Synthesis of Water-Soluble Polyacrylics Modified Silica Sol–Gel Materials

Yen Wei,* Wei Wang, Dachuan Yang, and Liguang Tang

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received March 22, 1994. Revised Manuscript Received June 23, 1994[⊗]

A series of new water-soluble polyacrylics modified silica gels has been prepared by hydrolysis of the polyacrylonitrile–silica hybrid sol–gel materials either in a 30% H_2O_2 solution containing K_2CO_3 catalyst or in aqueous KOH solution of various concentrations. The hydrolytic reactions in H_2O_2–K_2CO_3 or at low KOH concentrations transform the nitrile groups of the polyacrylonitrile component in the polyacrylonitrile–silica hybrid materials to highly hydrophilic amide and/or carboxyl groups without affecting the polymer backbones that are still immobilized in the silica matrix. The same reactions can also be used to change the hydrophilicity of the surface of the polyacrylonitrile–silica hybrid materials.

Introduction

In the past decade, a new class of organic–inorganic hybrid/composite materials has been prepared via sol–gel reactions of metal alkoxides with a variety of organic compounds or polymers in the presence of an acid or base catalyst at relatively low temperatures.[1] There are two major families of these organic-modified sol–gel materials: (1) organic–inorganic composites in which the organic or polymer components are trapped in the inorganic networks and (2) organic–inorganic hybrid materials in which the organic or polymer components are covalently bonded to the inorganic networks. There are many papers describing the sol–gel reactions of metal alkoxides in the presence of soluble polymers, such as poly(vinyl alcohol), polyacrylamides, polymethacrylates, polyoxazolines, methacrylic or acrylic acid polymers, etc., to afford the organic–inorganic composite materials.[2,3] We are interested in the organic–inorganic hybrid materials. We have developed a general method for the preparation of polymer sol–gel precursors containing the reactive alkoxysilyl groups via chain copolymerization of 3-(trimethoxysilyl)propyl methacrylate[4] with other vinyl monomers (e.g., methyl methacrylate[5,6] and styrene[7]). This approach makes it possible, in principle, to incorporate any conventional vinyl polymers into the inorganic matrices at molecular level through the sol–gel reactions. Many physicochemical properties of the hybrid materials could be varied by choosing appropriate vinyl polymers and their compositions in the inorganic matrices. Recently, we reported a successful synthesis of polyacrylonitrile–silica hybrid sol–gel materials (PAN–SiO_2), in which the polymer chains are uniformly distributed in and covalently bonded to the silica matrix.[8] The polyacrylonitrile component in the hybrid materials was found to undergo pyrolysis toward the formation of carbon fibers of micro- or nanostructures in the silica matrix.[8]

In this article, we present the synthesis of a series of new water-soluble polyacrylics modified silica gels via a hydrolysis of nitrile (–CN) groups in the polyacrylonitrile–silica hybrid materials that were prepared by the acid-catalyzed sol–gel reactions of poly[acrylonitrile-*co*-3-(trimethoxysilyl)propyl methacrylate] (PAN–MSMA) with tetraethyl orthosilicate (TEOS) at room temperature. The hydrolytic reactions convert the nitrile group to amide ($-CONH_2$) and to carboxyl ($-COOH$ or $-COO^-$) groups while leaving the polymer main chain intact. The resultant polyacrylamide and poly(acrylic acid or salt), though both are water-soluble polymers,[9] are still immobilized in the SiO_2 matrix without apparent phase separation. Since the PAN–MSMA chain in the SiO_2 matrix contains both hydrolyzable nitrile and ester groups, the hydrolysis of the ester groups may not be desirable because it breaks the

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

[1] For leading references and reviews, see: (a) Schmidt, H.; Sieferling, B.; Philipp, G.; Deichmann, K. In *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; p 651. (b) Schmidt, H. *J. Non-Cryst. Solids* **1989**, *112*, 419. (c) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science, the Physics and Chemistry of Sol-Gel Processing*; Academic Press: San Diego, 1990. (d) Ulrich, D. R. *J. Non-Cryst. Solids* **1990**, *121*, 465. (e) Wilkes, G. L.; Huang, H.; Glaser, R. H. In *Silicon-Based Polymer Science*; Advances in Chemistry Series 224; Ziegler, J. M., Fearon, F. W., Eds.; American Chemical Society: Washington, DC, 1990; pp 207–226. (f) Calvert, P. *Nature* **1991**, *353*, 501. (g) Wen, J.; Mark, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (2), 362. (h) Pope, E. J. A.; Asami, M.; Mackenzie, J. D. *J. Mater. Res.* **1989**, *4*, 1018. (i) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.

