

Perfluorosulfonic Ionomer Solution in *N,N*-Dimethylformamide

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ABSTRACT: The morphology of perfluorosulfonic ionomer molecules in *N,N*-dimethylformamide was investigated at different concentrations. Rheological, dynamic light scattering (DLS), and scanning electron microscopy (SEM) measurements were performed on the prepared perfluorosulfonic ionomer solutions or films. The ionomer molecules shrank from rodlike granules to spherelike ones at relatively low concentrations, and the spherelike granules aggregated together to form aggregates at higher concen-

trations, with capillary liquid bridge force as the driving force. As the solvent evaporated slowly at room temperature, the SEM image showed that the film was loosely stacked by granules and that aggregates formed in the solution. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2892–2898, 2008

Key words: films ionomers; light scattering rheology solution properties

INTRODUCTION

Perfluorosulfonated ionomer (PFSI) with the trademark Nafion was first synthesized by E. I. DuPont Co. via the copolymerization of perfluoro[2-(2-vinyl-oxy-1-methylethoxy) ethane sulfonyl] fluoride (PSVE) with tetrafluoroethylene (TFE) in 1962. The chemical structure of this material consisted of a polytetrafluoroethylene backbone and regularly spaced long perfluorovinyl ether pendant side chains terminated by sulfonic groups, as shown in Scheme 1.

PFSIs have unique properties, including a high ionic conductivity and thermal and chemical stability. They have attracted great attention in academic and industrial research and have been applied successfully in chloro-alkali processes, fuel cells, sensors, water treatment, membrane reactor, gas separation, and so on.^{1,2}

PFSIs are also used in the solution form. An important method for the preparation of PFSI membranes is the so-called solution-cast process, in which a membrane is formed after the solvent is evapo-

rated from a PFSI solution. After Robert B. Moore and Charles R. Martin³ developed a solution processing procedure that produced solution-cast PFSI membranes that had excellent mechanical properties, it was found to be a good method for the preparation of chlor-alkali membranes⁴ and for the coating of modified electrodes,⁵ membranes for proton-exchange membrane fuel cells and direct methanol fuel cells,^{6,7} and recast membranes.⁸

However, most studies related to PFSI have been focused on the performance of membranes. There have been only a few studies about the nature and structure of PFSI solutions. Commercial Nafion solutions are prepared and dissolved in ethanol/water or 2-propanol/water mixture solvents, and most of the studies on the solutions have been focused on these systems.^{9–18} The most accepted conformational model of Nafion molecules in aqueous solution was suggested by Szajdzinska-Pietek et al.¹⁹ They showed that Nafion molecules aggregated and formed fringed rodlike structures in aqueous solvents. These primary rodlike structures then aggregated again through fringed side chains to form secondary ionic aggregations. Lee et al.⁹ got the same results after a study on the properties of Nafion in low aliphatic alcohol/water mixture solvents with dynamic light scattering (DLS).

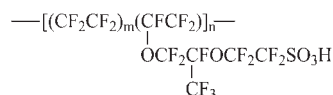
It is known that membranes made from solutions of ethanol/water or 2-propanol/water mixture solvents without annealing are brittle and have poor mechanical properties. Furthermore, they are soluble

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Scheme 1 Nafion polymer structure after conversion to the sulfonic acid form.

at room temperature in a variety of polar organic solvents, whereas as-received Nafion membrane is insoluble in all solvents.^{3,20,21} However, membranes made from solutions of high-boiling-point solvents such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide, or ethylene glycol are comparable to the as-received Nafion membranes.^{3,20,22} In their work, Silva et al.²² reported that membranes cast from DMF-based solutions gave conductivity performances comparable to those of Nafion 112 and 115. Solutions of PFSIs in DMF must have particular properties. For a fundamental understanding of the process from solution to membrane, it is important to have a detailed knowledge of the PFSI/DMF solution properties to be able to improve the performance of the membranes made from such solutions.

EXPERIMENTAL

Materials

Except for PFSI, the following chemicals were used: DMF, NaOH, NaCl, and HCl. All chemicals were reagent grade. Before use, DMF was dried and distilled twice under reduced pressure. All other reagents were used as received without further purification. TFE and perfluoro[2-(2-fluorosulfonylethoxy) propyl vinyl ether] were provided by Shandong Dongyue Polymer Materials Co., Ltd. (Zibo, China); the purity was more than 99.999%.

