Conductive Thin-Film Composite Hydrogels: Trapping an Anionic Polyelectrolyte in a Polyaziridine Host Matrix

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Acid-catalyzed polymerization of sufficiently concentrated aqueous solutions of a trifunctional aziridine monomer affords hydrogels. Dynamic mechanical analysis has been used to demonstrate that composite hydrogels, obtained when the polymerization is effected in the presence of poly(sodium styrenesulfonate), have a composition dependent modulus. A region rich in the polyelectrolyte has a modulus which exceeds that of the "host" homogeneous polyaziridine hydrogel. This is consistent with ionic bonds between protonated sites on the polyaziridine matrix and sulfonate groups on the included polyelectrolyte augmenting the structural stability of the hydrogel. Thin films were prepared from coatings of the incipient hydrogel solutions. When the coatings are dried to a water content of 20%, water-insoluble thin films are obtained provided a critical weight fraction of the monomer is exceeded. Conductive thin films can be obtained, provided a critical weight fraction of polyelectrolyte is exceeded. FTIR analysis of the coatings in the attenuated total reflectance mode shows that conductivity increases as tight ion pairing decreases between the polyelectrolyte and its counter ions in the matrix. The S-shaped dependence of the normalized conductivity on the composition of the thin films is independent of the state of hydration of the film. Effective medium percolation theory, (EMPT), generally fits the S-shaped compositional dependence of the conductivity but overestimates the rate of growth of the conductivity beyond the critical point.

Introduction

Hydrogels have been characterized as infinite three dimensional polymeric networks which contain considerable amounts (e.g., >20%) of water. Hydrogels having pendent ionizable groups have been reviewed and their methods of synthesis summarized.[1] We describe a method to prepare these materials which has yielded novel hydrogels. Our approach employs an acid polymerizable trifunctional aziridine monomer[2−4] to entrap anionic polyelectrolytes, e.g., sodium poly(styrenesulfonate). Composite hydrogels are formed when the monomer is polymerized in the presence of the polyelectrolyte. Since polymerization of the monomer itself affords a hydrogel, the question arises as to whether the polyelectrolyte is merely a passive guest, topologically trapped in the host polyaziridine matrix, or actively contributes to the strength of the hydrogel. The mechanical strength of the hydrogels as a function of composition was determined by DMA to distinguish between the possibilities.

Thin films can be obtained by coating the incipient hydrogel solutions onto support materials. On drying, clear and colorless coatings are obtained. The properties of the thin-film coatings are critically dependent on composition. Provided the weight fraction of monomer exceeds a critical value, the coatings are immune to water wash. Provided the polyelectrolyte exceeds a critical weight fraction the coatings are conductive.

Conductive, water-insoluble thin films of covalently cross-linked polyelectrolytes have found application as antistatic coatings.[5] These coatings have generally employed minimal levels of trifunctional cross-linking agents which have not been regarded as a potential host phase for the polyelectrolyte.

Experimental Section

Chemicals. A commercially available trifunctional aziridine monomer was used, pentaerythritoltris[β-(N-aziridinyl) propionate], available as XAMA-7 from Sanncor Ind., Leominster, MA. The monomer was analyzed at 6.51 meq of aziridine/g or at 92.7% of theory and used as is.[6] The anionic polyelectrolyte used was poly(sodium styrenesulfonate), NaPSS, M_w= 500 000, available from National Starch Corp. as Versa TL 78-7063.

Gels. Ten gel samples were prepared. Sample compositions were obtained from a distance based mixture design selected using Design-Expert software.[7] See the Results and Discussion for composition constraints (%water, %monomer, %polyelectrolyte) [log modulus]: (77.5, 5.0, 17.5) [3.41], (60, 15, 25) [4.65], (60, 27.5, 12.5) [6.32], (72.5, 27.5, 0) [4.98], (60, 40, 0) [5.62], (85, 5, 10) [4.28], (85, 15, 0) [5.32], (66, 28, 6)

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[6.52], (70, 5, 25) [2.91], (72, 16, 12) [6.31]. Solutions at the above compositions were adjusted with stirring to pH 9.0 by addition of 3 N sulfuric acid, and aliquots were rapidly transferred to sealable plastic vials.