[2] (a) Messermith, P. B.; Stupp, S. I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 536. (b) Novak, B. M.; Ellsworth, T. I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 698. (c) Landry, C. J. T.; Coltrain, B. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 514. (d) Saegusa, T. *J. Makromol. Sci., Chem. A* **1991**, *28*, 817.

[3] (a) Miller, T. M.; Brennan, A. B. *Polym. Mater. Sci. Eng.* **1994**, *70*, 276. (b) Roger, C.; Hampden-Smith, M. J. *J. Mater. Chem.* **1992**, *2*, 1111. (c) Nakanish, K.; Soga, N. *J. Non-Cryst. Solids* **1992**, *139*, 1; (d) **1992**, *139*, 14.

[4] Other alkoxysilyl containing vinyl monomers (e.g. trimethoxysilyl ethylene and (styrylethyl)trimethoxysilane) are also under investigation in our laboratory.

[5] (a) Wei, Y.; Bakthavatchalam, R.; Whitecar, C. K. *Chem. Mater.* **1990**, *2*, 337. (b) Wei, Y.; Bakthavatchalam, R.; Yang, D. C.; Whitecar, C. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (3), 503. (c) Wei, Y.; Wang, W.; Yeh, J.-M.; Wang, B.; Yang, D.; Murray, J. K., Jr. *Polym. Mater. Sci. Eng.* **1994**, *70*, 272.

[6] Wei, Y.; Yang, D. C.; Bakthavatchalam, R. *Mater. Lett.* **1992**, *13*, 261.

[7] Wei, Y.; Yang, D. C.; Tang, L. G.; Hutchins, M. K. *J. Mater. Res.*, **1993**, *8*, 1143.

[8] Wei, Y.; Yang, D. C.; Tang, L. G. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 273.

[9] Teot, A. S. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1982; Vol. 20, p 217.

0897-4756/94/2806-1737$04.50/0

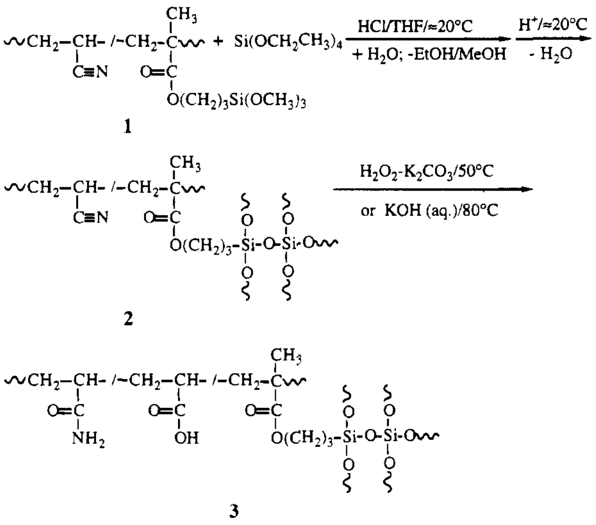
original covalent links between the polymer chain and the inorganic component in the hybrid materials. Therefore, several catalytic systems have been investigated to achieve good chemoselectivities of the hydrolysis reactions.

