Controlled Sulfonation of Poly(*N*-vinylcarbazole)

Suhua Wang,[†] Zhaohua Zeng,[†] Shihe Yang,*,[†] Lu-Tao Weng,[‡]
Philip C. L. Wong,[‡] and Kachun Ho[‡]

Department of Chemistry, Materials Characterization and Preparation Facility, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received October 28, 1999; Revised Manuscript Received February 9, 2000

ABSTRACT: Poly(*N*-vinylcarbazole) (PVK) was sulfonated with acetyl sulfate. SIMS and XPS measurements of the sulfonated PVK show that the sulfonation occurs on the carbazole moiety and that the degree of sulfonation (DS) increases linearly with the ratio of the sulfonating agent to PVK. The DS of PVK could be controlled within a range from 12% to 28% by varying the reagent ratio. GPC measurements demonstrate that the molecular weight of PVK did not change substantially after sulfonation. UV−vis and photoluminescence spectra indicate that the sulfonation caused little change in the electronic structure of the PVK molecules but reduced significantly its photoluminescence quantum efficiency.

Introduction

Poly(*N*-vinylcarbazole) (PVK) is an effective hole-transport organic semiconductor.[1−5] It has been extensively studied as a potential electronic and optical material.[6−11] To date, the exploitation of PVK as an active material component for applications has been based mainly on doped PVK or blends of PVK and semiconductor nanoparticals.[2,4,9] Surprisingly, very little work has been done on chemical modification of PVK up until now.[12,13] To broaden its scope in optoelectronic device applications, however, it is necessary to functionalize the peripheral of the PVK polymer in such a way that it becomes chemically compatible with other components in a hybrid system.

We have recently started to develop a versatile synthetic approach to derivatize the carbazole groups of PVK. This stems from our general interest in synthesizing nanocomposites of inorganic and organic semiconductors through chemical hybridization.[14,15] In the present work, we sulfonated PVK on the carbazole units. We used acetyl sulfate as a sulfonating agent. Acetyl sulfate is widely used to sulfonate polystyrene and other polymers with aromatic rings or unsaturated carbon−carbon bonds.[16−21] In principle, fuming sulfuric acid (SO_3) could also be used to sulfonate PVK,[22−24] but it was not used in the present case due to possible degradation/cross-linking of PVK molecules and also because of laboratory safety concerns.

One of the challenges in the sulfonation of PVK is the selection of a suitable solvent. Conventional solvents for sulfonation of polystyrene such as hexane, 1,2-dichloroethane, petroleum ether, etc., cannot be used here because PVK precipitates in these solvents due to protonation of the carbazole units in the presence of the sulfonating agent. We identified THF as a suitable solvent for the sulfonation of PVK and successfully avoided the precipitation problem. A variety of spectroscopic techniques were employed to characterize the sulfonation products. In particular, XPS and SIMS provided the vital molecular information necessary for both qualitative and quantitative analysis regarding the structural characteristics of the sulfonation products.

Table 1. Conditions and Results of the Sulfonation Reaction of PVK

reagent and solvent	sulfonating agent (mL)	products (label)	M_w/M_n (from GPC)
PVK (250 mg)	0	PVK-00	53 071/41 927
THF (5 mL)	0.39	PVK-30	53 063/41 850
	0.52	PVK-40	53 508/42 248
	0.65	PVK-50	*a*
	0.78	PVK-60	*a*

[a] For highly sulfonated PVK samples, the molecular weight was difficult to measure because of their poor solubility in THF.

Experimental Section

Preparation of Sulfonating Agent. First, 0.76 mL (8.1 mmol) of acetic anhydride (99+%, Aldrich) was dissolved in 4.0 mL of 1,2-dichloroethane in a 50 mL flask. Then, 0.28 mL (5.0 mmol) of 95% sulfuric acid ($\rho = 1.84$ g/mL) was added dropwise at 10 °C, and a transparent colorless solution was obtained. The concentration of acetyl sulfate in this solution was 1.0 M.[25] The solution was stored for later use in the sulfonation of PVK.