Gelation of the solutions occurred shortly after the transfer and moduli were determined after 2 weeks aging in the sealed vials at room temperature.

Thin Film Coatings. A (50/50 w/w) solution of the monomer was prepared in anhydrous isopropanol at 20 °C. A quantity of this solution necessary to give the appropriate weight fractions[8] of the monomer was added, with stirring, to an acidified 2% aqueous solution of the polyelectrolyte. Sufficient 3 N sulfuric acid was added to give a final solution pH = 7.5. (An equimolar amount of ammonium sulfate can be used in place of the sulfuric acid.) The aqueous polyelectrolyte solution contained 0.1% Olin 10G nonionic surfactant as a coating aid. Solutions were coated within 1 min of mixing. Substrates for the coatings were PE coated paper available from Schoeller-Tech, Pulaski, NY, and gelatin subbed PET film base from Eastman Kodak, Rochester, NY. Hand coatings were prepared using a #24 wire rod.[9] Machine coatings were prepared via a cascade coater. Coatings were water washed by immersion at a flow of 10 L/min for 2 min. Film thickness was determined by optical microscopy.

Dynamic Mechanical Analyzer (DMA). The mechanical strength of the hydrogels was studied using a Perkin-Elmer DMA-7 dynamic mechanical analyzer. All tests were run isothermally at 20 °C with a 5mm diameter parallel plate. To accommodate the wide range of moduli, the creep recovery mode was used. The creep stress was set at 141 Pa for 4 min, and the recovery stress was set at zero. The modulus reported is the maximum value of the creep modulus, *G*, during the test interval.

FTIR Spectra. Spectra of thin films were recorded using a Nicolet Magna-IR 550 Spectrometer. Coated samples were recorded in the ATR mode using a Spectra-Tech contact sampler with a 45° ZnSe flat sampling plate and a Gripper sample clamp.

Surface Resistivity/Conductivity. Surface resistivities, ϱ (Ω/sq), of thin films were measured as a function of weight fraction NaPSS (X), using a Hiresta-IP resistivity meter (Mitsubishi Petrochemical Co.) using the HR100 probe. All readings were taken in a controlled-humidity chamber after conditioning for 4 h at either 50% RH or 30% RH. (X, $\log \varrho_{50}$, $\log \varrho_{30}$): (0.0, 13.623, 14.146), (0.1, 13.415, 13.833), (0.2, 13.415, 13.799), (0.3, 12.591, 13.255), (0.4, 11.176, 12.079), (0.5,10.633, 11.591), (0.6, 9.732, 10.544), (0.7, 9.462, 10.176), (0.8, 8.785, 9.322), (1.0, 8.000, 8.756). Plotted conductivities, σ $(\Omega/\mathrm{sq})^{-1}$, are the reciprocals of the measured surface resistivities.

Haze. Haze levels were determined with a Gardener haze meter.

Results and Discussion

Hydrogels. Gel strength as a function of gel composition is illustrated in the map of the log creep modulus shown, (Figure 1). The compositional range of the map was constrained by a variety of factors. The weight percent water in the formulation of the gels ranged from 60 to 85%, since higher water content compositions did not gel and lower water content mixtures were difficult to stir. The trifunctional aziridine monomer content ranged from 5 to 40% as lower weight percents of the monomer did not afford gels. The NaPSS weight percent ranged between 0 and 25% as higher weight percents were difficult to stir. Within the bounds of these constraints a 10-point mixture experimental design was selected (see Experimental Section). Solutions at the design composition points were mixed, and aliquots were rapidly transferred to sealable plastic storage capsules where they gelled. Creep moduli were determined after 2 weeks of aging, and the design space was fitted to a regression model.