Experimental Section

Materials and Instrumentation. Tetraethyl orthosilicate (TEOS, Aldrich), tetrahydrofuran (THF, HPLC grade, Aldrich), hydrogen peroxide (30% aqueous solution, Fisher), potassium carbonate (Fisher), *N,N*-dimethylformamide (DMSO, Fisher), tetrafluorophthalic acid (Aldrich), and tetrachlorophthalic acid (TCl) were used as recieved. Acrylonitrile (AN, Aldrich) and 3-(trimethoxysilyl)propyl methacrylate (MSMA, Aldrich) were purified following the standard procedure and distilled under reduced pressure prior to use. The polymer precursor, poly[acrylonitrile-*co*-3-(trimethoxysilyl)propyl methacrylate] (PAN–MSMA), was prepared by free-radical copolymerization of acrylonitrile with 3-(trimethoxysilyl)propyl methacrylate using benzoyl peroxide as initiator at 75 °C in nitrogen.[8] The copolymer consisted of 85 and 15 mol % of AN and MSMA units, respectively, as determined from ^{1}H NMR and thermogravimetric analysis (TGA), and had a number-average molecular weight of 4700 as determined from gel-permeation chromatography (GPC) using polystyrene calibration. The transparent, monolithic polyacrylonitrile–silica (PAN–SiO_2) hybrid materials were prepared from an aqueous HCl-catalyzed sol–gel reactions of TEOS with PAN–MSMA in THF at room temperature as previously reported.[8] The SiO_2 contents in the materials were 84, 72, 61, 54, 42, 39, and 14 wt %. The Fourier-transform infrared spectra of KBr powder-pressed pellets were recorded on a Perkin-Elmer 1600 FTIR spectrometer. The diffuse reflectance FTIR spectra were measured on the same instrument equipped with a diffusion reflectance accessory. The assignments of IR bands were made based on the literature.[10,11] TGA runs were taken on a DuPont 9900TA system with a 951 TGA module in air at a programmed heating rate of 20 °C/min. The GPC measurements were performed on a Waters GPC IIA equipped with a Model 590 solvent delivery module, a refractometer as detector and an Ultrastyragel linear column using THF as eluant. Proton NMR spectra were recorded on an IBM Bruker WM-250 FT-NMR spectrometer operating at 250 MHz with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. Contact angles were measured at 22 °C using triply distilled water with a droplet volume of ca. 0.05 mL. The values were recorded about 5 min after the droplet was applied to the surface of the hybrid samples.

Hydrolysis of PAN–SiO_2 Hybrid Materials with H_2O_2. The nitrile (–CN) groups in PAN–SiO_2 were converted to water-soluble amide (–$CONH_2$) groups with excess 30% H_2O_2 under catalysis of potassium carbonate in a mixed solvent of either acetone–water or DMSO–water following the literature procedures reported for small molecular nitriles.[12] The PAN–SiO_2 sample could be a fine powder or a thin film. For a typical example, 0.05 g of finely ground powder of the PAN-SiO_2 sample containing 72 wt % SiO_2 and 0.17 mmol of nitrile groups was placed in 0.5 mL of mixture solvents of acetone and water (50/50, v/v) in a 25-mL round-bottom flask equipped with a condenser and a magnetic stirring bar. Then 0.15 mL of 30 wt % aqueous H_2O_2 (1.33 mmol) and 0.05 g (0.36 mmol) K_2CO_3 were added to the system with stirring. The reaction mixture was heated to and kept at 50 °C for 4 h. After cooling to room temperature, the reaction mixture was neutralized with 1 N HCl followed by filtration. The white solid hydrolysis product was thoroughly washed with distilled water and methanol followed by drying in vacuo at 90 °C overnight.

Scheme 1



Hydrolysis of PAN–SiO_2 Hybrid Materials with KOH. The PAN–SiO_2 hybrid materials were also hydrolyzed in aqueous KOH of various concentrations (i.e., 1, 10, 20, or 30 wt %) at 80 °C for either 1 or 3 h. The hybrid samples subjected to the hydrolysis were either in a fine powder form or in a monolithic disk form. The purpose of employing the disk samples was to limit the hydrolysis to only the surface of the PAN–SiO_2 hybrids and therefore to modify the surface properties of the materials. As a typical procedure for the hydrolysis of PAN–SiO_2 disk, a monolithic disk (0.8 g) of the sample with the SiO_2 content of 72 wt % was placed in ca. 50 mL of 1 wt % aqueous KOH solution at 80 °C for 1 h. The mixture was then cooled to room temperature and was neutralized with 2 M HCl. The product was thoroughly wasbhed with water and methanol and was dried in vacuo at 60 °C overnight. Similar procedure was used to hydrolyze the hybrid samples in powder form. For the hydrolysis at high concentrations of KOH (i.e., ≥10 wt % in this study), a PAN–SiO_2 sample (e.g., 0.8 g of the sample with the SiO_2 content of 72 wt %) was ground into a fine powder and then suspended in ca. 50 mL of 10% KOH aqueous solution. The mixture was heated to 80 °C under magnetic stirring. The color of solution changed from colorless to reddish, deep red and then to yellowish in ca. 1 h. After 1 or 3 h, the solution was cooled to room temperature and neutralized with 2 M HCl to pH~8. The hydrolysis product was precipitated in methanol and dried at 100 °C in vacuo overnight.