PFSI preparation

The PFSI precursor was prepared by the copolymerization of TFE and perfluoro[2-(2-fluorosulfonylethoxy) propyl vinyl ether] in fluorocarbon solvent with a perfluoroacyl peroxide initiator,^{23,24} as shown in Scheme 2. After the copolymerization, the product was separated, rinsed, and dried. The white powder was melt-extruded and granulated with a twin-screw extruder. Then, the perfluorosulfonated precursor with the functional group $\text{---SO}_2\text{F}$ was added to a 29 wt % aqueous sodium hydroxide solution and refluxed at 100°C for 48 h to chemically convert the $\text{---SO}_2\text{F}$ groups to $\text{---SO}_3\text{Na}$ groups. Next, the ionomer was washed to neutrality with an amount of water, and we converted the Na^+ -type ionomer to H^+ -type by immersing it in a 2M aqueous HCl solution for 24 h. We rinsed the ionomer again and dried it under vacuum at 80°C for 12 h. The ion-exchange

capacity of the perfluorosulfonic ionomer was determined by titration to be 0.95mequiv/g.

Solution preparation

H^+ -type perfluorosulfonic ionomer was dissolved in DMF with an autoclave at 230°C for 4 h to prepare a solution with concentration of about 50 mg/g. Solutions containing higher than 50 mg/g perfluorosulfonic ionomer were obtained with a rotary vacuum evaporator in our experiment. The concentrations of the concentrated solutions were measured by evaporation and careful weighing. Solutions with concentrations of less than 50 mg/g were diluted with DMF at the boiling point of the solvent.

Viscoelasticity analysis

The rheological properties of the solutions were examined with a rheometer (Gemini 200, Bohlin, United Kingdom) with a plate (radius = 15 mm). The temperature was controlled at $30 \pm 0.1^\circ\text{C}$ by an external thermal bath. The experiments were carried out in a DMF saturated environment to prevent the evaporation of solvent from the solutions. The steady viscosity (η) was measured under a stress of 0.2 Pa, and the reduced viscosity (η_r) was calculated as follows:

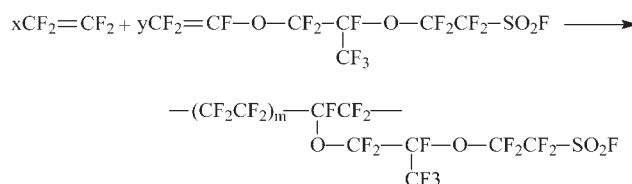
$$\eta_r = \frac{\eta - \eta_0}{\eta_0} \quad (1)$$

where η is the measured viscosity of the solutions and η_0 is the viscosity of solvent.

DLS

DLS measurement was carried out with a Zetasizer Nano instrument (ZEN1600, Malvern, United Kingdom) at 30°C. The laser was a He-Ne ion laser (633 nm, operated at 20 mW). The correlation length was the result of the intensity average. It was calculated as follows:

$$L = \sum_{i=0}^{\infty} (L_i \times I_i) \quad (2)$$



Scheme 2 Synthesis of perfluorosulfonated precursor with TFE and perfluoro[2-(2-fluorosulfonylethoxy) propyl vinyl ether]. m is about 5–7.

where L is the calculated correlation length, L_i is the measured correlation length, and I_i is the corresponding intensity.

Scanning electron microscopy (SEM) measurements

SEM was carried out on a Fei Sirion 200 (Fei Co. Hillsboro, Oregon) scanning electron microscope, and the images were taken at low vacuum after a thin gold film was sputtered on the sample.

RESULTS AND DISCUSSION

Perfluorosulfonic ionomer/DMF solutions showed different rheological properties at different concentrations. In polar solvents, the shape of ionomer molecules is determined by the balance of electrostatic repulsion and surface tension.²⁵ For the PFSI/DMF solution at a concentration of 0.01 mg/g, as shown in the plot of conductivity versus concentration (Fig.1), the perfluorosulfonic ionomer ionized well. The counterions dispersed into the solvent and interacted weakly with the sulfonic groups. The anions on the perfluorosulfonic ionomer interacted strongly without the screening of the counterions. The long-range interaction, that is, coulomb repulsion, was larger than the short-range attraction, that is, surface energy. Under the influence of the unscreened coulomb repulsion between PSVE monomers, the ionomer macromolecules assumed a strongly elongated rodlike conformation. The average hydrodynamic radius of the perfluorosulfonic molecules was more than 300 nm.