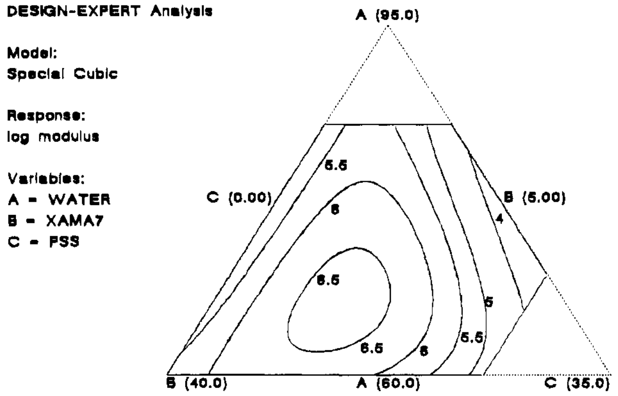

Figure 1. Logarithm of the creep modulus, log *G*, as a function of initial composition in weight percent. Plotted are the maximum values of log *G* determined from a creep recovery in parallel plate experiment run 4 min isothermally at 20 °C. The creep stress was 141 Pa. The experiment was a 10-point distance-based mixture design, and the data were fit to the special cubic model in the three composition variables.

In Figure 1, consider that at constant weight percent monomer, the polyelectrolyte is replaced solely by water as the weight percent polyelectrolyte decreases. Since gels formed even where the polyelectrolyte was completely replaced by water, we regard the polyelectrolyte as a guest in a host polyaziridine matrix. That is, at a sufficiently high fixed weight percent monomer an infinite three-dimensional polyaziridine network forms which may optionally include the polyelectrolyte. The polyelectrolyte is not a passive guest, however, as an interaction between the host and the polyelectrolyte which strengthens the gels is evident from the behavior of the modulus at constant weight percent water. Gel strength is optimal, at a fixed weight percent water, for compositions which include the polyelectrolyte. The increased gel strength is attributed to the formation of ionic bonds between protonated sites on the polyaziridine host and the negatively charged sulfonate groups of the included polyelectrolyte. Given the poor nucleophilicity of the sulfonate group, strengthening of the network via covalent bond formation between the monomer and the polyelectrolyte is unlikely.[10]

Thin-Film Hydrogels. Thin-film coatings were prepared by coating dilute solutions of the monomer, polyelectrolyte, and acid catalyst on a corona treated polyethylene substrate.[11] Coatings were air dried to a water content of 20% and were on the order of 1 μm thick. Control coatings were prepared from solutions having only the monomer and catalyst and from a solution with only the polyelectrolyte. The coatings were washed with deionized water. FTIR spectra, in the ATR mode, were taken of the thin-film coatings prior to and after washing (Figure 2). These spectra clearly revealed that the coated monomer polymerized and was immune to water wash, whereas the polyelectrolyte

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(8) Weight fraction of coated matrix solids.The weight matrix solids is the sum of the weights of the monomer and the anhydrous polyelectrolyte, 1.35 g/m^2.

(9) RDS Corp., Webster, NY.