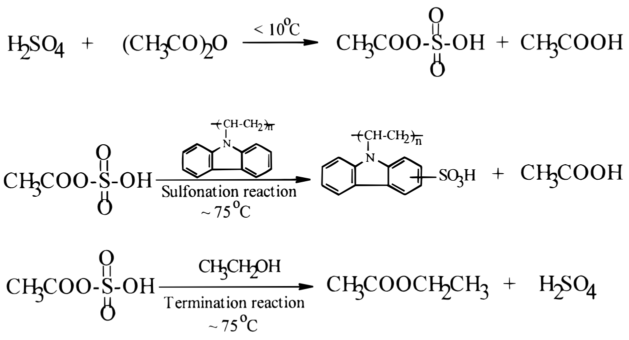
Sulfonation of PVK. PVK (secondary standard, Aldrich) was dried in a vacuum oven at 50 °C for 10 h before use. A 250 mg sample of PVK was dissolved in 5.0 mL of THF at room temperature. Five identical solutions were prepared in this way. Different amounts of the sulfonating agent were added dropwise into each of the above five PVK solutions, which were stirred magnetically (Table 1). The resulting five solutions were labeled as PVK-00, PVK-30, PVK-40, PVK-50, and PVK-60. The solutions were next heated on a water bath kept at ~75 °C and refluxed for 5 h, after which 1.0 mL of ethanol was added to terminate the sulfonation reaction (Scheme 1). At this stage, ~20 mL of cyclohexane was added to the solution to precipitate the sulfonation products. The precipitate was vacuum filtrated, washed with ethanol (for samples with a ratio of sulfonation agent to carbazole of PVK smaller than 40%) or cyclohexane (for samples with a ratio of sulfonation agent to carbazole of PVK larger than 40%), and dried overnight in a vacuum oven at 50 °C. Finally, a light gray powder was obtained. The sulfonated PVK with a low degree of sulfonation is soluble or partially soluble in nonpolar solvents such as 1,2-dichloroethane and cyclohexane. On the other hand, the sulfonated PVK with a relatively high degree of sulfonation is soluble or partially soluble in polar solvents such as ethanol. Sulfonation of PVK was also carried out at different water bath temperatures, but the optimum water temperature for the sulfonation of PVK was found to be 75 °C. This water bath temperature retained the refluxing

---

[†] Department of Chemistry.
[‡] Materials Characterization and Preparation Facility.
* Corresponding author. E-mail address: chsyang@ust.hk.

10.1021/ma991815z CCC: $19.00

Scheme 1. Sulfonation Reaction of PVK



condition of the THF solution (THF has a boiling point of 66 °C at 1 atm). The sulfonated PVKs reported in this work were all synthesized under the reaction conditions described above.

Characterization. FTIR spectra of the pristine PVK and sulfonated PVK samples were recorded using a Perkin-Elmer 16 PC spectrometer. The FTIR samples were prepared by mixing 1.5 mg of a PVK sample and 200 mg of a finely ground KBr powder and then pressing the mixture into a pellet. For comparison, we also prepared FTIR samples by casting a THF solution of sulfonated PVK to a film on a KBr pellet. UV–vis absorption spectra were obtained using a Milton Roy Spectronic 300 spectrometer using THF solution samples. Photoluminescence spectra (PL) of the solutions were measured on a SLM AMINCO spectrofluorometer with an excitation wavelength of 340 nm. Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI7200 system and a PHI5600 system, respectively. The pristine PVK and sulfonated PVK samples were prepared by spin-coating the THF solution on a silicon substrate. Nuclear magnetic resonance spectra were recorded on a Bruker ARX 300 MHz spectrometer using CD_3Cl as a solvent.

In the gel permeation chromatography (GPC) analysis (Waters 2690 separations module with a Waters 410 differential refractometer), THF was used as the carrier solvent. We used a column from Waters styragel HT, which was packed with high-performance fully porous, highly cross-linked styrene–divinylbenzene copolymer particles. The molecular weight data of the original PVK and the sulfonated PVKs were obtained by calibration with linear polystyrene standards (Polymer Standards Service–U.S.A. Inc., manufactured for Waters Corp.).

