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A Comparison of Mechanical and Electrical Percolation during the Gelling of Nafion Solutions

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ABSTRACT: Rheological and impedance measurements are performed on Nafion solutions at relatively high concentration. The viscosity scales with the Nafion volume fraction as $\eta_r \propto \varphi^{0.59}$, up to $\varphi = 2.5\%$. At higher fractions the viscosity diverges. At $\varphi = 2.5\%$ the storage modulus exhibits scaling behavior with the frequency ($G' \propto \omega^{0.81}$), and the solution behaves as a gel. The results for the viscosity seem to fit the Zimm, rather than the Rouse, model. For the sodium form of Nafion the conductivity behaves qualitatively the same as the viscosity, with $\sigma \propto \varphi^{0.89}$, and can be described by a percolation network of conductors and superconductors. Above $\varphi = 2.5\%$ a sharp increase is observed, and the conductivity scales with the frequency as $\sigma \propto \omega^{0.75}$. For Nafion in the proton form at volume fractions higher than 2.5% no sharp increase is observed in the conductivity, and the conductivity is independent of frequency. This indicates that in the proton form no electrical percolation takes place. It is discussed how these results can be used to improve the properties of recast membranes.

Introduction

Perfluoro-sulfonated ionomers have unique properties with respect to stability, solubility, and ionic conductivity and are therefore applied as membrane separators in for instance chlor-alkali electrolysis and fuel cells.[1−3] Solutions of such ionomers, with Nafion as its archetype, have particular properties as well. It is important to understand these properties in order to be able to improve the performance of membranes, when formed via a casting process from a solution. There have been several studies on relatively dilute solutions of Nafion which indicate the existence of rodlike aggregates of almost constant size,[4,5] in coexistence with loose ionomers.[6] These two entities seem to be in an equilibrium, such that at higher Nafion concentration the aggregates become more abundant.[7] The special point leading to this behavior seems to be the combination of a very hydrophobic fluorcarbon backbone and small side chains containing sulfonic acid groups, which become charged when put into contact with a hydrophilic solvent. Relatively little is known about Nafion solutions at higher concentration. It has been proposed that a physical cross-linking might occur.[6] This is similar to what is observed for other associating polymers which form a physical gel at higher concentration.[8,9] Since Nafion is an ionomer, this is of particular interest as it opens the way for a comparative study of electrical and mechanical properties of a gel, which has been a subject of several theoretical papers.[10−12] In this paper we therefore compare the mechanical and electrical properties of Nafion solutions. Both Nafion in the proton and the sodium forms are studied to see whether the difference in performance observed for Nafion membranes in those two forms[13] can be related to structural differences in solution.

Experimental Section

Sample Preparation. Nafion 117 membranes from DuPont (Wilmington, DE) were cut into pieces and cleaned in a 10% hydrogen peroxide solution at 50 °C for 10 min. The Nafion in the proton form was cleaned further in a 10% solution of nitric acid for 10 min. To obtain Nafion in the sodium form, the membranes were put in a 2% solution of NaOH for 10 min. The NaOH solution was changed three times, and it was checked that in the last step the pH was above 9. The cleaned membranes, in either sodium or proton form, were dissolved in a 50/50 mixture of ethanol/water, using an autoclave at 230 °C for 4 h. This solution was transferred into a rotary vacuum evaporator to obtain a highly concentrated solution, which was poured out into Petri dish. This dish was put into a drying oven at 70 °C. The resulting Nafion film was taken off by a scalpel and transformed into a powder in a mortar. The powder was dried in a vacuum oven for 3 h at 80 °C before being dissolved in a 3:1 (v:v) mixture of 2-propanol and water. This mixture was chosen after it was found that Nafion in its sodium form does not dissolve in pure 2-propanol, and this mixture gave rise to little interference of electrode polarization in impedance spectroscopy. Before being used, the solutions were filtered by using a paper filter and a Büchner funnel.