Results and Discussion

As depicted in Scheme 1, the synthesis of new water-soluble polyacrylics modified silica gels (**3**) was achieved by hydrolysis of the polyacrylonitrile–silica hybrid materials (**2**), which in turn were obtained from HCl-catalyzed sol–gel reactions of PAN–MSMA (**1**) with TEOS. The polyacrylic component in the new materials (**3**) contains water-soluble amide (–$CONH_2$) and/or carboxyl (–COOH or –COO^-) side chains.

The hydrolysis of the PAN-SiO_2 hybrid materials (**2**) was performed under various conditions. It was reported[12–14] that small nitrile compounds can be readily converted to the corresponding amides by treating the nitrile compounds with an excess of 30% H_2O_2 using potassium carbonate as a catalyst. The hydrolysis occurs chemoselectivity on nitrile groups while leaving ester groups in the compounds intact.[12] We have

---

(10) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; pp 95–180.

(11) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Wiley: New York, 1958; pp 161–220.

(12) Katritzky, A. R.; Pilarski, B.; Urogdi, L. *Synthesis* **1989**, 949.

(13) Kabalka, G. W.; Deshpande, S. M.; Wadgaonkar, P. P.; Chatla, N. *Synth. Commun.* **1990**, *20*, 1445.

(14) Cacchi, S.; Misiti and D.; Torre, F. L. *Synthesis* **1980**, 243.

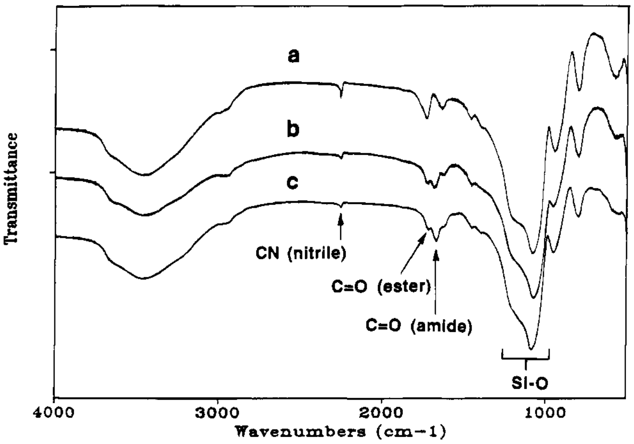


Figure 1. FTIR spectra of the polyacrylonitrile–SiO_2 hybrid sol–gel materials with SiO_2 contents of 72 wt % before (a) and after the treatment with H_2O_2–K_2CO_3 in acetone–water solvent for 2 h (b) and 4 h (c).

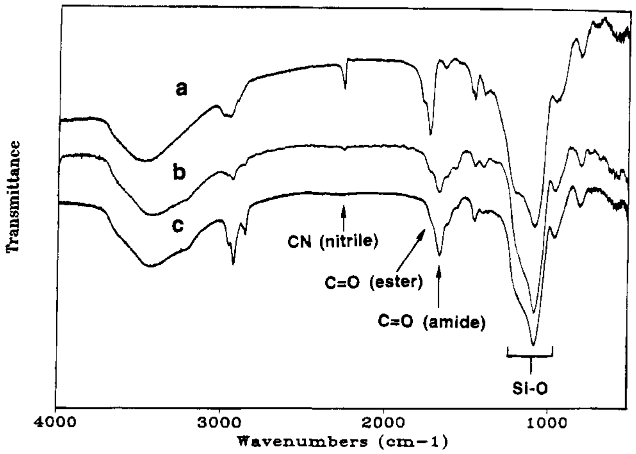


Figure 2. FTIR spectra of the polyacrylonitrile–SiO_2 hybrid sol–gel materials (PAN–SiO_2) with SiO_2 contents of 42 wt % before (a) and after the treatment with H_2O_2–K_2CO_3 in acetone–water solvent for 4 h (b) as well as after the treatment with H_2O_2–K_2CO_3 in DMSO–water solvent for 2 h (c).