Results and Discussion

FTIR was the first spectroscopic tool we used to identify our successful sulfonation of the PVK polymer. Presented in Figure 1 are the FTIR spectra of the pristine PVK and the sulfonated PVK with different DS. The samples were prepared as pellet mixtures of PVK or sulfonated PVK and finely ground KBr powder. Measurements on films of PVK or sulfonated PVK on KBr pellets yielded identical spectra. By comparing the above three spectra, it is clear that in the spectra of the sulfonated PVK (traces b and c) new peaks at 1175, 1055, and 688 cm^{-1} can be ascertained which are absent in the spectrum of the pristine PVK (trace a). Furthermore, the relative intensity of these new peaks increases with the increasing DS. The peaks at 1175 and 1055 cm^{-1} are ascribable respectively to the asymmetric and symmetric stretching vibrations of O=S=O,[26] and the peak at 673 cm^{-1} can be assigned to the stretching vibration of S–O. The results presented above all indicate that the sulfonic acid groups $-SO_3H$ have been successfully incorporated into the PVK polymer. The question as to whether the sulfonic acid groups are linked to the carbazole units or the polymer backbone will be addressed by XPS and SIMS measurements.

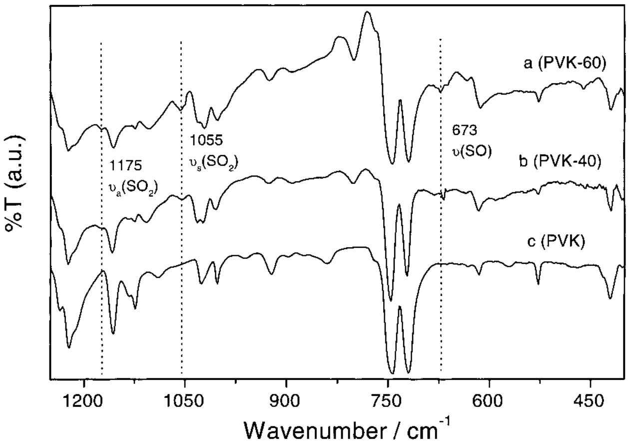


Figure 1. FTIR spectra of sulfonated PVKs: (a) PVK-60, (b) PVK-40, and (c) pristine PVK. The vertical dash lines indicate the vibration frequencies of the $-SO_3H$ groups in the PVK polymer.

GPC results show that the molecular weight of the sulfonated PVK decreases only slightly with the increasing DS (Table 1). This was not expected because the incorporation of the sulfonic acid groups should have increased the molecular weight of PVK. The slight decrease in molecular weight may indicate that the individual sulfonated PVK conglomerate is more compact than the parent PVK molecule due to the formation of hydrophilic domains. More importantly, one can conclude on the basis of the GPC results that neither cross-linking nor degradation occurred to a significant extent during the sulfonation reaction of PVK. For samples (PVK-50 and PVK-60) with higher degrees of sulfonation, GPC measurements were difficult due to their poor solubility in THF. This poor solubility results from the introduction of an increasing number of polar sulfonic acid groups into PVK. With high degrees of sulfonation, PVK-50 and PVK-60 are soluble in ethanol, and they become swollen in water.

Pure PVK and sulfonated PVKs are analyzed by XPS and SIMS.[27] XPS analysis showed that, in addition to carbon and nitrogen of pure PVK, sulfur was detected on all sulfonated PVKs. This indicates that sulfur has been attached to PVK. As an example, Figure 2 presents an S 2p XPS spectrum obtained with PVK-60 (DS = 28%), which shows a peak at about 168.7 eV. This binding energy was also observed for other sulfonated PVKs. The observed binding energy (168.7 eV) is close to that of sulfur in poly(sodium 4-styrenesulfonate) (168.3 eV).[28] This suggests that sulfur in the sulfonated PVKs exits in a form similar to sulfonate (SO_3). However, as this binding energy is also close to that of sulfate groups in polymers (~189 eV),[29] it is difficult from the XPS data alone to conclude whether sulfur exists in sulfonate or sulfate form and determine whether sulfur is attached to carbazole units or the backbone of the PVK polymer.