At concentrations from 0.01 to 0.5 mg/g, the ionization degree of the ionomer molecules decreased, but the number of the cations in the solution

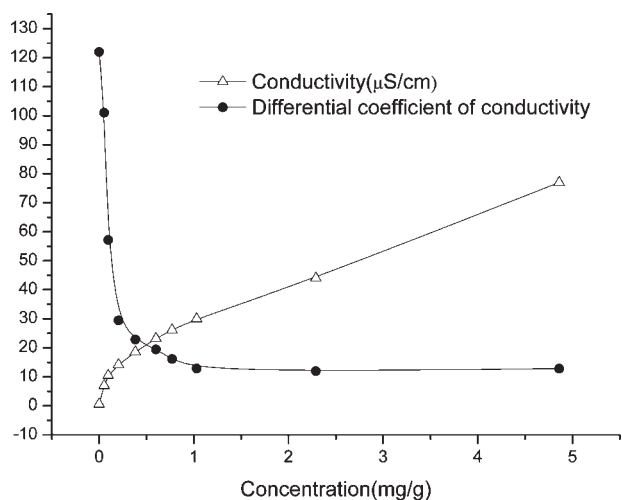


Figure 1 Conductivity and differential coefficient of conductivity of H⁺-type PFSI/DMF solutions at low concentrations.

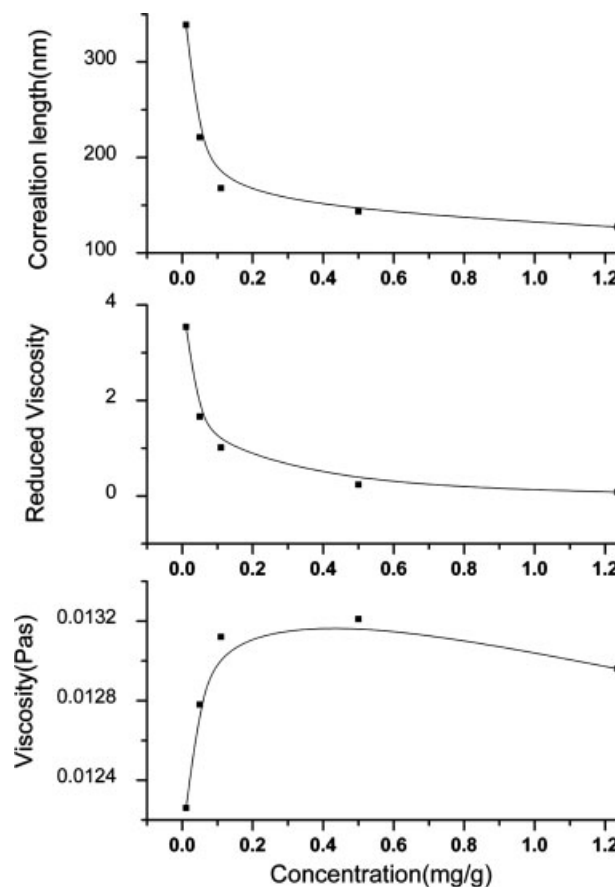


Figure 2 Correlation length, η_r , and viscosity of H⁺-type PFSI/DMF solutions, discussed concentration is from 0.01 to 0.5 mg/g.

increased, so the conductivity increased, and the differential coefficient of conductivity decreased as a result. As shown in Figure 2, the viscosity increased with the concentration because of the increase in the quantity of the molecules in the solution. Simultaneously, with the increase in the screening effect of the counterions, which resulted from the decrease in ionization, the repulsion of the sulfonic groups decreased gradually. Coulomb repulsion decreased, whereas surface energy increased. The molecule chains shrank, and the hydrodynamic radius of the perfluorosulfonic molecules decreased. As a result, the correlation length of the molecules and η_r of the solutions decreased with increasing concentration.

