

Photochemically Generated Polyacrylonitrile–Silica Nanocomposites: Optimized Fabrication and Characterization

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Nanocomposites of polyacrylonitrile in a porous silica matrix (Vycor) were generated by the photopolymerization of acrylonitrile inside the nanopores of the matrix. The amount of polymer incorporated could be controlled by photoinitiator concentration and by the irradiation time. Studies of the changes in pore volume and surface area of the matrix as a function of polymer loading lead to a model for pore filling in which the polymer forms plugs across the diameter of the pore, leaving closed void areas behind. The microenvironment of the polymer phase as related to the model for pore filling is investigated by the use of fluorescent probe molecules. Finally, the crystallinity and relative molecular weight distribution of the nanophase polyacrylonitrile are also reported.

There has been considerable interest in hybrid inorganic–organic polymer composite materials in which one of the composite phases is present in dimensions that are nanoscale or smaller.¹ This interest is driven by the unique properties of these materials, which can differ significantly from the components in their pure form or from composites in which both of the phases have macroscopic dimensions. In the case where silica constitutes the inorganic phase, many of these studies have focused on the dramatic enhancement in mechanical properties that is realized for organic polymers in which silicate nanoparticles have been dispersed.² At the other extreme, the incorporation of organic polymers into the nanoscale voids of layered and porous silica matrices has been explored for linear and nonlinear optical applications, holographic memory, and protective coatings.^{3–7}

Our own investigations into this latter category of materials have yielded polymer–silica nanocomposites through the photoinduced polymerization of vinyl and acetylenic monomers inside the pores of sol–gel-derived silica. This work has generated monolith silica-containing polyacetylene and low surface energy coating containing polyvinylidene fluoride.^{8,9} These studies have suggested that photopolymerization potentially affords

a significant degree of control over the placement of the polymer phase in the matrix through the application of photolithographic techniques. This could lead to the fabrication of engineered optical materials such as graded refractive index glasses and holographic storage media. We present here a study of the photoinduced incorporation of polyacrylonitrile in porous Vycor glass to produce a polyacrylonitrile–silica nanocomposite. Polyacrylonitrile was selected because it can be thermally reduced to carbon, which can ultimately afford carbon–silica nanocomposite materials. This study addresses some basic scientific aspects of the photochemical polymerization of acrylonitrile in a nanoporous environment with the goal of achieving control over the quantity and placement of the polymer phase.

Experimental Section

Acrylonitrile (Aldrich) was distilled immediately prior to use to remove the inhibitor. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and azobisisobutyronitrile (AIBN) were acquired from Acros and Aldrich, respectively, and used as received. 6-Propionyl-2-(dimethylamino)naphthalene (Prodan) was purchased from Molecular Probes and used as received. Porous 7930 Vycor disks, purchased from Chand Metallurgical, were cleaned in a tube furnace under O₂ at 500 °C and stored in an inert atmosphere box until used. All Vycor samples were from the same lot. The surface area and pore volume of the Vycor samples were determined through gas physisorption measurements.

Polymer Incorporation. Photopolymerization of acrylonitrile was accomplished with 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photocatalyst.¹⁰ Thermally initiated polymerization was accomplished using AIBN. In a typical polymerization, porous Vycor glass samples were taken from the 500 °C tube furnace under an O₂ atmosphere and evacuated to ~10^{−4} Torr. The samples were submerged in a N₂ degassed solution of 4 wt % initiator/acetone in the inert

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atmosphere of a glovebag. The acetone was removed under vacuum, leaving the initiator in the pores of the Vycor. The evacuated Vycor samples with initiator were transferred to a glovebox for weighing. Inside the glovebox the samples were placed into individual 50-mL Erlenmeyer flasks sealed with rubber septa to ensure an N_2 atmosphere. The distilled acrylonitrile solution was degassed with N_2 during this process. Then 5 mL of the degassed acrylonitrile was syringed into the flasks to submerge the Vycor samples. The flasks were then placed in front of the UV lamp equipped with a 324-nm cutoff filter for a period of 2.5, 5, 10, 20, and 30 min. The bulk polymer was removed from the Vycor samples and excess monomer was removed by placing the samples under vacuum. The polymerized samples were taken back into the glovebox for re-weighing. Reported weight gain per gram of Vycor is the average of three independent determinations; the reported error is the standard deviation of these measurements.