extended this method in the hydrolysis of the nitrile groups in the PAN–SiO_2 hybrid sol–gel network (**2**). The reactions were carried out heterogeneously by suspending a finely ground powder of **2** in 30% H_2O_2 in the presence of K_2CO_3 in a mixed solvent of acetone and water (50/50, v/v) at 50 °C. Because of the microporous nature of the unsintered sol–gel materials,[1] the reagents (e.g., H_2O_2) could diffuse into the inorganic matrix and react with the organic component. To further ensure high conversions of the nitrile groups in such a heterogeneous system, a reaction time of 4 h has used instead of 30 min for the hydrolysis of small nitrile compounds.[12] Throughout the entire reaction period, the system maintained heterogeneous and no apparent dissolution of the particles of the hybrid materials was observed.

The products were characterized with FT-IR spectroscopy in comparison with the materials before the hydrolysis. Figure 1 shows typical IR spectra of the hybrid materials before and after the hydrolysis under various conditions. For the sample with the organic content of 28 wt % before the hydrolysis (Figure 1a), the characteristic stretching bands of the C≡N and C=O groups from the acrylonitrile and methacrylate units appeared at 2242 and 1732 cm^{-1}, respectively. The broad bands at 1000–1200 cm^{-1} with the peak absorption at 1080 cm^{-1} are assigned to the Si–O (i.e., Si–O–Si and Si–O–C) stretching absorptions and that at 795 cm^{-1} to O–Si–O bending. After the hydrolysis for 2 h (Figure 1b), the intensity of the band at 2242 cm^{-1} for the nitrile (CN) group decreased significantly. A longer reaction time of 4 h (Figure 1c) resulted in a further decrease in the intensity of the nitrile band. A new strong band appeared at 1673 cm^{-1}, which can be assigned to the amide C=O stretching absorption. The absorption bands of the ester C=O, Si–O–C, and Si–O–Si remained essentially unchanged. These results indicate that the nitrile groups in the PAN–SiO_2 hybrid materials have been successfully converted to the water-soluble amide ($CONH_2$) groups. The ester groups in the methacrylate units remain largely intact during the hydrolytic reactions and therefore the new polymer chains containing amide groups are still immobilized in and linked to the silica matrix. It should be noted that there are some unhydrolyzed nitrile groups in the materials as evidenced by the residual absorption at 2242 cm^{-1} even after the reaction for 4 h (Figure 1c). We have also found that the conversion of nitrile to amide groups, as judged from the relative intensities of the residual nitrile band, is related to the organic–inorganic composition of the PAN–SiO_2 hybrid materials. An increase in the organic polymer content results in a relatively weaker nitrile absorption band and therefore a higher conversion. As shown in Figure 2, the nitrile band of the sample with the organic content of 58 wt % (Figure 2a) almost disappeared upon hydrolysis for 4 h (Figure 2b). This is probably because the hydrophilic reagents (e.g., H_2O_2) could more easily diffuse into the particles of the hybrid materials where there are more already formed hydrophilic amide groups after the reactions started.

The hydrolytic reactions were also carried out in a mixture solvent of DMSO and water (50/50, v/v) instead of that of acetone and water. The reactions appear to be faster with higher conversions of nitrile groups. As exemplified in Figure 2c, the hydrolysis in DMSO–water for only 2 h resulted in a nearly complete disappearance of the nitrile band at 2242 cm^{-1}. This observation could be interpreted based on the fact that DMSO is a good solvent for both the reagents and the organic polymer component in the hybrid materials so that the diffusion of the reagents into the materials should be facilitated leading to the faster reactions and higher conversions. Recently, a solvent-free method for hydrolysis of small nitrile compounds was reported.[15] By treatment with tetrahalophthalic acids, the nitriles could be chemoselectively hydrolyzed in the presence of ester groups. We attempted to apply this method in the hydrolysis of the PAN–SiO_2 hybrid materials and found it may not be desirable for our purpose. To obtain a good yield, this method calls for high reaction temperatures of 135–180 °C and excesssively long reaction time of 4–6 days.[15] At the temperatures above the melting point of the reagents (e.g., 152–154 °C for tetrafluorophthalic acid), the hybrid materials became brown-black in a few hours (e.g., 8 h), indicating that the polyacrylonitrile component in the materials is

---

(15) Rounds, W. D.; Eaton, J. T.; Urbanowicz, J. H.; Gribble, G. W. *Tetrahedron Lett.* **1988**, *29*, 6557.