As shown in Figure 3, at concentrations from 0.5 to 5 mg/g, with the increase of counterions in the solution, the screening effect of the counterions increased, and the electrostatic repulsion of the sulfonic groups became smaller than the surface energy. The hydrodynamic radius of the perfluorosulfonic ionomer molecules decreased, and the correlation length decreased as a result. The ionomer molecules shrank and gradually took the shape of sphere-like

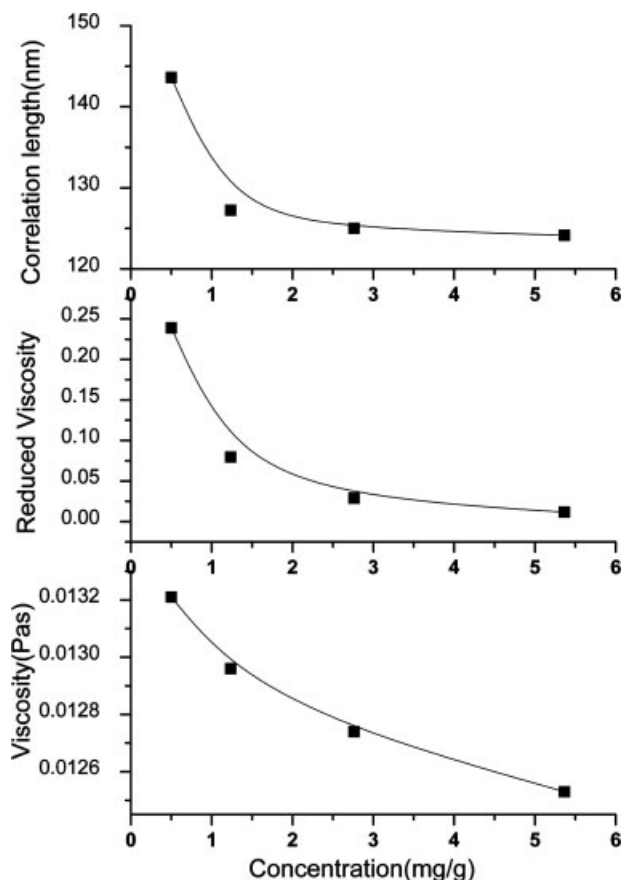


Figure 3 Correlation length, η_r , and viscosity of H^+ -type PFSI/DMF solutions, discussed concentration is from 0.5 to 5 mg/g.

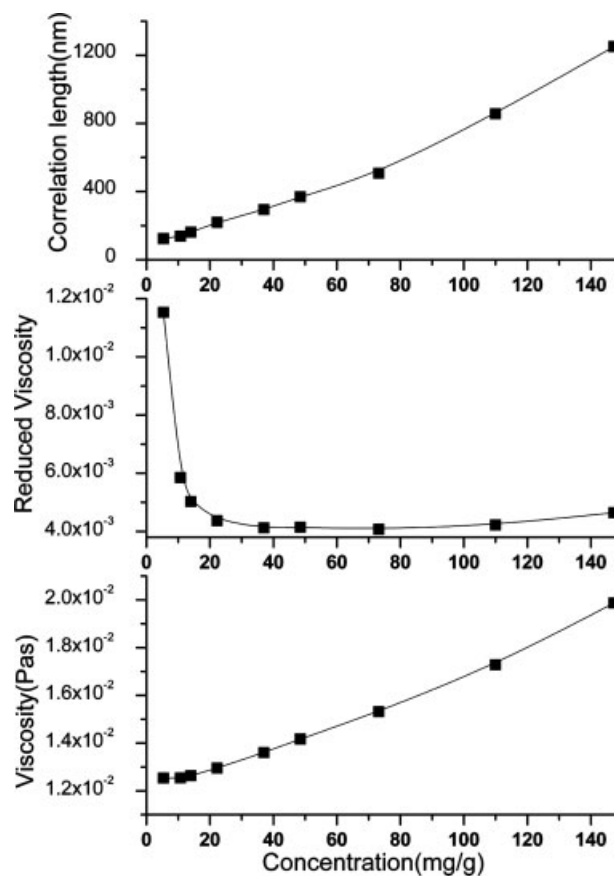


Figure 4 Correlation length, η_r , and viscosity of H^+ -type PFSI/DMF solutions, discussed concentration is from 5 to 150 mg/g.

globules, and the η_r and the viscosity of the solutions decreased as well.

