they would affect the water evaporation rate during the electrospinning. Usually the process was accomplished at ambient temperature (about 20−25 °C) with humidity below 50%. The PPV/PVA fibrous membrane was obtained after thermal elimination at 80 °C in vacuum. The cross-linking process of the membrane was adapted from the literature.[35] The PPV/PVA membrane was placed in the glutaraldehyde (GA)/HCl acetone solution for 24 h, followed by washing and drying to give the PPV/CPVA membrane. The reaction scheme for the cross-linking is shown in Scheme S1, Supporting Information. As discussed in the literature,[36] one aldehyde group reacts with two hydroxyl groups to form a five member ring, using acid as the catalyst. Two aldehyde groups in GA react with two pairs of −OH groups on the two neighboring polymer chains, respectively, to form the cross-linking site. To drive the acetalization to completion, excess cross-linking agent was added. However, there was a small amount of a residual −OH group since the isolation of a single −OH between a pair of acetal structures would exist.[37] More discussion about characterization of the PVA cross-linking has been reported previously.[38] About 1% (in mass percentage) of PPV in the PVA matrix should have very little influence on the cross-linking reaction. With strict control of each step during the preparation, the photophysical properties were reproducible for membranes obtained from different batches.

Figure 2 shows the SEM and confocal microscopy images of the PPV/PVA and PPV/CPVA fibrous membranes. Both membranes displayed a clear fibrous structure with uniform diameters of around 200 nm, as well as uniform and strong fluorescence emission. For comparison, Figure S1, Supporting Information, shows the SEM images for different fibrous membranes composed of PVA, cross-linked PVA (CPVA), pre-PPV/PVA, or pre-PPV/CPVA, respectively. All these fibers had very similar morphology. Most fibers were straight with a diameter of around 200 nm. Therefore, the addition of a small amount of pre-PPV (transformed into PPV after thermal elimination) into the PVA matrix had negligible influence on the fibrous morphology. In addition, the thermal treatment and the cross-linking reaction did not destroy the fibrous structure. PPV produced after thermal elimination endowed the fibers with strong fluorescence emission, and the fluorescence still remained after the cross-linking reaction.

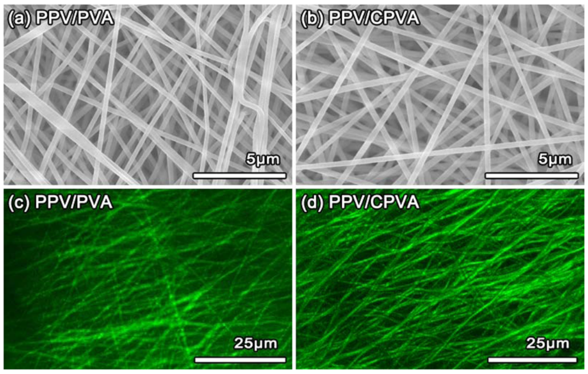

**Figure 2.** SEM (a, b) and confocal fluorescence (c, d) images of the PPV/PVA and cross-linked PPV/PVA (PPV/CPVA) fibrous membranes.

The solid-state fluorescent spectra of PPV/PVA and PPV/CPVA fibrous membranes were obtained with the same experimental parameters, as shown in Figure S2, Supporting Information. The two membranes gave very similar excitation and emission spectra. The excitation spectra are in the range of 280−480 nm, having a peak around 392 nm and several shoulders. The emission spectra are in the range of 430−620 nm, having a peak around 486 nm and a shoulder around 508 nm. Both excitation and emission spectra displayed very typical profiles for PPV materials. Thus, the cross-linking reaction had no significant influence on the PPV emission, which is consistent with confocal microscopic observation.

**3.2. Sensing Application.** The sensing tests of PPV/PVA and PPV/CPVA fibrous membranes were carried out on solvents routinely used in our lab, including water, ethyl ether, acetone, methanol, ethanol, tetrahydrofuran (THF), triethylamine, *N*,*N*-dimethylformamide (DMF), dichloromethane, chloroform, carbon tetrachloride, benzene, toluene, xylene, chlorobenzene, and pyridine. To ensure the reproducibility/consistency of the fluorescence measurements before and after the addition of the solvent, the whole process has been carried out carefully as noted in the Experimental Section. The emission spectra (recorded right after the solvents were added into the cuvette) were shown in Figure S3, Supporting Information. Upon addition of any solvent, the fluorescence was quenched or enhanced with a negligible change in the spectra profile and emission wavelength. Figure 3 showed the fluorescence responses of the PPV/PVA membrane and the PPV/CPVA membrane toward these solvents, based on the intensity change at the emission maximum. All the aromatic solvents studied greatly quenched the fluorescence of both membranes, while all nonaromatic organic solvents studied had much smaller influence on the emission. Ethyl ether, acetone, methanol, and ethanol had a slight enhancement effect on the fluorescence of both membranes. DMF, dichloromethane, chloroform, and carbon tetrachloride displayed a small quenching effect on both membranes. THF and triethylamine slightly quenched the emission of PPV/PVA, while slightly