Gas Physorption. Nitrogen adsorption-desorption measurements were performed at 77 K with a Micromeritics ASAP 2010 sorptometer. Prior to measurement, all samples were degassed for 12 h at 110 °C. Adsorption and desorption isotherms over a range of relative pressure (P/P^0) of 0.01–0.95 were collected for all samples. Surface areas were determined from the Brunauer–Emmett–Teller (BET) equation in a relative pressure range between 0.01 and 0.10.¹¹ Pore volumes reported are single-point volumes.¹² Micropore surface areas were estimated from t-plot analysis in the range $0.30 < t < 0.50$ nm by use of the Harkins–Jura correlation.¹³ All isotherms are described using IUPAC nomenclature.¹⁴

Fluorescence Spectroscopy. Emission spectra were collected on a Spex Fluorolog II equipped with 0.22-m double monochromators (Spex 1680) and a 450-W Hg/Xe lamp. Excitation was through the halved face of a Vycor disk with emission collected at a right angle. All reported spectra were corrected for the lamp profile and the detector response. Spectra reported in wavenumber units were corrected for the band-pass variability in data collected at fixed wavelength resolution by application of the standard λ^2 multiplicative factor.¹⁵

Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. PAN was liberated from the Vycor matrix by dissolving it in aqueous HF. For mass spectrometry, 5 mg of polyacrylonitrile (PAN) was dissolved in 1 mL of *N,N*-dimethylformamide (DMF) (HPLC-grade Fischer Scientific, St. Louis, MO). Ten microliters of this solution was dissolved in 9:1 DMF:acetonitrile with 1 mM added sodium trifluoromethane sulfonate (98% Aldrich Chemical, Milwaukee, WI). The above solution was directly infused at a flow rate of 500 nL/min into a microelectrospray ionization source with an emitter voltage of 3.5 kV and a tube lens voltage of 0.37 kV.¹⁶ Ions were accumulated in the external octapole of a home-built 9.4-T electrospray ionization Fourier transform ion cyclotron resonance (ESI FT-ICR) mass spectrometer for 15 s prior to injection into an open cylindrical cell.^{17,18} The external rf-only octapole ion trap and rf-only octapole ion guide were set to 1.5 MHz at 153 V_{p-p}.¹⁹ Ions were transported to

the cylindrical cell, frequency-sweep-excited, and the time-domain signal was direct-mode-detected. Data were collected with a MIDAS 160 Data station.^{20,21} A time-domain signal consisting of 36 co-added transients was zero-filled once, Hamming-apodized, fast Fourier-transformed followed by magnitude-mode calculation, and frequency-to- m/z converted by the usual two-term calibration equation.^{22,23} The polymer ion mass for each ion distribution was calculated by MIDAS analysis version 3.10b.²⁰

CHN Analysis. Performed on a CE Instruments ThermoQuest NC 2500.

XRD Analysis. The X-ray diffraction measurements were performed with Ni-filtered Cu K α radiation using a Siemens D500 diffractometer with a diffracted-beam graphite monochromator.

Results and Discussion

A principal goal of this study is to understand how the polyacrylonitrile (PAN) fills the nanopores of the matrix upon photopolymerization and to establish the conditions under which a maximum filling can be realized. Further, it is important to determine whether varying specific parameters of the polymerization process can control the amount of polymer incorporated into the matrix. Porous Vycor glass was used because of its relatively narrow and consistent pore size distribution, which has an average diameter of 9.95 nm and a total pore volume of 0.218 cm³/g (as determined from gas physisorption).

Prior studies of the thermal polymerization of methyl methacrylate in porous Vycor have suggested that relatively complete pore filling can be realized simply by submerging the monolith into a solution of the monomer and catalyst and then heating to initiate polymerization.²⁴ Similar results are observed with acrylonitrile in Vycor. In particular, two Vycor monoliths were weighed and then immersed in an acrylonitrile solution containing 1% azobisisobutyronitrile (AIBN) for a period of 20 min. At the end of this time, one sample was removed from the solution while the other was left submerged. Both samples were then heated to 70 °C for a period of 12 h to initiate the polymerization. After polymerization, the monolith that had been removed from the solution was evacuated (10^{-3} Torr) for a period of 30 min to remove unreacted monomer and then weighed. On the basis of the pore volume of Vycor and the density of bulk PAN (1.184 g/mL), complete filling of the available pore volume should result in a weight gain of approximately 0.237 g of polymer per gram of Vycor.²⁵ Weight gain in the PAN/Vycor polym-