As shown in Figure 4, as the concentration of the solutions increased from 5 to about 150 mg/g, the correlation length increased linearly with increasing concentration and increasing viscosity. In such a concentration region, the aggregation of the perfluoro-sulfonic ionomer granules dominated the system. The viscosity increased with increasing dimension of the aggregations. For η_r , although the dimension increased with the concentration, the total number of the aggregates in the solution did not change as greatly as the dimension. So η_r did not change much at concentrations from 20 to 150 mg/g.

As the concentration increased from 150 to 260 mg/g, as shown in the plots in Figure 5, the viscosity and η_r increased sharply. This was assigned to the aggregation of the aggregates to bigger ones. The plots of the distribution of the correlation lengths at different concentrations in Figure 6 shows that with increasing concentration, the small peak shifted gradually into big peaks; simultaneously, the big peak shifted to a larger correlation length, and the intensity increased. This suggests that more small

sphere-like granules aggregated together to form big aggregates. At a concentration of 189 mg/g, the small peak of the granules disappeared and only big

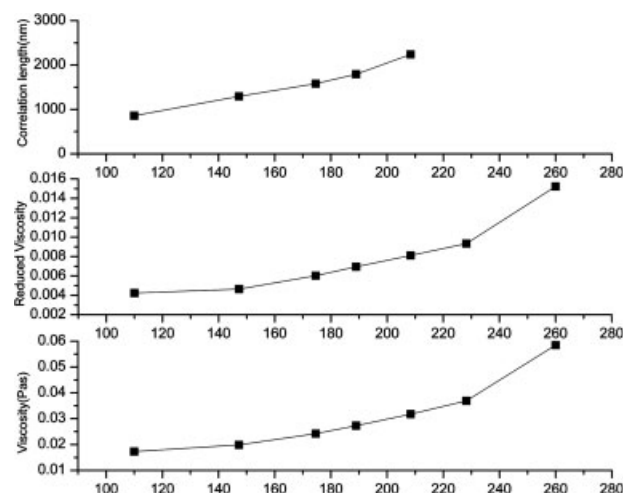


Figure 5 Correlation length, η_r , and viscosity of H^+ -type PFSI/DMF solutions, discussed concentration is from 150 to 260 mg/g.

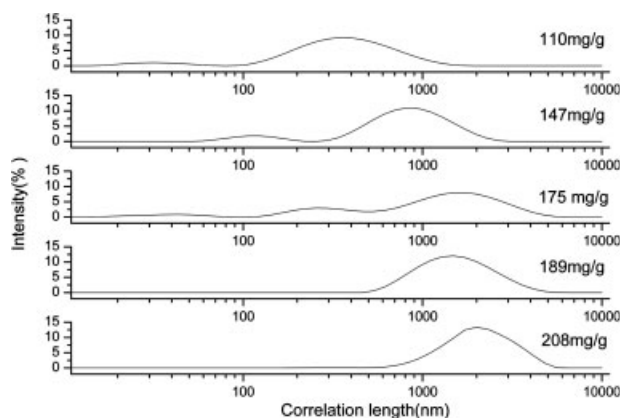


Figure 6 Correlation length distributions of H⁺-type PFSI/DMF solutions at different concentrations, the concentration is from 110 to 208 mg/g.

aggregates existed in the solution. When the concentration was higher than 208 mg/g, the aggregates interacted with each other, and it was not possible to gather the correlation length information with DLS any more.