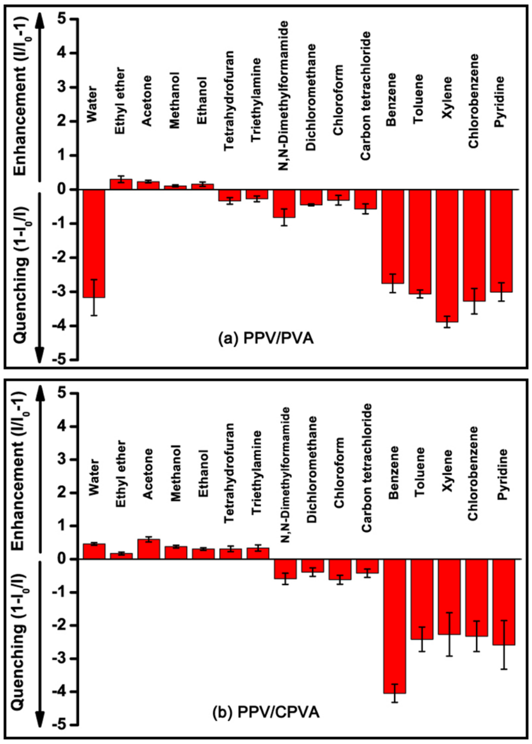

**Figure 3.** Fluorescence intensity changes at the emission maximum for PPV/PVA (a) and PPV/CPVA (b) membranes upon exposure to different solvents. The error bars shown are based on the calculated standard deviations from the average value of at least three measurements with membranes from different batches. The excitation was set at 395 nm.

enhancing the emission of PPV/CPVA. Besides the organic solvents, the influence from water was also evaluated. Interestingly, the emission of the PPV/PVA membrane was greatly quenched, and the extent of quenching was comparable to those for aromatic solvents. However, the emission of PPV/CPVA was slightly enhanced by the addition of water, and the enhancement was similar to those of nonaromatic solvents. The sensing behavior toward mixed aromatic and nonaromatic solvents was also evaluated by using THF/toluene as the representative solvent. The fluorescence spectra of the PPV/CPVA membrane upon exposure to the mixed solvent in different ratios are shown in Figure S4, Supporting Information. For all the spectra obtained with pure THF, the THF/toluene mixture in different ratios, and pure toluene, significant fluorescence quenching appeared only when the toluene became the dominant component of the mixture (THF/toluene $\leq$ 1:1).

The results from the sensing experiments indicate the aromatic solvents can be easily and rapidly distinguished from nonaromatic organic solvents by the fluorescence intensity change of the membrane. The interference from water can be avoided if the cross-linked membrane is used. The recognition of aromatic solvent can be attributed to the $\pi-\pi$ interaction between the aromatic solvent and the PPV backbone, which results in strong fluorescence quenching. The various fluorescent responses toward different nonaromatic solvents can be attributed to the different weak interactions between solvent and PPV. The large difference between PPV/PVA and PPV/CPVA membranes in the fluorescence response upon addition of water is because water can actually destroy the un-cross-linked membrane, as will be more discussed later.

The reversibility of the sensing behavior and the reusability of the material are key performance indexes if the material is incorporated as the detecting tip into a sensory device or used directly as a reusable testing strip. The reversibility study of both PPV/PVA and PPV/CPVA membranes toward toluene, as a representative for aromatic solvents, is shown in Figure 4.