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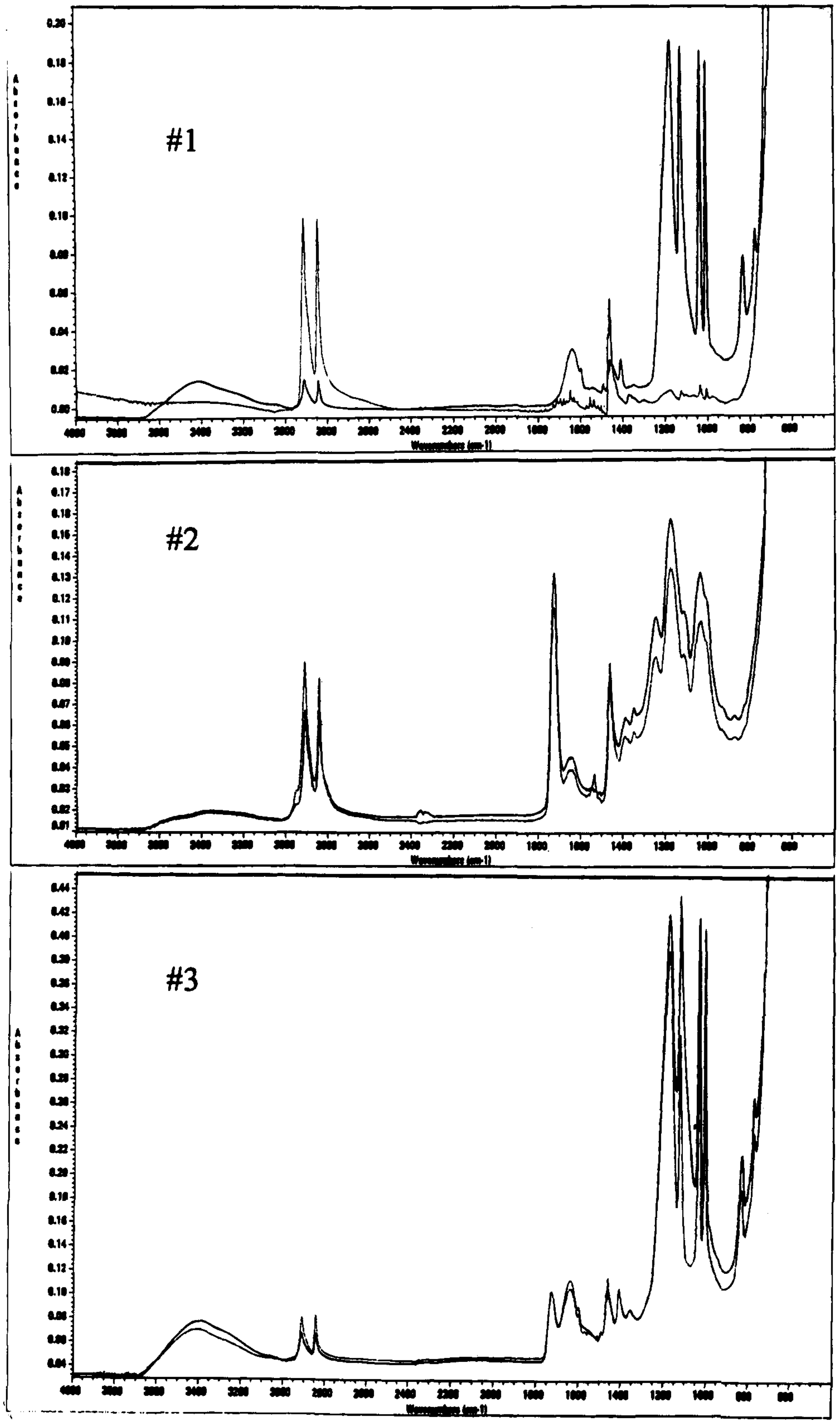

Figure 2. FTIR spectra, in the ATR mode, of thin film coatings on a corona-treated polyethylene substrate. The spectra were recorded pre and post water wash. The postwash spectra are the lower traces. (1) Sodium poly(styrenesulfonic acid); (2) Polymerized monomer; (3) Composite at 0.46 weight fraction monomer. The polyelectrolyte itself washes off whereas the polymerized monomer and composite coatings are immune to water wash.

coating was washed off. In composite coatings having sufficient monomer, the polyelectrolyte was retained through the water wash, entrapped by the polymerized monomer. To quantify the level of monomer sufficient to retain the polyelectrolyte, a 4 μm thick gelatin indicator layer was coated over the dried matrix. Figure 3 is a plot of measured haze against weight fraction monomer in the matrix. Cross sections of the clear composite coatings, with a monomer weight fraction in excess of 0.15, reveal a distinct hydrogel layer under a