When the concentration was higher than 150 mg/g, under a shear stress of 0.2 Pa, the plots of η versus time began to fluctuate periodically and clearly. This was because the aggregates in the concentrated solution formed rods under stress like the rouleaux formed in human blood,^{26,27} as pictured approximately in Figure 7. With increasing concentration, the number of the rods and the average number of aggregates in each rod increased, which made the average viscosity increase from 0.07 to 0.15 Pa s under the same stress of 0.2 Pa, and the amplitude and periodicity both increased, as shown in Figure 8(a,b). The aggregates did not form rods in a static solution due to the electrostatic repulsion between the aggregates, but under appropriate shear stress, the outside forces overcame the electrostatic repulsion and induced the formation of the aggregated rods. The rods tumbled and orbited in the solution with the shear stress and resulted in sine-wave-like plots of viscosity versus time. If the shear stress was larger than a certain critical value, the rod was broken up into short rods and individual aggregates, both the periodicity and amplitude of fluctuation of the plot decreased, and the viscosity decreased to 0.12 Pa s, as shown in Figure 8(c), under a shear stress of 0.8 Pa. If the shear stress was supercritical, the aggregates dispersed in the solution separately, and the viscosity decreased lower than 0.12 Pa s, and the plot lost the periodical fluctuation, as shown in Figure 8(d), under a shear stress of 1.2 Pa.

As the concentration of the perfluorosulfonic ionomer solution increased to 300 mg/g, we could not obtain η under small shear stress. The aggregates

were crosslinked together to form a network system. Figure 9 shows the storage modulus (G') and the loss modulus (G'') of the 300 mg/g perfluorosulfonic ionomer/DMF solution at 30°C. The plots of G' and G'' were similar to each other, and G' and G'' crossed over at some point, which indicated the formation of a transient network and physical gel.^{28,29} In such a solution, the concentration of perfluorosulfonic ionomer was high, which resulted in a low ionization degree of the ionomer. The screening effect of the counterions increased, and the electrostatic repulsion of the aggregates decreased accordingly. At the same time, the distance of the aggregates became smaller with desolvation, so it was easy for the aggregates to aggregate together with capillary liquid bridge force to form a transient network, as depicted approximately in Figure 10.

As the concentration of the solutions increased, the Witten–Scander model could be used to depict the aggregation of the aggregates very well. The Witten–Scander model is a variant of the Eden model, whose initial state is a seed particle at the origin of a lattice. A second particle is added at some random site at a large distance from the origin. This particle walks randomly until it visits a site adjacent to the seed. Then, the walking particle becomes part of the aggregate. Another particle is now introduced at a random distant point, and it walks randomly until it joins the aggregate and so forth.³⁰ In the solution of the perfluorosulfonic ionomer/DMF, the particle was the perfluorosulfonic granule or aggregate. The driving force for aggregation was capillary liquid bridge force.

Gebel et al.²¹ proposed that films reconstructed at room temperature may be considered to be “a compact nearly dried solution.” To get a direct visual observation of the aggregates formed in the solution,

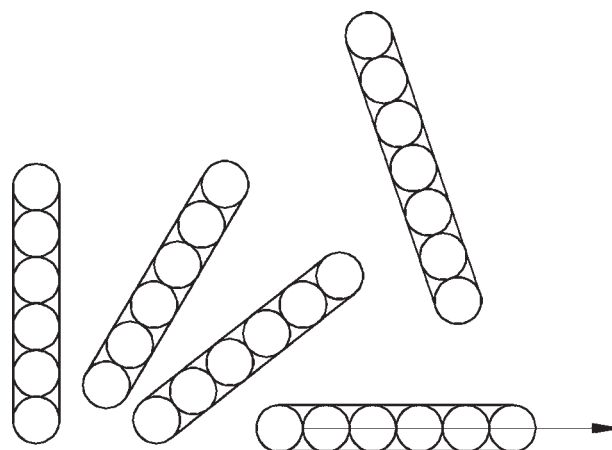


Figure 7 Approximation for the rods formed by aggregation at low shear rates in concentrated H⁺-type PFSI/DMF solutions.