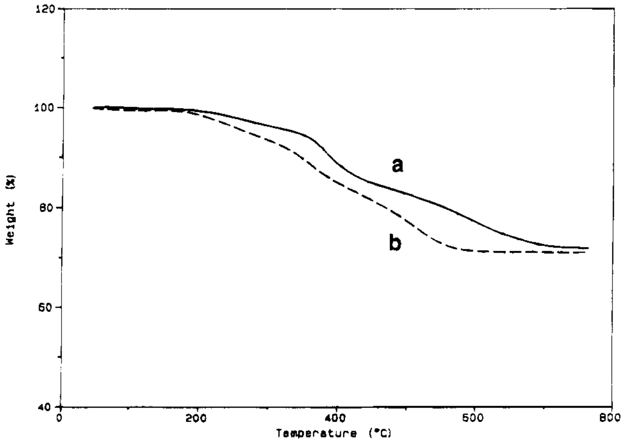


Figure 3. TGA curves of the polyacrylonitrile–SiO_2 hybrid sol–gel materials with SiO_2 contents of 72 wt % before (a) and after the treatment with H_2O_2–K_2CO_3 in acetone–water solvent for 4 h (b).

decomposed to form conjugated heterocyclic structures.[16] Currently, we are investigating the hydrolysis of the hybrid materials by tetrahalophthalic acids in the presence of solvents.

The water-soluble polyacrylics modified silica materials were further characterized by TGA technique in comparison with the PAN–SiO_2 hybrids before the hydrolysis. Typical TGA curves measured in air are shown in Figure 3 for a PAN–SiO_2 sample (a) before and (b) after the hydrolysis with H_2O_2–K_2CO_3 in acetone–water for 4 h. The organic polymer component in the hybrid materials decomposes in a temperature range of ca. 200–700 °C. The decomposition approaches completion at temperatures above 700 °C. The residual powdery substance after the TGA runs has no analyzable carbon or hydrogen content and its IR spectrum is essentially the same as SiO_2 glass. Therefore, the SiO_2 content in the hybrid materials can be measured as the weight remained at 750 °C in the TGA curves. The sample was found to have SiO_2 contents of 72 and 71 wt % before (Figure 3a) and after (Figure 3b) the hydrolysis, respectively. This suggests that about all of the organic contents were retained during the hydrolytic reactions. When the SiO_2 content in the PAN–SiO_2 hybrid materials was lowered, the hydrolysis was found to result in decreases in the organic content to some extent. For example, the PAN–SiO_2 sample with 61 wt % SiO_2 content lost about 10 wt % of its organic content after the hydrolysis. As illustrated in the structure **3** of Scheme 1, the covalent links between the polymer chains and the inorganic SiO_2 matrix are provided by the ester groups of the methacrylate units in the polymer. Since the hydrolysis may not be 100% chemoselective, some of the ester groups might have been hydrolyzed as well. Thus, some of the polymer chains might be no longer linked to the silica matrix and be leached out from the material resulting in the observed loss of the organic content. As the organic content is increased (i.e., the SiO_2 content is lowered) in the PAN–SiO_2 hybrid materials, there are fewer links between the polymer chains and the silica matrix and, therefore, more polymer chains may be leached out, leading to greater loss of the organic content.

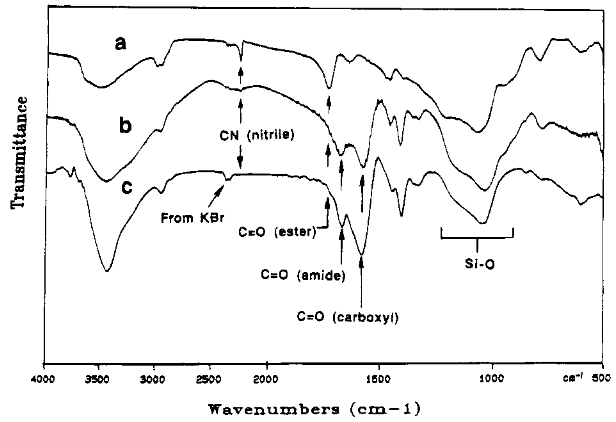


Figure 4. FTIR spectra of hydrolytic products of the polyacrylonitrile–SiO_2 sol–gel hybrid material with SiO_2 content of 39 wt % before (a) and after the treatment with 10% (b) and 20% (c) of aqueous KOH.