Rheology. At relatively high Nafion concentrations, rheological measurements were performed with a Haake CV 100 rheometer (Haake, Karlsruhe, Germany), having a Couette type geometry. The temperature was controlled via the heating mantle, and solvent evaporation was minimized by working in a solvent saturated environment. In the oscillatory measurements it was verified that the results were independent of the amplitude at three different amplitudes (between 0.1° and 10°). At intermediate volume fractions rotational measurements displayed a linear stress to strain rate dependence at low shear rates from which the viscosity was determined. At lower volume fractions this linearity was observed in the whole range of shear rates covered (<300 s^{-1}), and the same viscosity could be determined by an Ubbelohde capillary viscometer. For low Nafion fractions (<0.2 vol %), we used an Ubbelohde viscometer of Schott, Hofheim a Ts., Germany, tube type I, which was thermostated in a water bath. To prevent solvent evaporation, the inlet of the Ubbelohde was connected to an Erlenmeyer containing solvent soaked cotton. The relative viscosity η_r is calculated as follows:

$$\eta_r = \frac{\eta - \eta_0}{\eta_0} \tag{1}$$

with η being the measured viscosity and η_0 the solvent viscosity.

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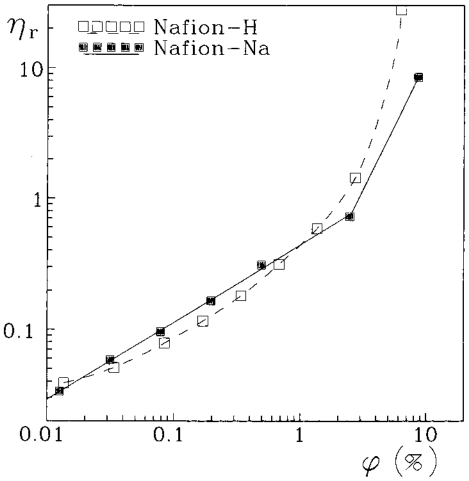

Figure 1. Relative viscosity as a function of Nafion volume fraction.

Table 1. Power Law Relations for the Nafion Volume Fraction and Frequency Dependence of Mechanical and Electrical Properties

	vol fraction dependence		freq dependence	
Nafion-H		$\sigma \propto \varphi^{0.89}$	$G' \propto \omega^{0.82}$	
Nafion-Na	$\eta \propto \varphi^{0.59}$	$\sigma \propto \varphi^{0.89}$	$G' \propto \omega^{0.81}$	$\sigma \propto \omega^{0.75}$

Impedance Measurements. For the impedance measurements we used a Solartron S-1260 frequency response analyzer (Solartron Instruments, U.K.). For several samples the amplitude of the voltage was changed from the normally used 0.1 V to 1 V which had no significant influence on the conductivity spectra. Two homemade measurement cells were used. For liquid samples a square cup type cell with copper electrodes on both sides at a spacing of 5 mm was used. For the gel samples we used two copper electrodes and a spacer, which could be separated to clean and put another sample. Also in this cell the electrode spacing was 5 mm. The cells were immersed into a water bath for temperature control, and it was checked that this had no influence on the impedance.

Results

Rheology. At room temperature (25 °C) samples with a fraction below 2 vol % reveal Newtonian behavior. For the sodium form the volume fraction dependence of the relative viscosity shown in Figure 1 can be fitted to a power law with the exponent indicated in Table 1. For the proton form on the other hand the dependence seems to deviate slightly from a power law. For fractions above 2 vol % the relative viscosity deviates strongly from a power law for both the sodium and proton forms. Moreover, at higher shear rates shear thinning occurs. The viscosity, determined by the slope of the stress against the strain rate at low strain rates, rapidly diverges as a function of volume fraction and at slightly higher volume fractions cannot be determined anymore. In our experimental setup this limit was reached at 8 vol %, where already at low strain rates the stress went over the maximum detectable value of 30 Pa. At a Nafion fraction of 2.5 vol % the frequency dependence of the storage modulus shown in Figure 2 can be described by a power law with an exponent as noted in Table 1. At the same fraction but at a temperature of 15 °C, the storage modulus becomes frequency-independent.