To address these issues, the SIMS technique, which can provide more molecular information, was used. SIMS results showed that new fragments were observed in the sulfonated PVKs. As an example, Figure 3 displays a negative SIMS spectrum obtained with PVK-60 (DS = 28%) which shows two intense peaks at m/z = 166 and 272. The peak at m/z = 166 corresponds to the carbazole unit while the peak at m/z = 272 corresponds to the molecular unit with sulfonate attached to aromatic ring (see molecular structure indicated in

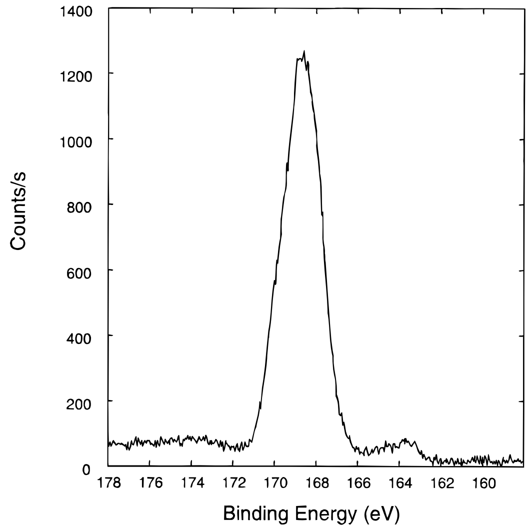


Figure 2. XPS S 2p spectrum of sulfonated PVK (PVK-60). The spectrum was recorded on a film sample that was spin-coated on a silicon substrate. THF was used as the solvent for spin-coating.

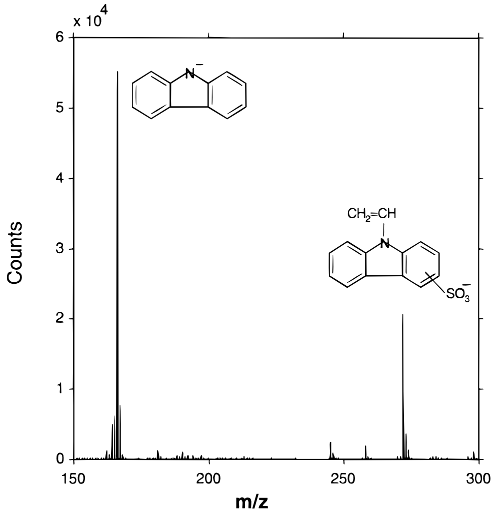


Figure 3. Negative ion SIMS spectrum of sulfonated PVK (PVK-60). The spectrum was recorded on a film sample that was spin-coated on a silicon substrate. THF was used as the solvent for spin-coating.

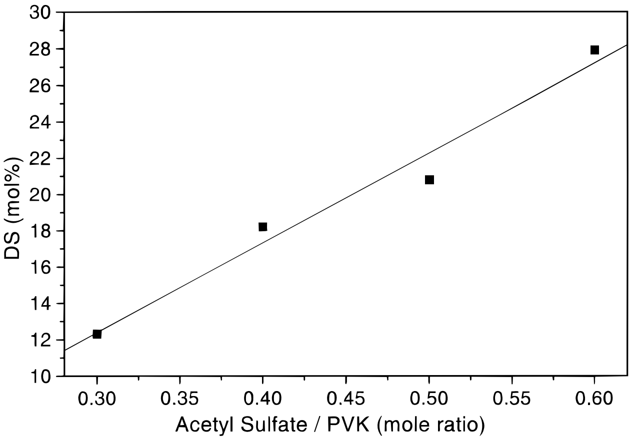


Figure 4. Variation of the degree of sulfonation (DS) of PVK as a function of the mole ratio of the sulfonation agent to the carbazole unit of PVK.