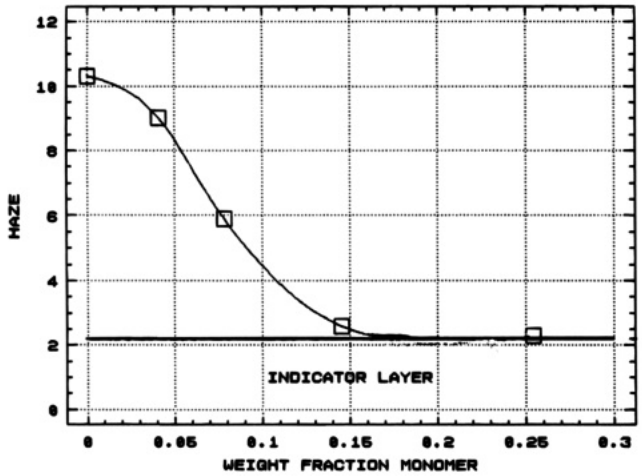

Figure 3. Haze as a function of weight fraction monomer in the hydrogel layer. A 4 μm indicator gelatin layer is coated over a previously coated and dried 1 μm hydrogel layer. At weight fractions of monomer greater than 0.2 the composite is as clear as the indicator layer alone.

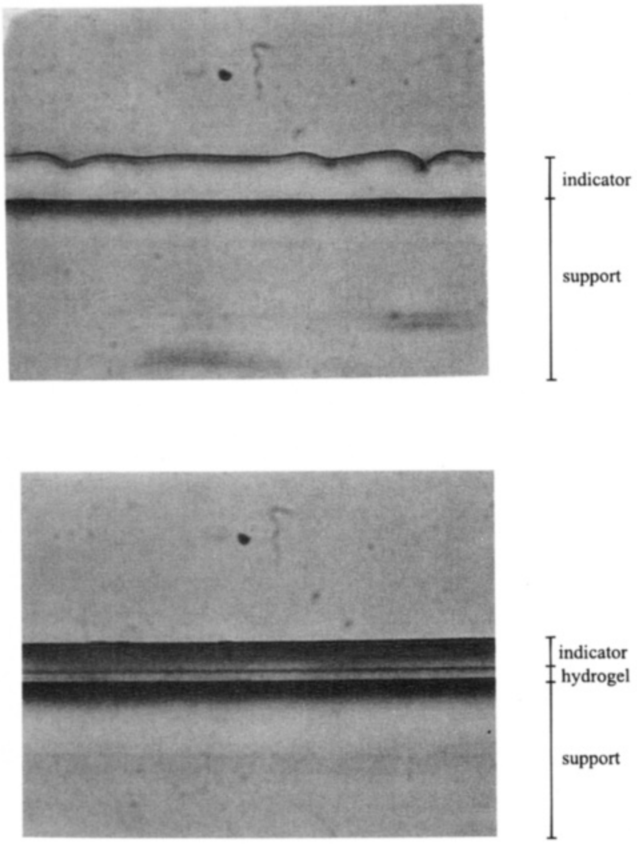

Figure 4. Cross sections of coatings enlarged 1000×. Sequential hydrogel and then indicator layer coatings were made on a polyester support. The hydrogel layers were coated at 1.0 g of NaPSS/m^2 but at varying monomer weight fractions. In the upper photograph, at a weight fraction monomer of 0.083, there is no distinct hydrogel underlayer. In the lower photograph, at a weight fraction monomer of 0.15, a distinct hydrogel underlayer is observed.

smooth flat indicator surface layer, whereas cross sections of the hazy coatings at lower weight fraction of the monomer exhibit a single layer with a buckled surface (Figure 4). Haze results from light scatter due to surface buckling in the resultant single layer of admixed polyelectrolyte and gelatin.[12] Above a critical weight fraction, a network of polymerized monomer provides the structural integrity to prevent admixing of the layers.