Impedance Spectroscopy. At fractions below 2 vol % the results from impedance spectroscopy are similar for the proton and sodium forms of Nafion. The conductivity spectra, shown in Figure 3, are characterized by one dispersion and regions with a relatively small frequency dependence at high and low frequencies. At low frequencies a real plateau region cannot be found, possibly due to electrode polarization. At high frequencies there is a plateau region for which the conductivity, shown in Figure 4, follows a power law as a function of the Nafion volume fraction. The exponents found by fitting the volume fraction dependence to a power law are shown in Table 1. At higher volume fractions, a large difference appears between the results for the proton and the sodium forms of Nafion. For the proton form the frequency dependence of the conductivity is qualitatively the same for Nafion fractions below or over 2 vol %. At fractions over 2 vol %, the volume fraction dependence of the conductivity in the plateau region only slightly deviates from the power law found at lower volume fractions. For the sodium form, on the other hand, a much more pronounced frequency dependence is found for the conductivity at higher Nafion volume fractions. For a Nafion volume fraction of 2.5% there is a large region in which the conductivity scales with the frequency as $\omega^{0.75}$.

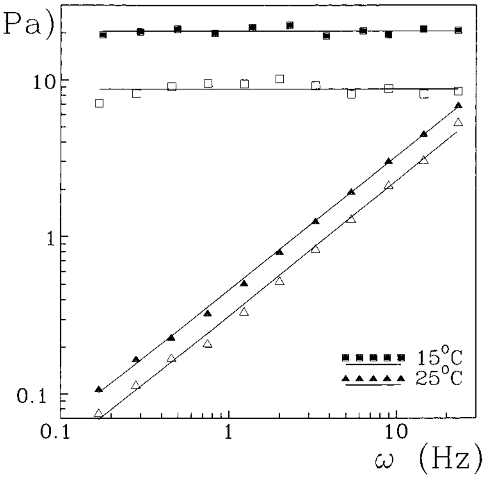

Figure 2. Storage modulus as a function of circular frequency at $\varphi = 2.5$ vol %: open symbols, Nafion-H; closed symbols, Nafion-Na.

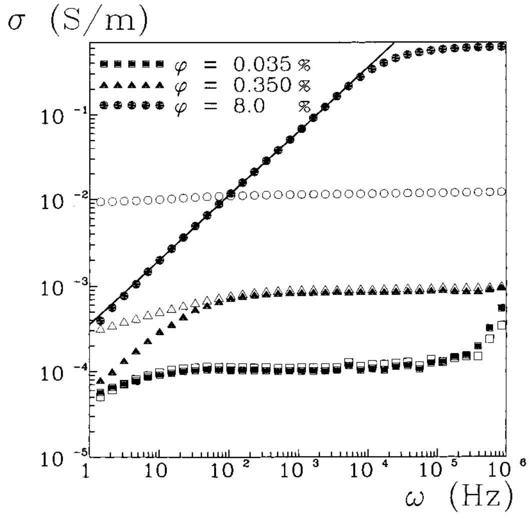

Figure 3. Conductivity as a function of circular frequency: open symbols, Nafion-H; closed symbols, Nafion-Na.

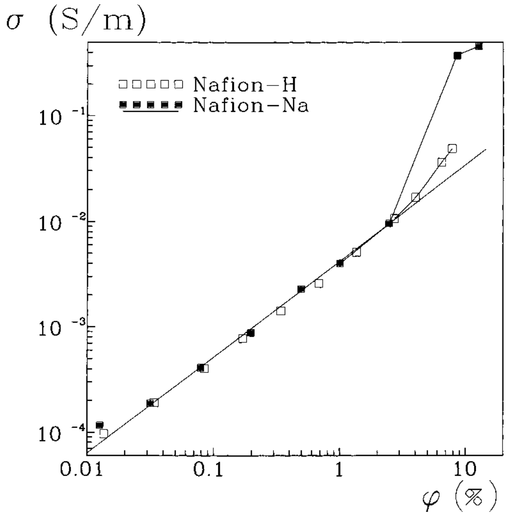

Figure 4. Conductivity at the plateau region as a function of Nafion volume fraction.