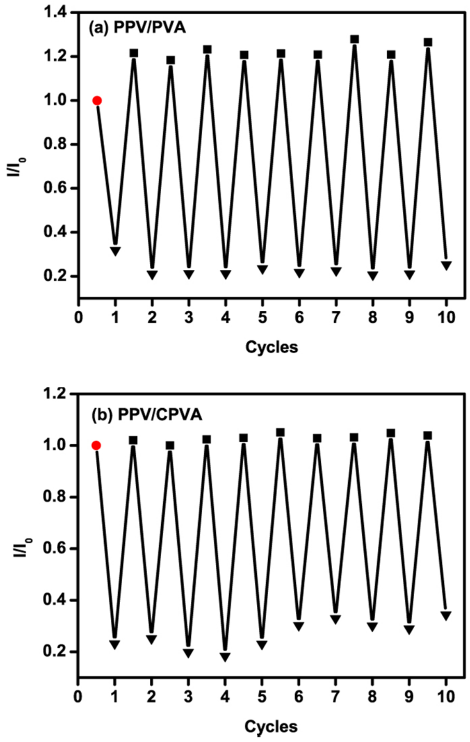

**Figure 4.** Reversibility study of PPV/PVA (a) and PPV/CPVA (b) fibrous membranes: the fluorescence intensity change $I/I_0$ vs "dry-immersed" cycles. The red circle represents the initial state of the membranes (intensity change $I/I_0$ = 1); the triangle represents the intensity change upon the addition of toluene; the square represents the intensity change of the dry state after removing toluene. The excitation was set at 395 nm.

Both membranes displayed good reversibility with pronounced "on/off" fluorescence response "without/with" the presence of toluene. A slight difference exists between the two membranes. For the PPV/CPVA membrane, the fluorescence after removing the solvent (the fluorescence "on" state) returned to a similar intensity as the initial fluorescence. However, for PPV/PVA, the fluorescence at the "on" state after removing the solvent was surprisingly increased, compared to the initial intensity. This difference may be attributed to the PPV chain reorganization that took place to some degree in the un-cross-linked membrane. Ethanol was used for accelerating the removal of toluene to arrive at a dry state, which would also facilitate the PPV chain movement. Such chain movement would be more limited in the cross-linked membrane and thus the membrane displayed more steady fluorescence. Nevertheless, such variation of the fluorescence at the "on" state for the PPV/PVA membrane had a minor effect on the recognition of aromatic solvents under the experimental conditions we employed. The cross-linked membrane may be more preferred since the presence of water has more interference to the sensing behavior of the noncrosslinked membrane.

The development of a facile method for on-site rapid recognition of aromatic solvents in the solvent wastes, expired solvents, or unlabeled solvents may facilitate the targeted recycling or post-treatment of these aromatic solvents. Photophysical methods are much easier to carry out than other spectroscopic techniques, such as NMR or IR, with respect to sample preparation and instrument requirements. However, no characteristic signal of common aromatic solvents can be obtained by direct UV−vis or fluorescence measurement. With the aid of the membranes, the class of aromatic solvents can be easily identified. To our knowledge, there is no other reported system specific for recognizing aromatic solvent from other solvents. There are some reports in the literature about sensing benzene or toluene in the vapor or in the liquid state, but other nonaromatic solvents or compounds also had a significant effect on the fluorescence of sensing materials.[39−43] In most studies, the fluorescence responses from aromatic solvents were usually used as a control for comparison but not the major analytes; a shift in the emission wavelength, or change in intensity ratio at different peaks/shoulders, is very common, and different solvents may give different responses. These responses might be advantageous in some ways, such as giving a more accurate signal "read-out" and providing a more direct visual view of the sensing result. However, in our system, the recognition of aromatic solvent can be done with one excitation wavelength and one emission wavelength. If the fibrous membranes are incorporated as the sensing tip into a small sensing device (such as a detection pen), the single excitation and the narrow detection wavelength range for all the solvents definitely can greatly simplify the setup. The whole classification (between aromatic and nonaromatic solvents) process can be easily accomplished by placing the sensing tip into the solvent, pressing a button for excitation, and then reading the output of the emission intensity. Though some methods, such as NMR and IR, may provide more detailed information about the chemical structure, the fluorescence response of fibrous PPV/PVA and PPV/CPVA membranes provides a method for easy classification of the solvents with a simple setup and no need for delicate sample preparation.