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erized while not immersed in the monomer solution was small (3.13%), indicating that little polymer incorporated. Consistent with the small weight gain, gas physisorption measurements indicated that the available pore volume had decreased by less than 0.6% from that of the Vycor control. For the immersed sample, meaningful weight gain data could not be obtained since the sample was encased in polyacrylonitrile; however, gas physisorption measurements of a powdered monolith yielded only slight adsorption and an isotherm that was essentially of Type II, which is characteristic of a nonporous solid (single-point pore volume was 0.006 cm³/g). These results indicate that, for acrylonitrile, reliance on monomer-catalyst diffusion into the pores to create a nanoscale polymer phase results in complete pore filling only when the monolith is totally submerged. The requirement that a constant source of monomer be present during the polymerization process to realize complete pore filling arises in large part from the fact that the polymer is significantly more dense than the monomer. As the polymerization proceeds, new monomer is required to fill the void produced from the density change. In the case of acrylonitrile, the polymer occupies only 68% of the volume occupied by the monomer. The obvious disadvantage to forming composites by immersing the monolith in the monomer is that the final materials will necessarily be encased in bulk polymer.

Initially, control studies carried out with DMPA at 4 wt % in neat deaerated acrylonitrile showed efficient polymerization with broadband irradiation ($\lambda \geq 320$ nm). To form nanocomposites, polymerization was carried out in Vycor monoliths immersed in neat deaerated acrylonitrile. However, since the polymerization was photoinitiated, bulk polymer could be prevented from encasing the monolith by depositing the catalyst separately into the pores of the Vycor and carrying out the irradiation under carefully masked conditions to prevent light from hitting the bulk solution. Catalyst impregnation into the Vycor was accomplished by immersing the monolith in a solution of DMPA in acetone (10 min) followed by evaporating the solvent at 50 °C under vacuum (10^{-3} Torr) to leave the catalyst behind in the pores. The catalyst-impregnated monolith was then immersed in deaerated acrylonitrile for a period of 2 min and then irradiated. This approach worked well, yielding reproducible polymer incorporation with little polymer formation observed in the surrounding solution or adhering to the outside of the monolith.

To evaluate the effects of photoinitiator concentration, Vycor samples were immersed in acetone solutions containing 0.5, 1, 2, and 4 wt % DMPA. For the 4% solution, evaporation of the solvent would be expected to leave 6.4 mg of DMPA per gram of Vycor (calculated from the available pore volume of the Vycor and the concentration of the photocatalyst solution), which corresponds to 0.49 wt % C. Elemental analysis of this material after removal of solvent yielded 0.58% carbon, which suggests that slightly more catalyst is left behind in the matrix. This is probably due to some selective adsorption of the DMPA to the walls of Vycor during infusion of the solution. Following the protocol outlined above, the samples were immersed in a neat, degassed volume of acrylonitrile. Photoinitiation in the monolith was carried out at fixed intensity for a period of 30 min.

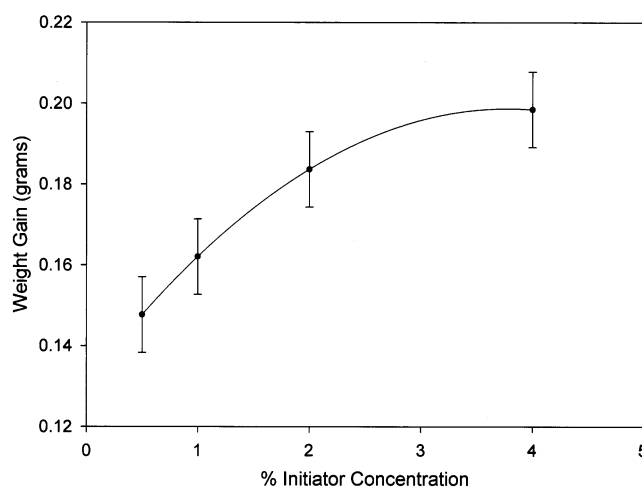


Figure 1. PAN weight gain per gram of Vycor as a function of DMPA concentration (irradiation time: 30 min).

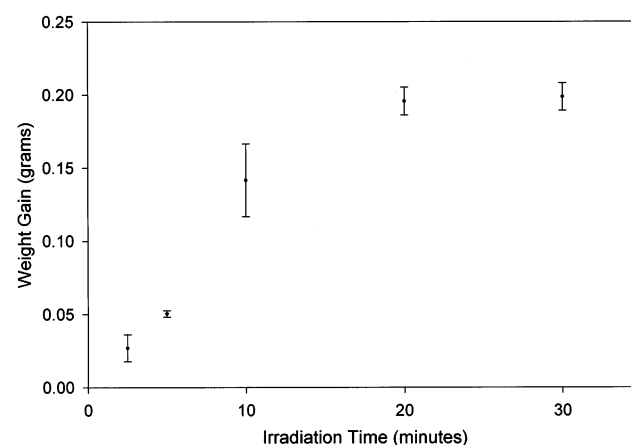


Figure 2. PAN weight gain per gram of Vycor as a function of irradiation time (4% DMPA).