The hydrolysis of the PAN–SiO_2 hybrid materials to afford the water-soluble polyacrylics modified SiO_2 materials was also performed in aqueous KOH under various conditions. The finely ground powder of the PAN–SiO_2 hybrid materials was treated in 1, 10, 20, or 30 wt % KOH at 80 °C for 1 or 3 h. The product was isolated by precipitation in methanol after neutralizing the reaction with HCl solution at room temperature. Figure 4 shows representative IR spectra of the hybrid material with 39 wt % SiO_2 before (a) and after hydrolysis at various concentrations of KOH (b and c). After the hydrolysis, the nitrile band at 2242 cm^{-1} for the nitrile group almost disappeared (Figure 4c) or its intensity significantly decreased (Figure 4b). Two new characteristic bands appeared at 1673 and 1570 cm^{-1}, which can be assigned to the C=O stretching vibration bands in the amide ($-CONH_2$) and carboxyl ($-COO^-$) groups, respectively. Again, the absorption bands of Si–O groups remained at 1000–1200 cm^{-1}. On the basis of these observations, it is concluded that the hydrolysis of the PAN–SiO_2 hybrid materials in KOH solution affords the new materials with water-soluble $CONH_2$ and COO^- groups. Upon hydrolysis, the band at 1732 cm^{-1} showed a decrease in the intensity and was almost merged as a shoulder into the broad amide C=O band at 1673 cm^{-1} (Figure 4). This suggests that the ester groups in the methacrylate units were also hydrolyzed to some extent to form water-soluble methacrylic acid or salt units. Such a hydrolysis may be a minor reaction at the low KOH concentrations (e.g., 1 wt %) as further evidenced by the following TGA results: Figure 5 shows TGA curves on the PAN–SiO_2 sample with the original SiO_2 content of 39 wt % (i.e., the organic content of 61 wt %) before (a) and after hydrolysis at various KOH concentrations (b–d). For comparison, the silica gel derived from the sol–gel reactions of TEOS alone is also given (Figure 5e). In general, the loss of the organic content is greater than that with H_2O_2 catalysis system. However, most of the polymer chains still remain in the materials at low KOH concentrations, suggesting that some of the ester links survived the hydrolysis. For example, at 10 wt % KOH concentration, the organic content changed from 61 to 43 wt % with less than 30% loss (Figure 5b). As the KOH concentration is increased, the organic content

---

(16) (a) Peng, F. M. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley: New York, 1985; Vol. 1, pp 426–470. (b) Coleman, M. M.; Petcavich, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 821.

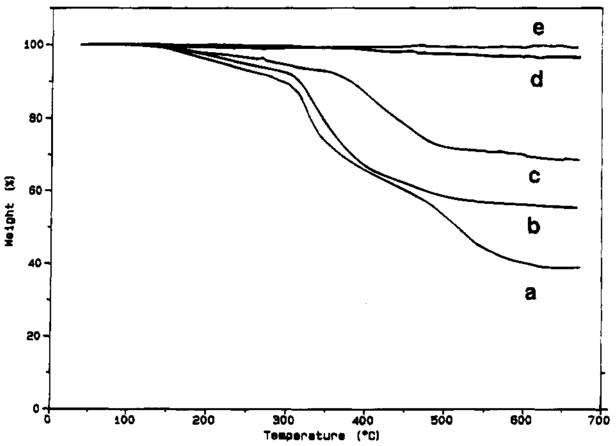


Figure 5. TGA curves of hydrolytic products of the polyacrylonitrile–SiO_2 sol–gel hybrid materials with SiO_2 content of 39 wt % before (a) and after the treatment with 10% (b), 20% (c), and 30% (d) of aqueous KOH. The TGA curve of the SiO_2 sol–gel material derived from TEOS alone is also shown (e).