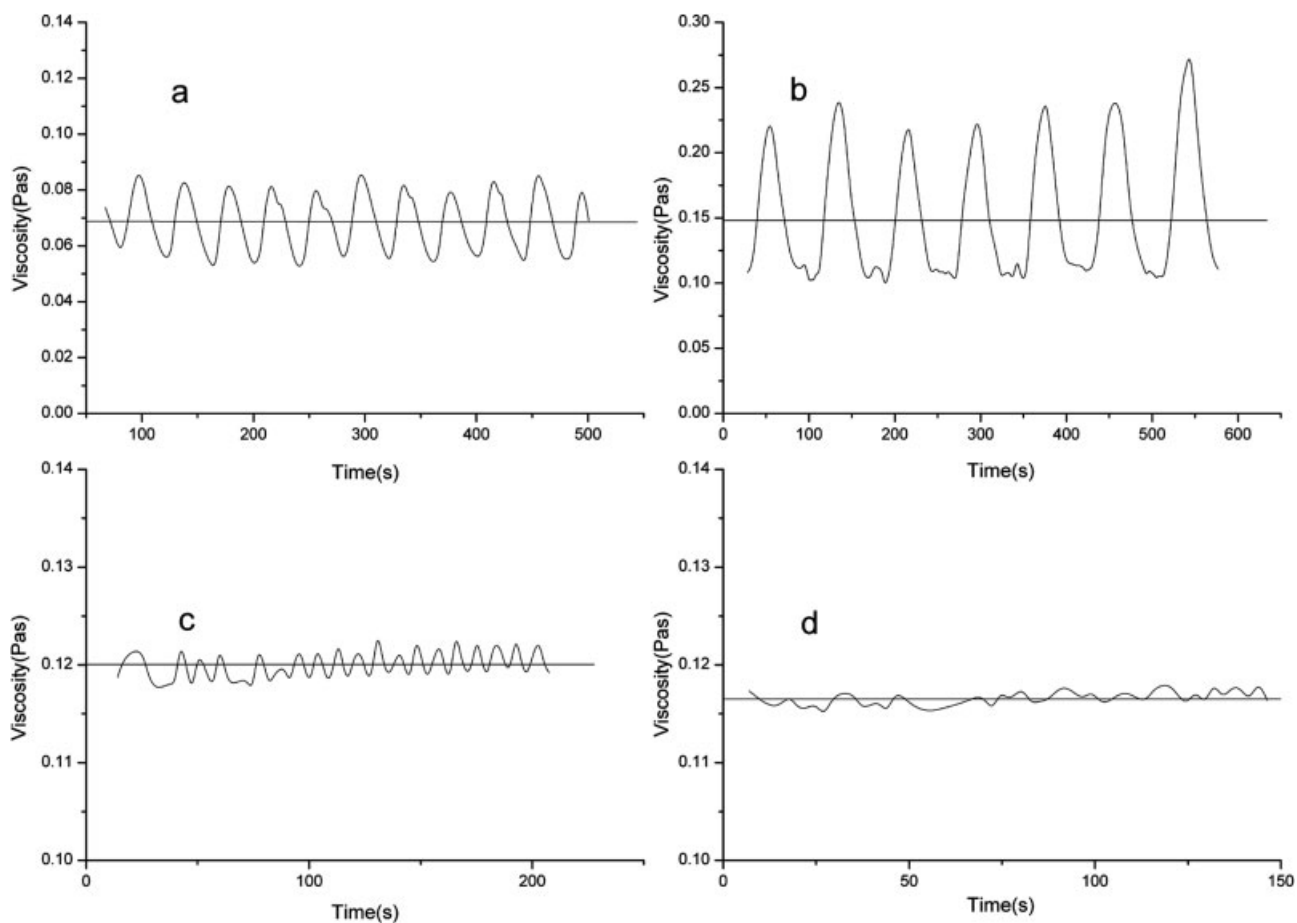


Figure 8 η of different H⁺-type PFSI/DMF solutions under different stress versus time, a: the concentration is 270 mg/g, the shear stress is 0.2 Pa; b: the concentration is 290 mg/g, the shear stress is 0.2 Pa; c: the concentration is 290 mg/g, the shear stress is 0.8 Pa; d: the concentration is 290 mg/g, the shear stress is 1.2 Pa.

a very thin film was prepared at room temperature. The film was prepared from a PFSI/DMF solution of with a concentration of 10 mg/g on a freshly cleaved