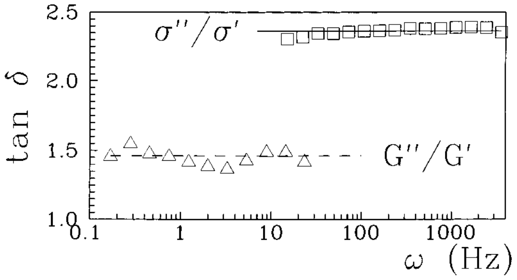

Figure 5. Tangent of the phase angle as a function of angular frequency for Nafion in the sodium form at $\varphi = 2.5$ vol %.

Table 2. Tangent of the Phase Angle Determined in the Frequency-Independent Region (See Figure 5) and the Corresponding Relaxation Exponent Δ Calculated According to Formula 3, for the Sodium Form of Nafion at 2.5 vol %

	$\tan \delta$	Δ
mechanical	1.46 ± 0.03	0.62
electrical	2.36 ± 0.01	0.74

Discussion

The rheological properties start to show a different behavior at Nafion fractions above 2 vol % compared to more dilute solutions. At this point the flow behavior starts to become non-Newtonian, and the viscosity rapidly increases as a function of the volume fraction. For slightly higher volume fractions complex rheological measurements show a higher storage (G') than loss modules (G''). For lower temperature the storage modulus becomes frequency-independent. These solidlike properties indicate the formation of a physical gel.[11,14] The critical phenomena that occur around a gel point are usually described by percolation theory.[10,15] The scaling laws which are predicted by this theory and to which our data can be compared are

$$\eta \propto \varphi^k \qquad G' \propto \omega^\Delta \tag{2}$$

For the volume fraction dependence the exponent k of 0.59, observed for the sodium form of Nafion, corresponds reasonably well with what is observed in several other systems and predicted by theory.[11,16] There are two theoretical models: The Zimm model taking into account hydrodynamic interactions between polymers in a mean field way predicts that $k = 0.65$. Recent data that appear to be described satisfactorily by this model include those on polyacrylamide[17] and pectine,[26] whereas references to older data can be found in ref 11. The Rouse model, on the other hand, neglects hydrodynamic interactions and predicts that $k = 1.35$. The better agreement of our result with the Zimm model suggests that hydrodynamic interactions are important in this system. At 25 °C, for the sample that appears to be near the gel point the storage modulus, G' depends on the frequency by a power law with an exponent, Δ, of about 0.81. This value of Δ is a bit high compared with the theoretical prediction of $0.61 \leq \Delta \leq 0.75$. A high value, however, confirms the better resemblance to the Zimm model for which Δ takes the value of the upper limit (i.e., 0.75). As can be seen in Figure 5, the ratio of G''/G', which equals the tangent of the phase angle, takes up a frequency-independent value of about 1.46 for low frequencies. This value can also be used to calculate Δ, via the relation[18,19]

$$G''/G' = \tan \delta = \tan \frac{\Delta\pi}{2} \tag{3}$$

The value of 1.46 for the tangent of the phase angle results in a Δ of 0.62 (Table 2), which is clearly lower than the value observed directly from the frequency dependence of G'. The difference between these two numbers can possibly be attributed to the limited frequency range in which the viscoelastic properties were measured and the limited time which was given to the gel to reach an equilibrium (±1 h).[20] Recent experiments on various physical gels yielded values for Δ of 0.62,[21] 0.69,[8] 0.70,[22] 0.72,[26] 0.75,[23] 0.78,[20] 0.8,[24] and 1.3,[25] whereas older data suggested a value around 0.7.[11] In this respect values found in this study by either method compare reasonably well with other experiments. At 15 °C the results are different. Here the storage modulus is frequency-independent, indicating elastic behavior in the frequency range probed. One could expect that in a wider frequency range G' exhibits a low-frequency domain in which its value is frequency-independent and a high-frequency domain where it increases with frequency by a power law. With an increase of temperature the crossover between these two domains will be expected to shift to lower frequencies, such as can be seen in measurements on pectin gels.[26] In this way a limited frequency domain can show a change from constant toward a power law frequency dependence. A possible explanation might be given in a recent publication of Rubinstein and Semenov[27] in which they take into account the lifetime of the connections between polymers. For a certain free energy of a connection (which depends on the temperature) they indeed find a scaling regime for which the storage modules is frequency-independent.