### 3.3. Structural and Morphological Study of the Fibrous Membranes as Binary Polymer Blends.

To gain a better understanding of the overall performance of the membranes for the sensing application, a more detailed structure and morphology investigation was carried out by considering the membranes as binary polymer blend materials. There are two major differences between PPV/PVA and PPV/CPVA membranes. First, the functional groups in the polymer matrix are different. Most −OH groups in PVA were converted into the acetal groups in CPVA. Second, the polymer architectures are different. The linear chains in PVA were changed into the cross-linked network in CPVA. As for the functional groups, both −OH and acetal groups are hydrophilic and both can interact with water easily. However, the linear chains in PVA can dissolve easily in water while the cross-linked network in CPVA can only swell in water. The appearances of PPV/PVA and PPV/CPVA membranes at the dry state (without water or solvents) look very similar under ambient light or UV light (Figure 5). The photophysical properties (such as excitation and emission spectra) for these two membranes are nearly the same, indicating that the cross-linking reaction has no significant influence on the PPV chains in the membranes. There is a small difference in the apparent color, which may be attributed to the different functional groups or polymer architectures. After some water drops were placed on each membrane, the PPV/PVA membrane shrank whereas the PPV/CPVA remained unchanged the shape. The images for neat PVA, CPVA, and PVA after 80 °C thermal treatment (TPVA) are also shown in Figure 5 for comparison. As expected, none of the three membranes have fluorescence. The shape of CPVA remained unchanged after it was in contact with water whereas the PVA and TPVA membranes were damaged to a certain degree. The damage of the PVA membrane is due to the dissolution of PVA in water. The above results suggest that the thermal treatment of the PVA membrane has no effect on improving its resistance to water, whereas the cross-linking reaction was very effective. The damage of the PPV/PVA membrane by water was slowed compared to pure PVA and TPVA membranes, suggesting the presence of PPV retarded the dissolution of PVA in water. The cross-linking of PVA further improved the water resistance of the PPV/CPVA membrane.

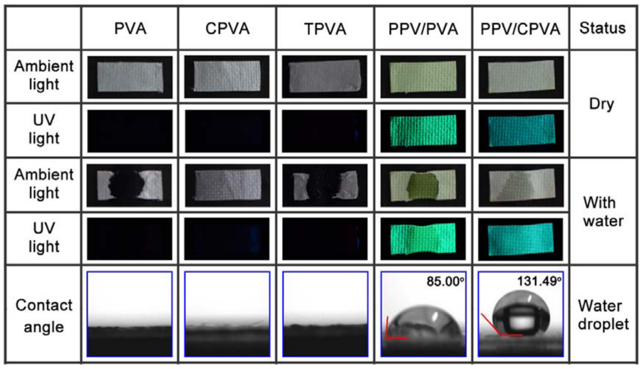

**Figure 5.** Digital photos under different conditions and contact angle measurements of the membranes. Contact angle images were obtained about 5 s after a water droplet was in contact with the membranes.

To further study the hydrophilicity/hydrophobicity of these materials, the contact angle measurements were carried out, as shown in Figure 5. The images were taken about five seconds after the water droplet was dropped onto each surface, to ensure the interaction between the water and the surface reached equilibrium. No contact angle was observed for PVA and TPVA, since PVA and TPVA dissolved in water easily. Even after cross-linking, the CPVA membrane displayed no contact angle, which was consistent with the formation of hydrophilic acetal groups. Interestingly, by adding only about 1% PPV into PVA, the contact angle was increased dramatically to 85°. Cross-linking the PVA in the presence of PPV further increased the contact angle to about 131°, and thus, the PVA/CPVA membrane was transformed into a hydrophobic material. The deformation process of the water droplet after it was in contact with the membranes was tracked by a series of pictures with a camera at different times (Figure S5, Supporting Information). The rates for water droplet deformation before the final disappearance were almost the same on PVA and TPVA membranes. Such a deformation/disappearance process was much longer for the CPVA membrane. With the addition of about 1% of PPV into the matrix, the situation changed greatly. For the PPV/PVA membrane, the water droplet deformed slightly at the beginning and then remained on the membrane. However, for the PPV/CPVA membrane, almost no deformation was observed for the water droplet on it.

The results in Figure 5 indicate that the addition of 1% PPV improves the hydrophobicity of the fibrous membrane. Comparing TPVA with PPV/PVA (both membranes were thermal treated), the addition of about 1% of PPV in the PPV/PVA membrane greatly retarded the dissolution of PVA in water and increased the contact angle. Comparing CPVA and PPV/CPVA, the addition of about 1% of PPV transformed the hydrophilic membrane into a hydrophobic one. As shown in the SEM (Figure 2 and Figure S1, Supporting Information), the morphology of the fibrous structure was very similar for all membranes. Such a dramatic change in the contact angle with the addition of 1% PPV implies that PPV would be the primary component on the surface of the fibers with PVA or CPVA as the matrix. The hydrophobic PPV-rich surface greatly reduced the hydrophilicity of the fibers.