decreases. When the PAN–SiO_2 hybrid materials were treated with 30% KOH solution, almost no organic component remained (Figure 5d), indicating the complete hydrolysis and removal of the water-soluble polymers from the SiO_2 matrices. It should be noted that the silica matrix could also be solubilized in strong base media.[17]

To limit the hydrolysis to the surface layers of the PAN–SiO_2 hybrid materials, we have also treated the monolithic samples with 1 wt % KOH at 80 °C for 1 h followed by neutralization, washing with water, and drying. Upon hydrolysis, the samples remained monolithic and transparent. The optical transparency suggests the absence of macroscopic organic–inorganic phase separation in the materials (i.e., the domain sizes should be at least lower than the wavelengths of visible light[1]). The diffuse reflectance FTIR showed the characteristic absorption band of the amide C=O groups at ca. 1673 cm^{-1}, indicating the hydrolysis on the surface of the sample. The surface property was further monitored by measuring the water contact angles before (θ_1) and after (θ_2) the hydrolysis. As demonstrated in Figure 6, the hydrolysis significantly increased the surface hydrophilicity of the hybrid materials as indicated by the decrease in the contact angles (i.e., $\theta_1 - \theta_2 > 0$). The higher polymer content in the materials leads to a greater extent (i.e., $\theta_1 - \theta_2$ value) of contact angle decrease. The decrease in the water contact angle upon hydrolysis is attributed to the presence of water-soluble carboxyl and amide groups on the surface of the hybrid materials.

In summary, we have successfully prepared a series of new water-soluble polyacrylics modified silica gels by hydrolysis of the polyacrylonitrile–silica hybrid materials. The hydrolytic reactions that convert nitrile groups to highly hydrophilic amide and carboxyl groups were carried out by treating the hybrid materials with H_2O_2 in the presence of K_2CO_3 or with aqueous KOH solution under various conditions. The treatment with H_2O_2–K_2CO_3 transformed the nitrile group to the amide groups with a good chemoselectivity, i.e., the ester groups in the polymer chains remained largely intact. The polymer backbones were still immobilized in the SiO_2 matrices. Conversions of the nitrile groups in DMSO–water solvent were higher than those in acetone–water solvent. The treatment with KOH also converted the nitrile groups to the amide and carboxyl groups without affecting the polymer backbones. At low KOH concentrations (e.g., 1 wt %), the polymer content in the product remained high. At high KOH concentrations, the loss of the polymer content in the materials was more significant, because the hydrolysis with KOH is not chemoselective as that with H_2O_2–K_2CO_3 and the ester groups in the polymer side chains might be hydrolyzed. The same hydrolytic reactions can also be used to increase the hydrophilicity of the surface of the PAN–SiO_2 hybrid materials. We are currently studying the ion transport and exchange properties of these polyacrylics-modified sol–gel materials and exploring their electrochemical and biochemical applications.

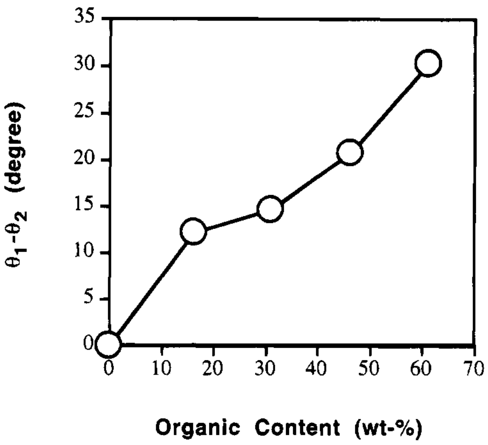


Figure 6. Relationship between the organic content and the charge in water contact angles of the polyacrylonitrile–silica hybrid materials before (θ_1) and after (θ_2) the KOH (1 wt %)-catalyzed surface hydrolysis at 80 °C for 1 h. The measurements were performed at 22 °C using triply distilled water with a droplet volume of ca. 0.05 mL.

Acknowledgment. We gratefully acknowledge the support of this work by the National Institutes of Health (Grant No. RO1-DE09848) and by E. I. DuPont de Nemours & Co., Inc. through a Young Faculty Award to Y.W. We thank the referees of this paper for many insightful comments and suggestions.

---

[17] Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry*; Wiley: New York, 1979.