Table 2. Degree of Sulfonation (DS) of PVK and Yield of Sulfonated PVK

samples	PVK-30	PVK-40	PVK-50	PVK-60
theoretical DS (%)	30	40	50	60
observed DS (%)	12.3	18.2	20.8	27.9
yield (%)	41.0	45.5	41.6	46.5

Figure 3). Pure PVK shows only the peak at $m/z = 166$ while all sulfonated PVKs show both peaks. These results clearly demonstrate that sulfur in the sulfonated PVKs exists in the form of sulfonate and the sulfonate groups are attached to aromatic ring. However, SIMS is unable to determine exactly which carbon in the aromatic ring has been directly bonded to the sulfonate groups.

Both ^1H and ^{13}C NMR spectra of the sulfonated PVK were obtained. Because CD_3Cl was used as the solvent, we could take NMR spectra for only slightly sulfonated PVK (PVK-10). The ^1H NMR spectrum of PVK-10 is very similar to that of the pristine PVK.[30] This is because the degree of sulfonation is too low (2.5% in terms of the carbazole unit and only 1.25% in terms of the benzene ring), and the relative intensity of the NMR peaks does not show any discernible changes after sulfonation. The ^{13}C NMR spectrum of PVK-10 is also similar to that of the pristine PVK,[30] but two new peaks appear at 125.8 and 119.4 ppm, respectively. These two peaks appear to be associated with the peaks of the pristine PVK at 124.9 ppm (carbons 2 and 7) and 118.4 ppm (carbon 4) but are displaced to lower field respectively by 0.9 and 1.0 ppm presumably due to substitution by the sulfonic acid groups. Therefore, we believe that sulfonation occurs in the meta position to the amine group in the carbazole unit. This is plausible because sulfonation is an electrophilic reaction, and the protonation on the amine groups would direct the electrophilic addition on its meta position in the carbazole unit.

From the S/C atomic ratio obtained by XPS, the degree of PVK sulfonation can be quantitatively determined. The results are tabulated in Table 2. It can be observed that the degree of PVK sulfonation varies from 12% to 28%.

Figure 4 plots the degree of sulfonation as a function of the mole ratio of the sulfonation agent to the carbazole unit of PVK. The plot is approximately linear, indicating that the degree of sulfonation of PVK is directly proportional to the relative amount of the sulfonation agent employed in the reaction. However, the sulfonation reaction was not complete under the conditions we adopted. For example, when the ratio of the sulfonation agent to carbazole of PVK was 0.60, the theoretical degree of sulfonation is calculated to be 60%. However, our XPS data give the degree of sulfonation to be only 28% (based on the C/S ratio) under this condition. The sulfonation yield can then be estimated to be 47%. One possible explanation for this relatively low yield is that the THF used for carrying out the sulfonation reaction may contain water, which can decompose the sulfonation agent. In addition, to some extent, increasing the reaction time can also improve the sulfonation yield.

UV–vis absorption spectra of the original PVK and the PVKs with different degrees of sulfonation (DS) are presented in Figure 5. As a reference, the spectrum of the pristine PVK is nearly the same as that reported in the literature.[31] A comparison of the spectra of the pristine and the sulfonated PVKs shows that the absorption spectrum of PVK in all the spectral regions we examined changes little after sulfonation. This

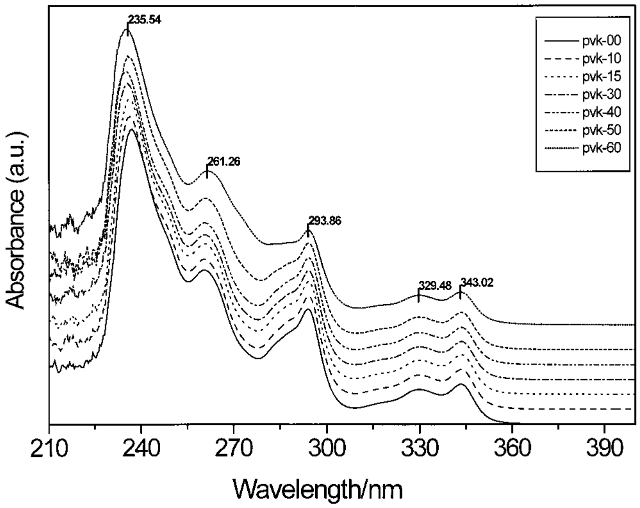


Figure 5. UV–vis absorption spectra of the PVK samples with various DS. THF was used as the solvent for the measurements.