The surface enrichment of PPV in the PPV/PVA and PPV/CPVA membranes can be explained by the surface energy difference between the two components in the binary blends. The surface enrichment of one component with lower surface energy in the binary polymer blends has been well-established both theoretically[44,45] and experimentally.[46−50] The structural and compositional factors can affect the difference in the surface energy of the components and thus the degree of the segregation.[44−50] External factors (such as solvents[46] or the temperature[47] during processing) also have a significant effect on surface enrichment. Increasing temperature facilitates such surface enrichment.[46] In one example, one component can reach 98% (in mass percentage) at the surface with an overall 50% of that component in the blend.[48] Theoretical studies suggested that such surface preference of one component is more pronounced when that component is "dilute" in the blend.[45] Since the surface energy of hydrophobic PPV would be much lower at the polymer−air interface than that of the hydrophilic PVA or CPVA matrix, it is very likely that most PPV chains would migrate to the surface during the thermal treatment.

To further support the notion of the PPV segregation on the surface of the fiber, we have characterized the fibrous membranes using a surface energy dispersive spectrometer (EDS) or cross-section TEM. The EDS and TEM results were not conclusive. The reason might be that PPV has no appreciable contrast from the matrix in the elements (except the oxygen element) or in the material density. X-ray photoelectron spectroscopy (XPS) is a very powerful technique for characterization of such surface enrichment.[47−50] We measured XPS on PVA, CPVA, PPV/PVA, and PPV/CPVA membranes (see Figure S6, Supporting Information). The relative intensity of the peak for the C−O bonding in PPV/CPVA or PPV/CPVA decreased, compared to that for the C−C bonding (see Supporting Information for a more detailed discussion). Such results suggested a reduction of the PVA or CPVA concentrations in the area close to the surface (the sample depth of XPS is about 5 nm for polymeric materials) due to the presence of about 1% of PPV. This is consist with the contact angle measurement, which may be more sensitive to the topmost surface layer with respect to the hydrophilicity/hydrophobicity change.[50] Therefore, our experimental results clearly showed that the surface of the PPV/PVA or PPV/CPVA fibers is covered by PPV. Such a PPV-rich surface may be ideal for the sensing application. The weak $\pi-\pi$ interaction is usually not able to provide strong and fast perturbation of emission if the distance between the fluorophore and the analyte is relatively far. The surface located PPV on the fiber can facilitate the fast and selective recognition of aromatic solvents based on the $\pi-\pi$ interaction between the PPV and the aromatic solvents.

Thermal studies, such as TGA and DSC, were also used to characterize the membranes. As shown in Figure S7, Supporting Information, the addition of about 1% of pre-PPV or PPV had a minor effect on the thermal stability or glass transition temperature ($T_g$) of the PVA. TGA curves showed PVA and CPVA were stable up to 250 and 270 °C, respectively. The $T_g$ was about 73.5 °C for PVA, and no glass transition was observed for CPVA. In our previous study,[13] fibrous membranes composed of substituent hydrophobic PPV and hydrophobic poly(methyl methacrylate) (PMMA) matrix were fabricated. Thermal treatment around the $T_g$ of PMMA resulted in the deformation of the fibrous structure. Interestingly, the 80 °C thermal treatment in the current study did not affect the fibrous structure. The thermal treatment would help the migration of PPV onto the surface, and the rigid PPV on the surface layer might prevent the deformation of the fibrous structure.

## 4. CONCLUSION

Fluorescent PPV/PVA fibrous membrane has been fabricated via electrospinning followed by thermal treatment. By dispersing the water-soluble PPV precursor polymer and the PVA matrix in an aqueous solution, the electrospining was accomplished in an environmentally friendly way. Cross-linked membrane PPV/CPVA was obtained by simply placing the PPV/PVA membrane in a sealed container with cross-linking agent for 24 h at room temperature. PPV/PVA and PPV/CPVA membranes displayed a negligible difference in morphological and photophysical properties. Both membranes displayed a large fluorescence quenching response upon exposure to aromatic solvents. Water was found to damage the PPV/PVA membrane due to the dissolution of PVA, and the cross-linked CPVA helped to prevent the damage of the membrane. Good reversibility in the sensing behavior was observed for both PPV/PVA and PPV/CPVA membranes. Both PPV/PVA and PPV/CPVA can be used for rapid recognition of aromatic solvents from other organic solvents routinely used in the research laboratories or chemical industry. The single excitation wavelength and the single detection wavelength make the recognition of the class of aromatic solvents very simple without complicated instrumentation. PPV/CPVA may be more robust for providing a long-term usage without worrying about the interference of water or humidity. Further, morphology and structural characterization of the fibrous membranes as binary polymer blends gave insight into the unique properties of the membranes. The contact angle measurement showed conclusively that the small amount of PPV improved the water resistance of the membrane significantly. Such a change suggested that the PPV chains would stay at the surface of the fiber and, therefore, would facilitate the fast and selective recognition of aromatic solvents based on the intimate $\pi-\pi$ interaction. The PPV-rich surface and the contact angle change could be explained by the surface enrichment of lower surface energy components in the polymer blends.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Cross-linking reaction scheme, photophysical spectra, XPS spectra, thermal analysis curves, pictures of a water droplet on the membrane at different times, additional SEM images, and discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Stacey, N.; Winder, C. *Occupational Toxicology*, 2nd ed.; CRC Press: Boca Raton, FL, 2004.