The uptake of polymer, measured by the weight gain of the monolith, increases nonlinearly as a function of starting photoinitiator concentration (Figure 1). A maximum weight gain of 20.9% was attained with a 4% catalyst solution. Gas physisorption analysis of this nanocomposite indicates that approximately 95% of the available volume is filled under these conditions. Using monoliths impregnated with 4 wt % solutions of DMPA, a series of polymerizations were carried out under fixed conditions and intensity but for varying irradiation times. The weight gain associated with each irradiation time, averaged over five independent determinations, is shown in Figure 2. From these data it can be seen that, under these conditions, incorporation of polymer increases with irradiation time up to 20 min, after which little change is observed. Significantly, for most irradiation times the standard deviation in the polymer uptake for multiple irradiation times is not excessively large (<10%), suggesting good reproducibility. Taken together, these results imply that good control over polymer incorporation is attainable photochemically.

The porous properties of the range of nanocomposites generated in this manner were analyzed by gas physisorption. Isotherms for the series of PAN loadings obtained at various irradiation times are presented in Figure 3. The isotherms are all of Type IV and the series shows a steady decrease in gas adsorption as a function of polymer filling. Control isotherms of pure bulk PAN

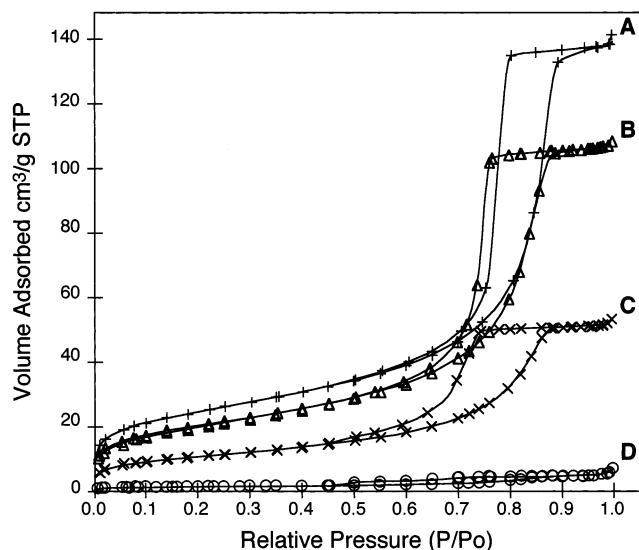


Figure 3. Gas physisorption (N_2) Isotherms of (a) Vycor, (b) 2.69% PAN/Vycor, (c) 14.16% PAN/Vycor, and (d) 19.87% PAN/Vycor.

samples are of Type II and show very little adsorption by nitrogen, suggesting that we are primarily observing adsorption to the available silica pore. The maximum polymer loading that was attained through photopolymerization was 0.209 g of polymer per gram of Vycor. If the density of bulk PAN is used, this mass would be predicted to occupy 88% of the available pore volume of a gram of Vycor. However, the measured single-point pore volume from gas physisorption indicates that in excess of 95% of the pore volume has been filled. A plot of the weight gain versus the single-point pore volume shows the relationship to be linear (Figure 4a). The magnitude of the slope of the line in Figure 4a is equal to the inverse of the density. Weighted regression analysis of the data yields an apparent density of 0.927 ± 0.042 g/mL, which differs from the measured density of the bulk by 20%. This suggests that either a less dense polymer phase is formed in the nanopores or that some of the available pore volume becomes inaccessible to gas physisorption, thereby giving a lower apparent density for the polymer phase (or some combination of these factors).