Simultaneously with the viscoelastic properties the electrical properties start to deviate above Nafion fractions of 2 vol % (Figure 4). At this point a deviation of high-frequency conductivity from a power law dependence on the volume fraction can be observed. The extent of this deviation is much larger for the sodium form compared to the proton form of Nafion. The exponent, s, of the power law dependence at low volume fractions of 0.89 for Nafion in the sodium form corresponds reasonably well to the theoretical prediction of $s = 0.835$[11] for a percolation network of conductors and superconductors and is in exact agreement with experimental data on an electron conductive gel.[28] This value is clearly different from the value for the volume fraction dependence of the viscosity, which complies with the idea that the classical concept[10,12] of an exact correspondence between the scaling forms for the conductivity and viscosity is not correct and that in fact $s > k$.[11,29,30] The agreement with the superconductor percolation model might be explained by the following: Ions experience a high resistance when travelling through the solution. Along the Nafion strands this resistance is several orders of magnitude lower, such that the formation of a Nafion network comes to expression in the conductivity as a percolation in which conductors are replaced by superconductors. For low volume fractions the conductivity is frequency-independent for most of the frequency range covered. The frequency response in this case is very similar for the proton and the sodium forms of Nafion. As a function of the Nafion volume fraction this similarity starts to vanish. This becomes especially clear at fractions above 2 vol %, at which the volume fraction dependence of the conductivity starts to be different for the proton and the sodium forms of Nafion. In the sodium form a very distinct frequency dependence can be observed at fractions above 2 vol %, in which the conductivity shows a power law dependence toward the low-frequency end of the spectrum. The exponent Δ_e, for the frequency dependence of the conductivity, of 0.75 is in very good agreement with theoretical predictions. The tangent of the phase angle is almost frequency-independent. From the exponent $\Delta_e = 0.75$ a value of $\tan \delta_e = 2.4$ can be calculated from the electrical equivalent of eq 3, which agrees well with the observed frequency-independent value of tangent of the phase angle (Figure 5 and Table 2). It is remarkable that the difference in the value of Δ, observed by calculating its value in these two ways for the mechanical properties, is not observed for the electrical properties. This can be partly understood by the more extended frequency range in which the electrical properties are monitored.

For Nafion in the proton form even at the highest Nafion volume fraction used a distinctive frequency dependence of the conductivity is not observed. This is accompanied by a relatively small deviation of the power law dependence in the volume fraction dependence of the conductivity at higher volume fractions (Figure 4). These two observations seem to suggest that, unlike in the sodium form, in the proton form there is no electrical percolation threshold, above which an ion conductive cluster is formed through the sample. However, judging from the scaling behavior, some kind of electrical percolation phenomenon takes place at low Nafion volume fractions. It seems therefore that at low volume fractions, for Nafion in both the proton and the sodium forms, conductive clusters are growing with the Nafion volume fraction, such that the scaling laws for percolation are observed. However, in the proton form as opposed to the sodium form no sample-spanning conductive cluster is formed at a certain volume fraction. For the mechanical percolation, on the other hand, the differences between Nafion in the proton and the sodium forms appear to be relatively small. One difference is the lack of a clear power law dependence of the viscosity with the volume fraction in the case of Nafion in the proton form. However, another important difference is that after evaporating the solvent from a solution of Nafion in the sodium form the resulting film is soluble in a 2-propanol/water mixture. A recast film of Nafion in the proton form, on the other hand, is insoluble in such a mixture.