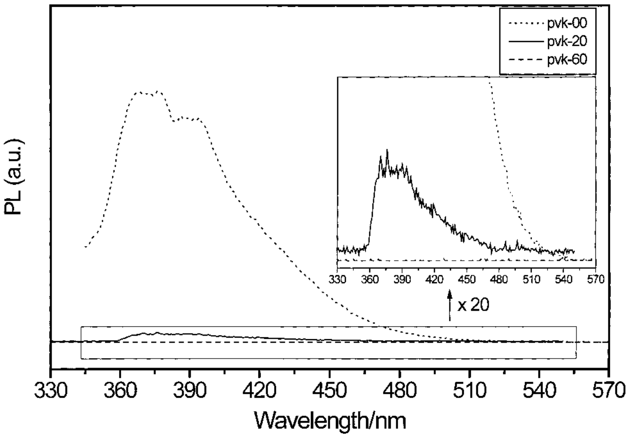


Figure 6. Photoluminescence spectra (PL) of the PVK samples with different DS. THF was used as the solvent for the measurements.

continues to be the case even though as much as 28% of the carbazole units of the pristine PVK were sulfonated (Figure 5). Small changes in peak shape and position may be recognized in the spectra, particularly for the ^1L_a band around 293 nm;[31] the shoulder becomes more and more obscured as the degree of sulfonation increases. Overall, the absorption spectra show that the introduction of the sulfonic acid groups on the carbazole units has a minimum effect on the electronic structure of the PVK molecules. This is exactly what we aimed to achieve for device applications of PVK: functionalization of PVK while retaining its bulk properties.

Photoluminescence spectra (PL) of the pristine PVK and the sulfonated PVK (PVK-20 and PVK-60) are shown in Figure 6. Although the PL spectra of the sulfonated PVKs are similar to that of the pristine PVK, the PL efficiency decreases significantly after sulfonation. As can be seen in Figure 6, the sample PVK-60 (DS = 28%) almost does not show any photoluminescence. Apparently, the sulfonation of the carbazole units, albeit accompanied by little change in electronic structure, does create a nonradiative energy transfer path. The nonradiative energy transfer path could be much faster than the luminescence process so that the photoluminescence is effectively suppressed. This suggests that control of the degree of sulfonation is important depending on the specific device applications of the PVK molecules.

Conclusion

In conclusion, we have successfully sulfonated PVK for the first time. The degree of sulfonation is controllable by using different molar ratios of the sulfonating agent to the carbazole unit of PVK. The sulfonated PVKs were characterized by a number of spectroscopic techniques. The results show that the sulfonation occurs on the carbazole moiety in PVK. The yield of the sulfonation products is estimated to be ~41–47%. The products were characterized by SIMS and XPS in terms of location and degree of sulfonation. The electronic structure of the sulfonated PVK was examined by UV–vis absorption spectra and photoluminescence spectra. The electronic structure of PVK incurs little changes, but photoluminescence efficiency decreases significantly after sulfonation. Synthesis of semiconductor nanocrystals using these sulfonated PVKs is in progress in our laboratory, and preliminary results are quite encouraging.

Acknowledgment. This work was supported by an RGC grant administered by the UGC of Hong Kong.