(2) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. Signaling Recognition Events with Fluorescent Sensors and Switches. *Chem. Rev.* **1997**, *97*, 1515−1566.

(3) Basabe-Desmonts, L.; Reinhoudt, D. N.; Crego-Calama, M. Design of Fluorescent Materials for Chemical Sensing. *Chem. Soc. Rev.* **2007**, *36*, 993−1017.

(4) McDonagh, C.; Burke, C. S.; MacCraith, B. D. Optical Chemical Sensors. *Chem. Rev.* **2008**, *108*, 400−422.

(5) Ding, L.; Fang, Y. Chemically Assembled Monolayers of Fluorophores as Chemical Sensing Materials. *Chem. Soc. Rev.* **2010**, *39*, 4258−4273.

(6) Ojida, A.; Mito-oka, Y.; Sada, K.; Hamachi, I. Molecular Recognition and Fluorescence Sensing of Monophosphorylated Peptides in Aqueous Solution by Bis(zinc(II)-dipicolylamine)-Based Artificial Receptors. *J. Am. Chem. Soc.* **2004**, *126*, 2454−2463.

(7) Ojida, A.; Takashima, I.; Kohira, T.; Nonaka, H.; Hamachi, I. Turn-On Fluorescence Sensing of Nucleoside Polyphosphates Using a Xanthene-Based Zn (II) Complex Chemosensor. *J. Am. Chem. Soc.* **2008**, *130*, 12095−12101.

(8) McQuade, D. T.; Pullen, A. E.; Swager, T. M. Conjugated Polymer-Based Chemical Sensors. *Chem. Rev.* **2000**, *100*, 2537−2574.

(9) Thomas, S. W., III; Joly, G. D.; Swager, T. M. Chemical Sensors Based on Amplifying Fluorescent Conjugated Polymers. *Chem. Rev.* **2007**, *107*, 1339−1386.

(10) Fan, L. J.; Zhang, Y.; Murphy, C. B.; Angell, S. E.; Parker, M. F.; Flynn, B. R.; Jones, W. E. Fluorescent Conjugated Polymer Molecular Wire Chemosensors for Transition Metal Ion Recognition and Signaling. *Coord. Chem. Rev.* **2009**, *253*, 410−422.

(11) Jiang, H.; Taranekar, P.; Reynolds, J. R.; Schanze, K. S. Conjugated Polyelectrolytes: Synthesis, Photophysics, and Applications. *Angew. Chem., Int. Ed.* **2009**, *48*, 4300−4316.

(12) Lv, F.; Feng, X.; Tang, H.; Liu, L.; Yang, Q.; Wang, S. Development of Film Sensors Based on Conjugated Polymers for Copper (II) Ion Detection. *Adv. Funct. Mater.* **2011**, *21*, 845−850.

(13) Song, J.; Zhang, W.; Miao, K.; Zeng, H.; Cheng, S.; Fan, L. J. Receptor-Free Poly (phenylenevinylene) Fibrous Membranes for Cation Sensing: High Sensitivity and Good Selectivity Achieved by Choosing the Appropriate Polymer Matrix. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4011−4016.

(14) Long, Y.; Chen, H.; Yang, Y.; Wang, H.; Yang, Y.; Li, N.; Li, K.; Pei, J.; Liu, F. Electrospun Nanofibrous Film Doped with a Conjugated Polymer for DNT Fluorescence Sensor. *Macromolecules* **2009**, *42*, 6501−6509.

(15) Tao, S.; Li, G.; Yin, J. Fluorescent Nanofibrous Membranes for Trace Detection of TNT Vapor. *J. Mater. Chem.* **2007**, *17*, 2730−2736.

(16) Huang, W.; Wang, X.; Jia, Y.; Li, X.; Zhu, Z.; Li, Y.; Si, Y.; Ding, B.; Wang, X.; Yu, J. Highly Sensitive Formaldehyde Sensors Based on Polyvinylamine Modified Polyacrylonitrile Nanofibers. *RSC Adv.* **2013**, *3*, 22994−23000.