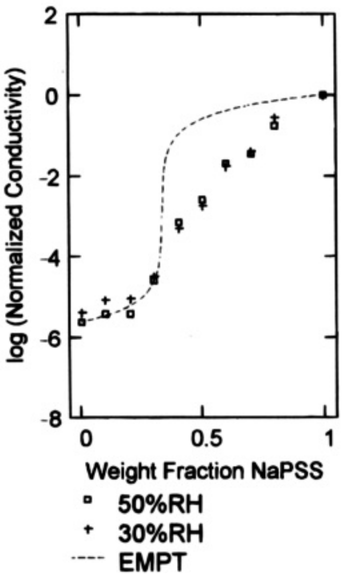

Figure 5. log [σ(X)/σ(1)] vs weight fraction NaPSS (X). Fixed coat weight of 1.35 g of matrix/m^2. Coatings were conditioned for 4 h at 50% or 30% RH. Curve is the fit of the EMPT model (eq1) to the data.

A thin film hydrogel at a composition immune to water wash, monomer weight fraction of 0.46, was extracted with anhydrous 2-propanol. The monomer was separately shown to be stable in the anhydrous 2-propanol. The extracts were analyzed for aziridine functionality by the method of Epstein[13] against control solutions containing the monomer. No aziridine functionality was detected in the extract. At the limit of detection extractable monomer is less than 0.28% of coated monomer.

The absence of extractable aziridine functionality is consistent with the polymerization of the monomer in the coating. Within the limits of detection, all of the coated monomer is bound within the hydrogel matrix. The requirement for a minimal weight fraction of the monomer to ensure immunity to water wash and to immobilize the polyelectrolyte suggests that sufficient polymerized monomer is required to form a spanning three dimensional network entrapping the polyelectrolyte.

Conductivity of Thin-Film Hydrogels. A series of coatings were made at a fixed total coat weight but at varying weight fractions of polyelectrolyte and monomer. Surface resistivities, measured at 50% and 30% RH, were strongly dependent on moisture content (see discussion Below and Experimental Section). However, a plot of the normalized conductivities at the two humidities vs weight fraction polyelectrolyte, (Figure 5) clearly indicates that the compositional dependence of the conductivity is independent of the state of hydration of the layer. The nearly S-shaped curve is characteristic of percolation behavior predicted by the effective medium percolation theory (EMPT).[14,15] Given the con-