References and Notes

(1) Regensburger, P. J. *Photochem. Photobiol.* **1968**, *8*, 429.
(2) Melz, P. J. *J. Chem. Phys.* **1972**, *57*, 1694.
(3) Pai, D. M. *J. Chem. Phys.* **1969**, *50*, 3568.
(4) Pfister, G.; Williams, D. J. *J. Chem. Phys.* **1974**, *61*, 2416.
(5) Gill, W. D. In *Photoconductivity and Related Phenomena*; Mort, J., Pai, D. M., Eds.; Elsevier: Amsterdam, 1976; p 332.
(6) Chan, H. S. O.; Ng, S. C.; Sim, W. S.; et. al. *Macromolecules* **1992**, *25*, 6029.
(7) Cao, Y.; Simth, P.; Heeger, A. J. *Synth. Met.* **1993**, *55*, 3514.
(8) Cao, Y.; Qiu, J.; Simth, P. *Synth. Met.* **1995**, *69*, 187.
(9) Wang, Y.; Herron, N. *Chem. Phys. Lett.* **1992**, *200*, 71.
(10) Brutting, W.; Berleb, S.; Egerer, G.; et al. *Synth. Met.* **1997**, *91*, 325.
(11) Touihri, S.; Safoula, G.; Bernede, J. C. *Polym. Degrad. Stab.* **1998**, *60*, 481.
(12) See, for example: Zamora, F.; Gonzalez, M. C. *J. Macromol. Sci., Phys. B* **1998**, *37*, 601.
(13) Cai, R. F.; Bai, X.; Chen, Y.; Huang, Z. E. *Eur. Polym. J.* **1998**, *34*, 7.
(14) Zeng, Z. H.; Wang, S. H.; Yang, S. H. *Chem. Mater.* **1999**, *11*, 3365.
(15) Wang. S. H.; Yang, S. H. *Langmuir* **2000**, *16*, 389.
(16) Makowski, H. S.; Lundberg, R. D.; Singhal, G. U.S. Patent No. 3,870,841, to Exxon Research and Engineering Co., U.S.A., March 11, 1975.
(17) Lundberg, R. D.; Makowski, H. S.; Westerman, L. U.S. Patent No. 4,014,847, to Exxon Research and Engineering Co., U.S.A., March 29, 1977.
(18) Lundberg, R. D.; Makowski, H. S. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 1821.
(19) Smith, P.; Eisenberg, A. J. *Polym. Sci., Polym. Lett.* **1983**, *21*, 223.
(20) Lundberg, R. D. *J. Appl. Polym. Sci.* **1982**, *27*, 4623.
(21) Feng, K.; Zeng, Z. H.; Ou-Yang, W.; Li, Z. M. *J. Appl. Polym. Sci.* **1997**, *64*, 1651.
(22) Kitano, K.; Mikuchi, T.; Terao, T. U.S. Patent No. 4,671,903, to Lion Corp., Japan, June 9, 1987.
(23) Miyatake, K.; Iyotani, H.; Yamamoto, K.; Tsuchida, E. *Macromolecules* **1996**, *29*, 6969.
(24) Miyatake, K.; Shouji, E.; Yamamoto, K.; Tsuchida, E. *Macromolecules* **1997**, *30*, 2941.
(25) Balas, J. G.; Gergen, W. P. U.S. Patent No. 5,239,010, to Shell Oil Co., U.S.A., Aug 24, 1993.
(26) (a) Brown, D. W.; Floyd, A. J.; Sainsburg, M. *Organic Spectroscopy*; John Wiley & Sons: New York, 1988; p 24. (b) Silverstein, R. M.; Clayton Bassler, G.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; John Wiley & Sons: New York, 1991; p 91.

(27) Weng, L.-T.; Wong, P. C. L.; Ho, K.; Wang, S. H.; Zeng, Z. H.; Yang, S. H., to be published.

(28) Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers*; The Scienta ESCA300 Database; John Wiley: Chichester, 1992.

(29) Weng, L. T.; Bertrand, P.; Stone-Masui, J. H.; Stone, W. E. E. *Langmuir* **1997**, *13*, 2943.

(30) Natansohn, A. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4257.

(31) (a) Okamato, K.; Itaya, A. Kusabayashi, S. *Chem. Lett.* **1974**, *10*, 1167. (b) Kadiri, A.; Fadouach, B.; Benail, B.; Boucetta, A. *Spectrochim. Acta* **1994**, *50A*, 851.

MA991815Z