(17) Yin, K.; Zhang, L.; Lai, C.; Zhong, L.; Smith, S.; Fong, H.; Zhu, Z. Photoluminescence Anisotropy of Uni-Axially Aligned Electrospun Conjugated Polymer Nanofibers of MEH-PPV and P3HT. *J. Mater. Chem.* **2010**, *21*, 444−448.

(18) Greiner, A.; Wendorff, J. H. Electrospinning: A Fascinating Method for the Preparation of Ultrathin Fibers. *Angew. Chem., Int. Ed.* **2007**, *46*, 5670−5703.

(19) Ramakrishna, S.; Fujihara, K.; Teo, W. E.; Yong, T.; Ma, Z.; Ramaseshan, R. Electrospun Nanofibers: Solving Global Issues. *Mater. Today* **2006**, *9*, 40−50.

(20) Li, D.; Xia, Y. Electrospinning of Nanofibers: Reinventing the Wheel? *Adv. Mater.* **2004**, *16*, 1151−1170.

(21) Fong, H.; Chun, I.; Reneker, D. H. Beaded Nanofibers Formed During Electrospinning. *Polymer* **1999**, *40*, 4585−4592.

(22) Wang, X.; He, G.; Fong, H.; Zhu, Z. Electron Transport and Recombination in Photoanode of Electrospun $TiO_2$ Nanotubes for Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2013**, *117*, 1641−1646.

(23) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Light-Emitting Diodes Based on Conjugated Polymers. *Nature* **1990**, *347*, 539−541.

(24) Burn, P. L.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Holmes, A. B. Studies on the Efficient Synthesis of Poly-(phenylenevinylene) (PPV) and Poly(dimethoxy phenylenevinylene) (dimethoxy-PPV). *Synth. Met.* **1991**, *41*, 261−264.

(25) Louwet, F.; Vanderzande, D.; Gelan, J.; Mullens, J. A New Synthetic Route to a Soluble High Molecular Weight Precursor for Poly(p-phenylenevinylene) Derivatives. *Macromolecules* **1995**, *28*, 1330−1331.

(26) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. Synthesis of Light-Emitting Conjugated Polymers for Applications in Electroluminescent Devices. *Chem. Rev.* **2009**, *109*, 897−1091.

(27) Chen, Y.; Qiu, T.; Zhao, W.; Fan, L. J. Realization of Fluorescence Color Tuning for Poly(p-phenylenevinylene) Coated Microspheres via a Heterogeneous Catalytic Thermal Elimination Process. *Polym. Chem.* **2015**, *6*, 1576−1583.

(28) Dong, H.; Nyame, V.; MacDiarmid, A. G.; Jones, W. E., Jr. Polyaniline/Poly(methyl methacrylate) Coaxial Fibers: The Fabrication and Effects of the Solution Properties on the Morphology of Electrospun Core Fibers. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3934−3942.

(29) Lee, C. C.; Lai, S. Y.; Su, W. B.; Chen, H. L.; Chung, C. L.; Chen, J. H. Relationship between the Microstructure Development and the Photoluminescence Efficiency of Electrospun Poly (9,9-dioctylfluorene-2,7-diyl) Fibers. *J. Phys. Chem. C* **2013**, *117*, 20387−20396.

(30) Chen, H. C.; Wang, C. T.; Liu, C. L.; Liu, Y. C.; Chen, W. C. Full Color Light-Emitting Electrospun Nanofibers Prepared from PFO/MEH-PPV/PMMA Ternary Blends. *J. Polym. Sci., Part B: Polym. Phys.* **2009**, *47*, 463−470.

(31) Bognitzki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H. Nanostructured Fibers via Electrospinning. *Adv. Mater.* **2001**, *13*, 70−72.

(32) Cotts, P. M.; Swager, T. M.; Zhou, Q. Equilibrium Flexibility of a Rigid Linear Conjugated Polymer. *Macromolecules* **1996**, *29*, 7323−7328.

(33) Zhao, W.; Song, J.; Shao, Y.; Zhang, W.; Au, A.; Fan, L. J. Preparation of Fluorescent Conjugated Polymer Films with Different Emission Colors: Investigation into the Influences of Chemical Structure and Morphology. *Macromol. Chem. Phys.* **2012**, *213*, 1913−1921.