Other details of nanopore filling by PAN can be elucidated from the quantities calculated from the gas physisorption data. In particular, even though the pore volume decreases linearly with polymer incorporation, the average pore diameter remains relatively constant at around 9.6 nm. In addition, there is a linear decrease in the BET surface area with polymer uptake (Figure 4b). Considering the details of how the pores are likely to fill, these results are counterintuitive. Assuming cylindrical pores (which is a good approximation for Vycor), if polymerization occurs from the center going out, with the polymer strands filling the pores longitudinally (as has been proposed for PMMA-silica nanocomposites), then the surface area should remain constant or, depending on the adsorption properties of the polymer, increase, particularly during the early stages of filling.^{26,27} Conversely, if polymer growth starts on

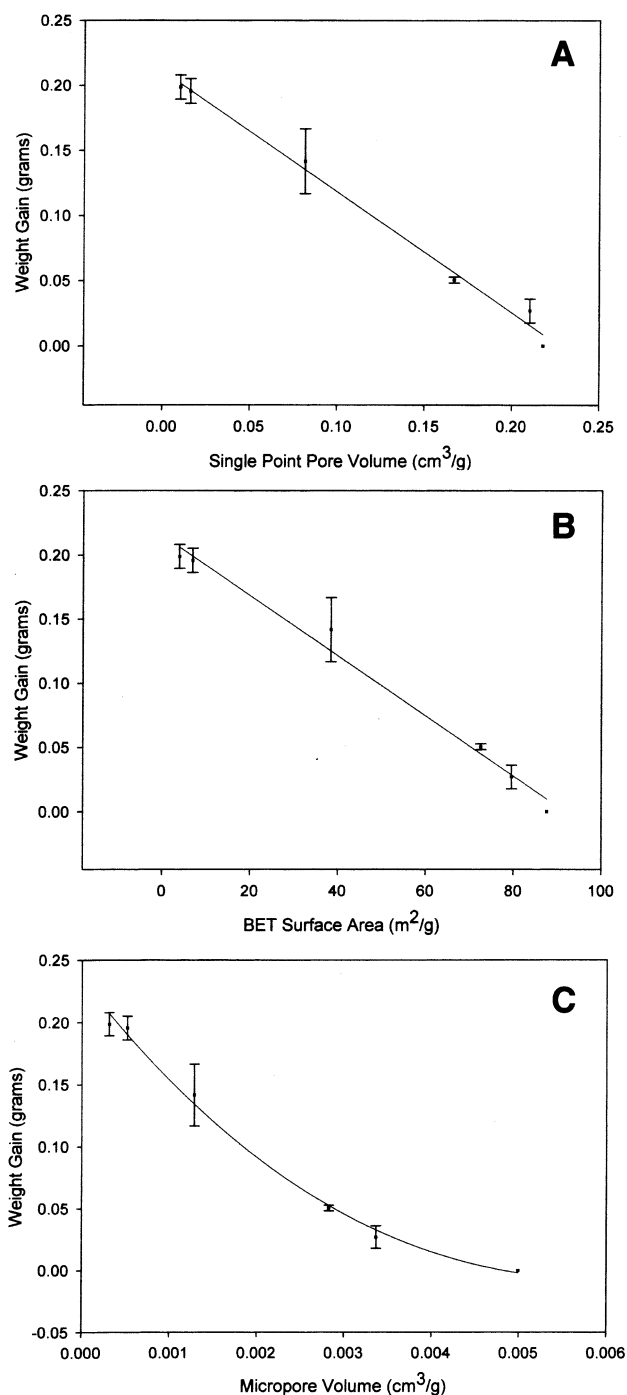


Figure 4. (a) Pore volume as a function of PAN uptake. (b) Surface area (BET) as a function of PAN uptake. (c) Micropore volume as a function of PAN uptake.

the surface of the pore and moves inward, the surface area should decrease approximately as the square root of the pore volume (assuming a cylindrical pore of decreasing radius). Intermediate models with polymer growth from a portion of the wall would follow other functional forms but none of them should show a linear dependence. Finally, a plot of the micropore volume, obtained from the t-plot, as a function of irradiation time (Figure 4c) shows a strongly nonlinear dependence that, empirically, is well fit by an exponential. This indicates

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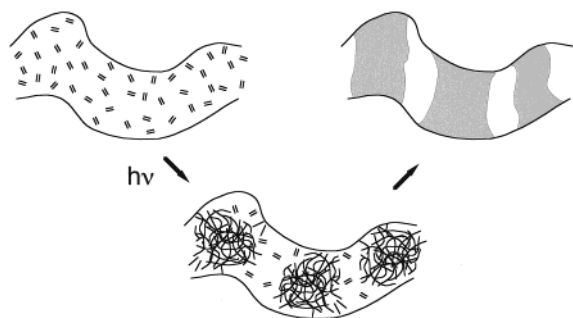


Figure 5. Model of pore filling in Vycor showing the depletion of monomer from the surrounding regions and the formation of polymer plugs and void spaces.

that the micropore region fills preferentially and is largely consumed in the early stages of the polymerization.