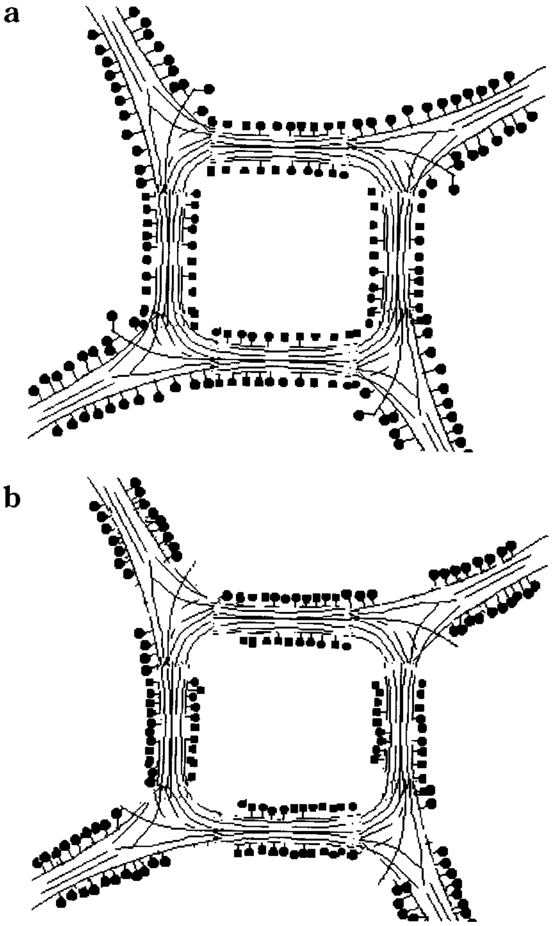

Figure 6. Drawing of a system that is over the percolation threshold with regard to both electrical and mechanical properties (a) and a system in which no electrical percolation takes place (b). In the situation drawn in (b) the sulfonic groups are closer together such that voids occur in the electrical path. These make the gel less conductive and insoluble in a hydrophobic solvent.

A possible explanation for these differences could be that in the proton form of Nafion clusters are formed in which the hydrophilic part is well screened off by a hydrophobic layer, such that they become insoluble in a hydrophilic solvent. This kind of micelle-like aggregate could give rise to a deviation from normal percolation, thus resulting in an upward departure from a power law dependence of the viscosity versus the volume fraction. It could also explain the lack of an electrical percolation threshold. In Figure 6 we depict this idea within the framework of the fringed rod model, proposed for the gelling of Nafion aggregates.[6] In Figure 6a the proposed situation for the sodium form is shown in which the sulfonic groups are distributed over the whole network, and mechanical percolation is accompanied by electrical percolation. Figure 6b shows the situation which might reflect the proton form, in which the sulfonic groups are clustered together and voids occur in the electrical path. Of course, we cannot rule out that the actual structure of the Nafion gels might be even more different in the proton and sodium forms of Nafion. Figure 6 is one example which could fit the data.

It would be interesting to see how the results described in this article can be used in membrane technology. An important method for the processing of membranes is recasting from a solution. This method consists of the dissolution of Nafion and the subsequent evaporation of the solvents on a glass substrate, such that a thin film is formed which is called the recast membrane. Recast membranes however have different properties than membranes as obtained after their synthesis in the factory. The most apparent differences are that recast Nafion is brittle[31] and has a much lower conductivity. This difference can partly be repaired by annealing, i.e., heating the recast membrane for a certain period.[32] Moreover, factors that affect the recast process positively are a high humidity during the process or the addition of a higher boiling point solvent to the solution from which the film is recasted.[33−35] These observations suggest that the recast membrane has a tendency to be in a glassy state out of its equilibrium, which has less favorable properties with respect to ionic conductivity and strength. If so, the recasting process might be improved if care is taken that the solvent is taken away very slowly when the system reaches the gel point at which the relaxation times will diverge. From the results in this paper this point is at about 2.5 vol % (5 mass %) of Nafion. The results in this paper suggest further on that electrical percolation is more easily obtained when sodium is used as counterion. It could therefore be favorable to use Nafion in its sodium form during recasting. If necessary, the sodium can be replaced by hydrogen once a stable film is formed.

Conclusions

Nafion in 2-propanol/water 3:1 (v:v) forms a physical gel at fractions higher than 2.5 vol %. For the sodium form of Nafion we could compare the volume fraction and frequency dependence of the viscoelastic and electrical properties to percolation theory. This seems to be the first time that the scaling behaviors of the viscosity and conductivity are measured directly on the same system, and the results suggests that there is no direct correspondence between them. For the proton form as opposed to the sodium form of Nafion no threshold for electrical percolation could be observed. This result suggests that it might be good to use the sodium form in the recasting process for Nafion membranes.