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(13) Epstein, J.; Rosenthal, R. W.; Ess, R. J. *Anal. Chem.*, **1955**, *27*, 1435.
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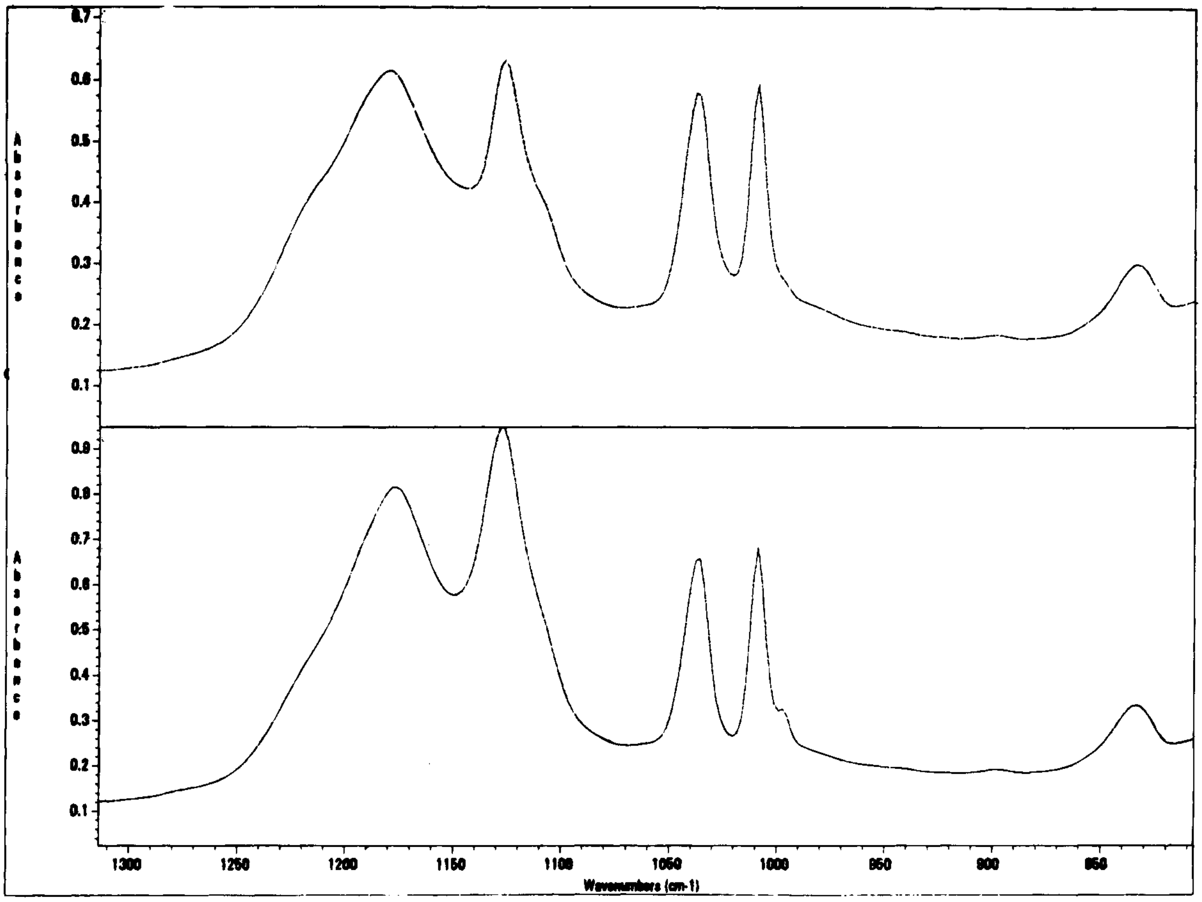

Figure 6. FTIR bands as a function of hydration. The coating conditioned at 80% RH (lower spectrum), had a measured surface resistivity of 1.6E11 Ω/square. Notable is the increase in the relative intensity of the 1127 cm^{-1} band as compared with the 50% RH coating (upper spectrum) with a surface resistivity of 1.0E12 Ω/square.

ductivities of a host, σ_1, and a conductive phase, σ_2, the conductivity of mixed phases, σ_m, at any composition is given by

$$\sigma_m = 0.25[K_2 - K_1X_2 + [(K_2 - K_1X_2)^2 + 8\sigma_1\sigma_2]^{1/2}] \tag{1}$$

where

$$K_1 = 3(\sigma_1 - \sigma_2) \tag{2}$$

$$K_2 = 2\sigma_1 - \sigma_2 \tag{3}$$

and X_2 is here taken as the weight fraction of the conductive phase. The EMPT model predicts an initial slow growth in conductivity, an "incubation region", followed by a percolation region where the conductivity rises rapidly as the conductive phase forms a spanning network in the host phase. The fit up to the percolation region is reasonable, but the growth in conductivity beyond the percolation threshold is not as rapid as predicted by the model. A like failure of EMPT theory was observed in ionic conductivity results for AgI-doped glasses discussed by Martin. He suggested that the conductivity in the pure bulk phase of AgI may overestimate its conductivity in diluted mixtures, weakening an EMPT assumption. Our results suggest that this observation may be generally valid.