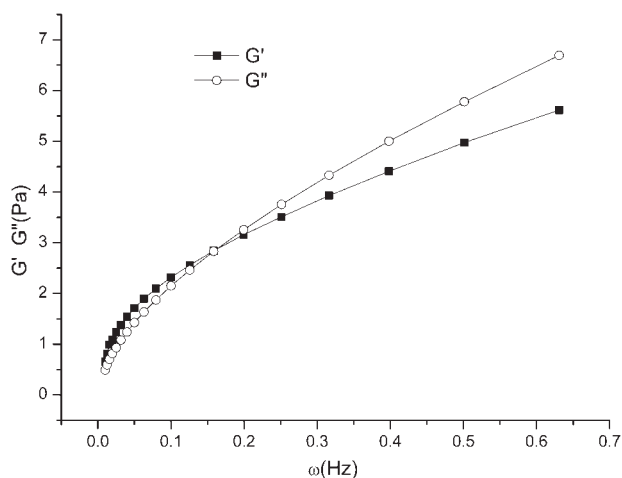


Figure 9 Dynamic modulus (ω) of H⁺-type PFSI/DMF solution at 30°C, the concentration is 300 mg/g.

mica substrate with a spin coater and then transferred into a glass desiccator to evaporate the solvent slowly at a room temperature of 0–10°C for 2 days. Figure 11 shows the SEM image of the film. The film was assembled primarily by spherelike granules of about 20 nm, and some of the granules aggregated to form aggregates of about 60–150 nm. We propose that the granules developed from the small particles in the solutions, whereas the aggregates developed from the aggregated granules.

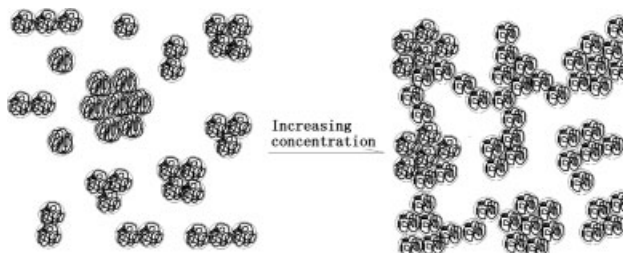


Figure 10 Approximation for the aggregates in the solutions at different concentrations.

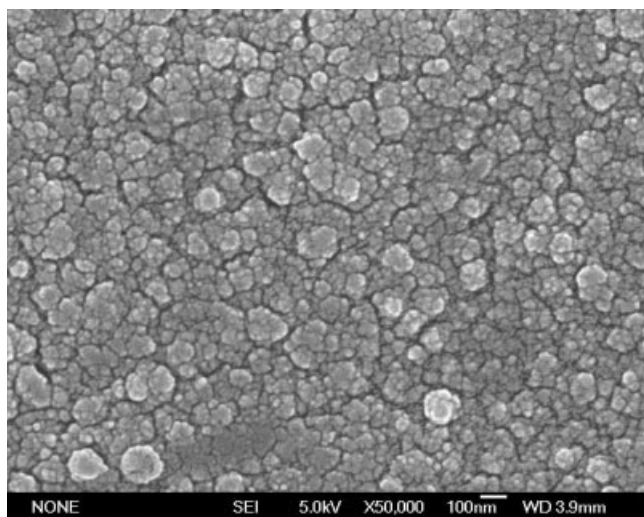


Figure 11 SEM image of thin H⁺-type PFSI film prepared at room temperature of 0–10°C.

CONCLUSIONS

The morphology of perfluorosulfonic ionomer molecules in DMF was different with concentration. As the concentration of the PFSI/DMF solution increased, the ionomer molecules shrank gradually at concentrations lower than 5 mg/g and aggregated together with capillary liquid bridge force to form bigger aggregates at concentrations higher than 5 mg/g. Accordingly, with increasing concentration, the viscosity of the solution increased first at concentrations from 0.01 to 0.5 mg/g, then decreased at concentrations from 0.5 to 5 mg/g, and increased again at concentrations over 5 mg/g. For concentrations over 150 mg/g, under a steady shear stress of 0.2 Pa, the aggregates overcame the coulomb repulsion to form rods like the rouleaux formed in human blood. When the concentration of the PFSI/DMF solution increased to 300 mg/g, the granules and aggregates were crosslinked together to form a network system. SEM image of the PFSI film prepared at room temperature showed that the film was loosely stacked by the granules and aggregates formed in the solution. So, to prepare solution-cast PFSI membranes with good mechanical strength and other properties, it is necessary to introduce proper methods to fuse the particles, such as the preparation of membranes at high temperature and high

solution concentration or the annealing of the membranes at high temperature.

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