References and Notes

(1) Hsu, W. Y.; Gierke, T. D. *J. Membr. Sci.* **1983**, *13*, 307.
(2) Srinivasan, S.; Manko, D. J.; Koch, H.; Enayetullah, M. A.; Appleby, J. *J. Power Sources* **1990**, *29*, 367.
(3) Heitner-Wirguin, C. *J. Membr. Sci.* **1996**, *120*, 1.
(4) Aldebert, P.; Dreyfus, B.; Gebel, G.; Nakamura, M.; Pineri, M.; Volino, F. *J. Phys. (Paris)* **1988**, *49*, 2101.
(5) Loppinet, B.; Gebel, G.; Williams, C. E. *J. Phys. Chem. B* **1997**, *101*, 1884.
(6) Szajdzinska-Pietek, E.; Schlick, S.; Plonka, A. *Langmuir* **1994**, *10*, 2188.
(7) Cirkel, P. A.; Okada, T.; Kinigasa, S. *Macromolecules* **1999**, *32*, 531.
(8) Bromberg, L. *Macromolecules* **1998**, *31*, 6148.
(9) Borchard, W. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1580.
(10) De Gennes, P. G. *J. Phys., Lett.* **1976**, *37*, L-1.
(11) Sahimi, M. *Mod. Phys. Lett. B* **1992**, *6*, 507.
(12) Daoud, M.; Lapp, A. *J. Phys.: Condens. Matter* **1990**, *2*, 4021.
(13) Okada, T.; Xie, G.; Gorseth, O.; Kjelstrup, S.; Nakamura, N.; Arimura, T. *Electrochim. Acta* **1998**, *43*, 3741.
(14) Hermans, P. H. In *Colloid Science*; Kruyt, H. R., Ed.; Elsevier: Amsterdam, 1949; Vol. II.
(15) Stauffer, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1354.
(16) Arbabi, S.; Sahimi, M. *Phys. Rev. Lett.* **1990**, *65*, 725.
(17) Yano, T.; Kumagai, H.; Fujii, T.; Inukai, T. *Biosci., Biotechnol., Biochem.* **1993**, *57*, 528.
(18) Gambon, F.; Winter, H. H. *Polym. Bull.* **1985**, *13*, 499.
(19) Mours, M.; Winter, H. H. *Macromolecules* **1996**, *29*, 7221.
(20) Schwittay, C.; Mours, M.; Winter, H. H. *Faraday Discuss.* **1995**, *101*, 93.
(21) Peyrelasse, J.; Lamarque, M.; Habas, J. P.; Bounia, N. E. *Phys. Rev. E* **1996**, *53*, 6126.
(22) Yu, J. M.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R.; Blacher, S.; Brouers, F.; L'Homme, G. *Macromolecules* **1996**, *29*, 5384.
(23) Li, L.; Aoki, Y. *Macromolecules* **1997**, *30*, 7835.
(24) te Nijenhuis, K.; Winter, H. H. *Macromolecules* **1989**, *22*, 411.
(25) Kobayashi, K.; Huang, C.; Lodge, T. P. *Macromolecules* **1999**, *32*, 7070.
(26) Axelos, M. A. V.; Kolb, M. *Phys. Rev. Lett.* **1990**, *64*, 1457.
(27) Rubinstein, M.; Semenov, A. N. *Macromolecules* **1998**, *31*, 1386.
(28) Chen, P.; Adachi, K.; Kotaka, T. *Polymer* **1992**, *33*, 1813.
(29) Limat, L. *Phys. Rev. B* **1988**, *38*, 7219.
(30) Benguigui, L.; Ron, P. *J. Phys. I* **1995**, *5*, 451.
(31) Gebel, G.; Aldebert, P.; Pineri, M. *Macromolecules* **1987**, *20*, 1425.
(32) Zook, L. A.; Leddy, J. *Anal. Chem.* **1996**, *68*, 3793.
(33) Moore, R. B.; Martin, C. R. *Anal. Chem.* **1986**, *58*, 2570.
(34) Striebel, K. A.; Scherer, G.; Haas, O. *J. Electroanal. Chem.* **1991**, *304*, 289.
(35) Tsusaka, K. *Toyota Chuo Kenkyusho R&D Rebyu* **1998**, *33*, 119.

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