As noted, the conductivity of the hydrogel thin film is strongly dependent on moisture content. FTIR spectra of coatings at a fixed weight fraction of polyelectrolyte were taken after conditioning at 80% and 50% RH, (Figure 6). Conditioning at high humidity leads to a strong increase in the relative absorbance intensity of a band at 1127 cm^{-1}, a softening of a shoulder band at 1108 cm^{-1}, and a decrease in surface resistivity. Hydration dependent IR bands for poly(styrenesulfonic acid) have been described in the literature,[16] where a band at 1128 cm^{-1} was observed only at high hydration, and a 1097 cm^{-1} band only with increased drying. The high-energy band was assigned to the in-plane skeleton vibration of a disubstituted benzene ring having a fully ionized sulfonate group and the low energy band to the same skeletal vibration for the protonated sulfonate substituent. On the basis of the observed humidity-dependent resistivities in our coatings, the 1127 cm^{-1} band is identified as the disubstituted benzene ring vibration involving fully ionized sulfonate groups. The corresponding counterions, both free and bound to the macroion, are mobile.[17] The 1108 cm^{-1} shoulder may correspond to the vibration where the counter ions are localized, i.e., tight ion-paired, and nonconductive.

The fit of the EMPT model to the compositional dependence of the normalized conductivity suggests that these thin-film conductive hydrogels are comprised of

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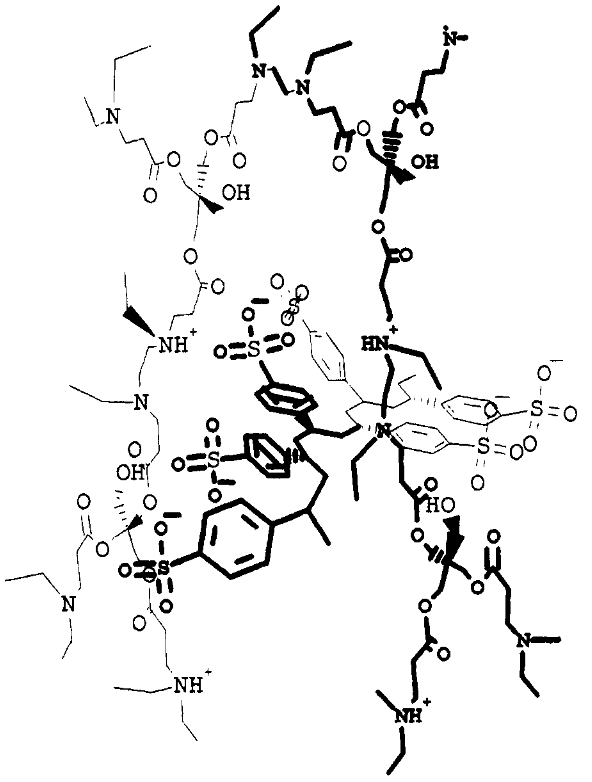

Figure 7. Representation of the composite hydrogel network showing a pore in the polyaziridine macrogel. The pore, occupied by polyelectrolyte, serves as a percolation channel for the bound but mobile counterions.

a randomly dispersed phase of macroions which, at a critical concentration, form a conductive network in the poorly conductive host poly(aziridine) phase (Figure 7).[18] The principal charge carriers accordingly are associated with the macroion network, i.e., the bound but mobile counterions.

Conclusions

The formation of hydrogels described in our work combines elements of gel formation seen between oppositely charged polyelectrolytes[19] and in the classical self-condensation reaction of trifunctional monomers.[20] The polyelectrolyte here is regarded as a guest in a polyaziridine host matrix since polymerization of aqueous solutions of the trifunctional monomer itself forms hydrogels. The polyelectrolyte however plays an active role in strengthening the hydrogel, which is attributed to ionic bond formation with the protonated polyaziridine host. Thin films of the composite hydrogels are readily prepared and are immune to water wash provided there is a sufficient initial weight fraction of the trifunctional monomer. The requirement for a critical weight fraction of monomer in order to immobilize the polyelectrolyte suggests the formation of a three-dimensional network entrapping the polyelectrolyte. A random conductor network of the polyelectrolyte forms provided the weight fraction of the polyelectrolyte exceeds a critical value. Within the range of the above critical weight fractions thin films which are both conductive and immune to water wash can be prepared.

The ability to prepare thin films of the hydrogel from aqueous coatings enhances the possibilities for new technology development. The precise molecular topology of these materials is under active study.

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