A model for nanopore polymer filling that explains these observations is shown schematically in Figure 5. Upon photoinitiation the polymer growth starts in a region of the pore and, in doing so, depletes monomer from the surrounding regions. This depletion both limits polymer growth in the longitudinal direction and creates void spaces. The polymer filling then occurs across the pore diameter to the wall. This model for pore filling through the formation of a series of discontinuous polymer plugs, depending on the average length of the plug, could yield a linear decrease in both surface area and pore volume. This model also explains why the average pore diameter remains constant as the pores are filled since the void space that was created during polymerization will have same pore diameter as the matrix. Finally, since some of this void space may be closed (trapped between polymer plugs), this could contribute to the lower apparent density of the polymer in the nanocomposite.

To further probe the microstructure of the composite material, we have employed the highly solvatochromic fluorescent molecule 6-propionyl-2-(dimethylamino)-naphthalene (Prodan).²⁸ This dye molecule has been applied previously to polymer–silica nanocomposites to probe their microenvironments by correlating the energy of the fluorescence with the dielectric properties of the medium in which the dye is dispersed. Figure 6 shows the emission bands and Table 1 compiles the emission maxima for Prodan in various independent components of the Vycor–PAN system and for the nanocomposite itself. For Prodan dissolved in neat acrylonitrile the emission maximum lies at 22 123 cm^{-1} ; however, upon infusion of this solution into the pores of the Vycor, the maximum shifts dramatically to lower energy ($\lambda_{\text{max}} = 20\,346\,\text{cm}^{-1}$) and there is no significant spectral overlap with the Prodan in acrylonitrile. Subsequent removal of the acrylonitrile from the pores by drying at 50 °C results in only a small hypsochromic shift in the emission energy, suggesting a slightly less polar environment. Clearly, even though the 9-nm pores of the Vycor are, in principle, large enough to contain completely solvated Prodan molecules, the spectra indicate that the dye interacts strongly and preferentially with the matrix. The origin of this preferential interaction

Relative Intensity Vs. Wavenumber

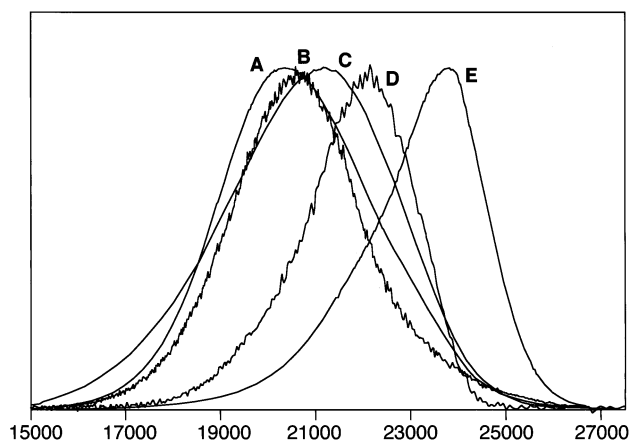


Figure 6. Emission spectra of Prodan in (a) acrylonitrile in Vycor, (b) Vycor (dry), (c) PAN/Vycor composite, (d) acrylonitrile solution, and (e) bulk PAN.

Table 1. Emission Maxima of Prodan in Various Environments Related to the PAN/Vycor System

environment	emission maximum (cm^{-1})
acrylonitrile	22123
acrylonitrile/Vycor	20346
Vycor (dry)	20570
PAN/Vycor	23781
bulk PAN	21142

and the concomitant spectral shift comes from strong specific interactions of the Prodan molecule with the hydroxyls on the surface of the silica. Such interactions have been reported previously in solvatochromism studies comparing protic and aprotic solvents.²⁹ They have also been observed in silica xerogels derived from tetramethyl orthosilicate.²⁷ After photopolymerization of an acrylonitrile/Prodan solution in the nanopores, the emission maximum shifts to 23 781 cm^{-1} , which suggests a less polar environment. The emission band itself (Figure 6) is quite symmetric but broad with a full-width at half-height of 3713 cm^{-1} . In comparison, Prodan dispersed in bulk polymer has a emission maximum at 21 142 cm^{-1} (Figure 6), indicative of a much less polar environment and, further, is quite asymmetric with a low-energy tail extending down to $\sim 19\,000\,\text{cm}^{-1}$. The Prodan emission band in the composite has significant overlap with the emission envelope of Prodan interacting with the silica surface (either dry or with acrylonitrile present), which suggests that the dye is still associated with the silica wall and is either trapped at the interface between the silica walls and the polymer phase or is in vacancies (or some combination of both of these). While the broad emission band of the dye in the composite does overlap somewhat with its emission band in pure polymer, the limited amount of overlap and the symmetry of the emission in the composite suggests that, at best, only a small amount of dye is dispersed into the polymer nanophase. These fluorescent probe results differ somewhat from prior results on poly(methyl methacrylate) composites, which finds dispersion into the polymer phase; however, this difference probably arises both from the difference in monomer and because the Vycor/PAN materials are