(34) Wang, S.; Zhao, W.; Song, J.; Cheng, S.; Fan, L. J. A Platform for Preparation of Monodispersed Fluorescent Conjugated Polymer Microspheres with Core-Shell Structures. *Macromol. Rapid Commun.* **2013**, *34*, 102−108.

(35) Wang, X.; Chen, X.; Yoon, K.; Fang, D.; Hsiao, B. S.; Chu, B. High Flux Filtration Medium Based on Nanofibrous Substrate with

Hydrophilic Nanocomposite Coating. *Environ. Sci. Technol.* **2005**, *39*, 7684−7691.

(36) Tomihata, K.; Ikada, Y. Crosslinking of Hyaluronic Acid with Glutaraldehyde. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3553−3559.

(37) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2004.

(38) Tang, C.; Saquing, C. D.; Harding, J. R.; Khan, S. A. In Situ Cross-Linking of Electrospun Poly (vinyl alcohol) Nanofibers. *Macromolecules* **2009**, *43*, 630−637.

(39) Qin, L.; Zheng, M.-X.; Guo, Z.-J.; Zheng, H.-G.; Xu, Y. One Non-Interpenetrated Chiral Porous Multifunctional Metal−Organic Framework and Its Applications for Sensing Small Solvent Molecules and Adsorption. *Chem. Commun.* **2015**, *51*, 2447−2449.

(40) Liu, T.; Ding, L.; He, G.; Yang, Y.; Wang, W.; Fang, Y. Photochemical Stabilization of Terthiophene and Its Utilization as a New Sensing Element in the Fabrication of Monolayer-Chemistry-Based Fluorescent Sensing Films. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1245−1253.

(41) Peterson, J. J.; Davis, A. R.; Werre, M.; Coughlin, E. B.; Carter, K. R. Carborane-Containing Poly (fluorene): Response to Solvent Vapors and Amines. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1796−1799.

(42) He, G.; Yan, N.; Kong, H.; Yin, S.; Ding, L.; Qu, S.; Fang, Y. A New Strategy for Designing Conjugated Polymer-Based Fluorescence Sensing Films via Introduction of Conformation Controllable Side Chains. *Macromolecules* **2011**, *44*, 703−710.

(43) Wang, J.-H.; Li, M.; Li, D. A Dynamic, Luminescent and Entangled MOF as a Qualitative Sensor for Volatile Organic Solvents and a Quantitative Monitor for Acetonitrile Vapour. *Chem. Sci.* **2013**, *4*, 1793−1801.

(44) Hariharan, A.; Kumar, S. K.; Russell, T. P. Reversal of the Isotopic Effect in the Surface Behavior of Binary Polymer Blends. *J. Chem. Phys.* **1993**, *98*, 4163−4173.

(45) Hariharan, A.; Kumar, S. K.; Russell, T. P. Surface Segregation in Binary Polymer Mixtures: A Lattice Model. *Macromolecules* **1991**, *24*, 4909−4917.

(46) Schmidt, J. J.; Gardella, J. A., Jr.; Salvati, L., Jr. Surface Studies of Polymer Blends. 2. An ESCA and IR study of Poly(methyl methacrylate)/Poly (vinyl chloride) Homopolymer Blends. *Macromolecules* **1989**, *22*, 4489−4495.

(47) Thomas, H. R.; O'Malley, J. J. Surface Studies on Multicomponent Polymer Systems by X-ray Photoelectron Spectroscopy: Polystyrene/Poly(ethylene oxide) Homopolymer Blends. *Macromolecules* **1981**, *14*, 1316−1320.

(48) Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. Preferential Surface Adsorption in Miscible Blends of Polystyrene and Poly (vinyl methyl ether). *Macromolecules* **1988**, *21*, 2166−2175.

(49) Liu, S.; Chan, C. M.; Weng, L. T.; Li, L.; Jiang, M. Surface Characterization of Poly (styrene-*co*-*p*-hexafluoro-hydroxyisopropyl-$\alpha$-methylstyrene)/Poly (4-vinylpyridine) Blends Spanning the Immiscibility-Miscibility-Complexation Transition by XPS, ToF-SIMS, and AFM. *Macromolecules* **2002**, *35*, 5623−5629.

(50) Liu, S.; Weng, L. T.; Chan, C. M.; Li, L.; Ho, K. C.; Jiang, M. Surface Characterization of Poly(styrene-*co*-*p*-hexafluorohydroxyisopropyl-$\alpha$-methyl styrene) Copolymers by ToF-SIMS, XPS and Contact Angle Measurements. *Surf. Interface Anal.* **2000**, *29*, 500−507.