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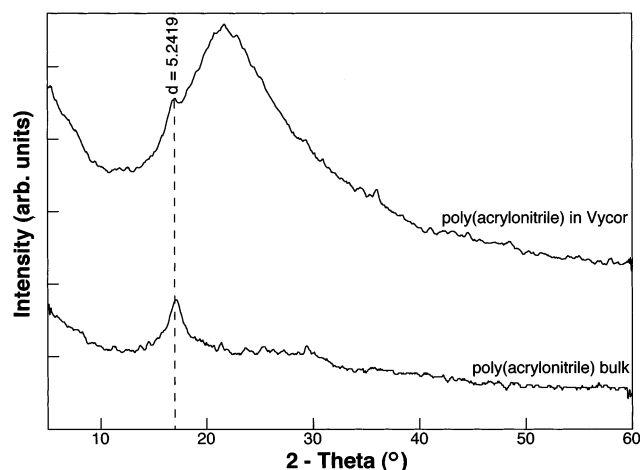


Figure 7. XRD of PAN in Vycor and of bulk photopolymerized PAN.

polymerized at room temperature, thereby suppressing thermal diffusion processes.²⁷ Notably, these results are completely consistent with the model for polymer filling proposed for these materials, though they certainly do not prove that model.

Properties of Nanoconfined PAN. It is of interest to compare the properties of PAN generated in the nanoscale confines to those of the bulk. Bulk PAN generated from thermal polymerization is a crystalline polymer with a characteristic X-ray diffraction peak at $d_{hkl} = 5.156 \text{ \AA}$.³⁰ An identical diffraction peak was found to be present in control samples of photopolymerized PAN (Figure 7), indicating similar crystallinity. It might be anticipated that the restrictions of the nanoscale

pores would inhibit the formation of crystallites in the nanocomposite. This is not the case; X-ray analysis of a PAN–Vycor nanocomposite (20.9% loading) shows the characteristic diffraction peak, resolved as a shoulder on the broad amorphous scattering peak due to the Vycor matrix (Figure 7). Clearly, the polymer does form some crystallites, even in the constraints of the 9-nm pores.

Finally, it is reasonable to suggest that the molecular weight of the polymer that forms in nanoconfinement will have a lower average molecular weight distribution. To determine this, the polymer phase was isolated by dissolving the matrix in HF and collecting the remaining solid. The isolated polymer was then investigated by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR). Figure 8 shows the ESI FT-ICR mass spectra for PAN produced by photopolymerization outside the glass monolith and the nanophase PAN recovered from the monolith. Both samples contain numerous chemically distinct species, but the spectral resolution (average resolving power $\sim 45\,000$) allows for the determination of each polymer ion distribution's charge state, based on the spacing between species differing by ^{13}C vs ^{12}C .³¹ Qualitatively, the two spectra are similar, but close examination of each reveals important details. The bulk PAN spectrum shows more ions between $1400 < m/z < 1600$ than the nanophase PAN spectrum. In this region the $5+$ ions predominate, corresponding to $[(\text{PAN})_n + 5\text{Na}]^{5+}$ ($n = 115\text{--}125$) ions in both the standard and sample. In the bulk PAN the ion distribution extends above $1800 \text{ } m/z$, corresponding to $[(\text{PAN})_n + 4\text{Na}]^{4+}$ ($n = 115\text{--}125$) ions. Few if any doubly, triply, or quadruply charged ions are

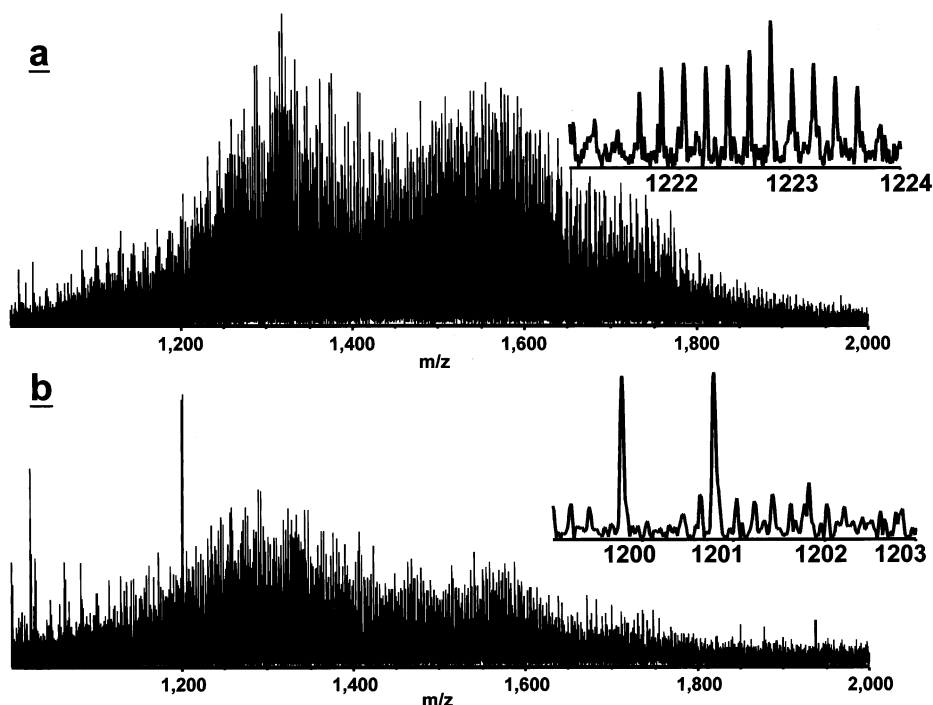


Figure 8. ESI FT-ICR mass spectra of PAN with added sodium trifluoromethane sulfonate. Top: Control PAN sample produced outside the Vycor monolith. The apparent bimodal distribution is in fact due to two charge state envelopes ($4+$ and $5+$) for the same sets of polymers (see text). The accompanying inset is an expansion around m/z 1223, showing an $[\text{M} + 5\text{Na}]^{5+}$ ion. Bottom: PAN sample produced from inside the Vycor. The centroid for the polymer distributions shifts to the left, indicating a higher quantity of lower molecular weight species. The accompanying inset shows low-molecular-weight singly charged ions around m/z 1202.

observed in that spectrum. Thus, the apparent multiple distributions in this spectrum are due to the multiple charge states rather than an unusually large polymer polydispersity. When the charge states of the polymer produced outside of the glass are taken into account, the PAN number-average molecular weight becomes 6400.3 Da.

The nanophase PAN shows interesting low-mass species that are not present in the control PAN. The spectrum (figure inset) reveals singly charged low-mass polymers. If only the 5+ and 4+ charge states are included, we obtain a number-average molecular weight of 6310.0 Da. However, taking the lower mass ions into account lowers the number-average molecular weight to 5397.5 Da, which is consistent with a lower average molecular weight for the nanophase PAN. It should be emphasized, however, that the molecular weight distribution observed through FT-ICR-MS does not represent the absolute molecular weight distribution of the polymer (which is, in general, much larger) but the distribution of the polymer that can be taken into the gas phase through electrospray. Notwithstanding this, the relative distributions suggest that polymerization within the nanopores limits polymer growth. This lower molecular weight distribution in all likelihood contributes to the lower apparent density determined for the nanocomposite from gas physisorption measurements.

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Conclusion

This study has provided some insight into the photochemical generation of polyacrylonitrile–silica nanocomposites. We have observed that high loadings of polymer can be incorporated into the silica matrix and, more importantly, that the amount of polymer phase incorporated can be controlled by the catalyst concentration and the irradiation time. This has allowed us to measure the pore volume and surface area as a function of the amount of polymer incorporation. These measurements show a linear decrease in both quantities as a function of polymer loading, which indicates that the apparent density of the incorporated polymer is significantly less than the bulk. These results have been interpreted in terms of a model for pore filling involving the formation of discontinuous polymer plugs that span the pore. The formation of these plugs can account for the linear decrease in pore volume and surface area and also indicates one possible origin of the apparent decrease in polymer density through the formation of inaccessible nanovoids. In addition, removal of the polymer from the matrix and measurement of the molecular weight distribution indicates that the polymer formed in the nanopores has a lower average molecular weight than bulk polymer formed under the same conditions. This lower molecular weight suggests that the polymer is, in fact, less dense, which suggests that several factors may contribute to the overall properties.

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