

Rheology of Concentrated Sulfonated Poly(ether ether ketone) Solutions

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ABSTRACT: Sulfonated polyether ether ketone (SPEEK), an ionic polymer, has been shown to be a potential candidate for fuel cell electrolyte as a proton exchange membrane. Rheological behavior of SPEEK solutions is of great interest to understand the molecular associations as well as due to implications in membrane processing. In this work, SPEEK of various degrees of sulfonation (58–80) was prepared and rheology of concentrated solutions of SPEEK was studied. The rheological properties were evaluated using steady and oscillatory shear. It was found that steady shear viscosity and storage modulus at any given concentration, is the highest for the lowest degree of sulfonation SPEEK solutions in *N*-methyl-2-pyrrolidone. The low frequency plateau in storage modulus was observed at some combinations of degrees of sulfonation and concentrations, indicating gel-like behavior in these SPEEK solutions. No significant change in rheological behavior was observed with different polar solvents. Increase of several orders of magnitude in viscosity, storage and loss moduli were observed with increasing concentrations. The role of hydrophobic aggregation and inter-chain associations in determining rheology of SPEEK solutions is argued based on comparisons with other material systems. The rheological behavior of SPEEK solutions with 70 as the degree of sulfonation, suggests crossover from hydrophobic-hydrophilic balance. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40044.

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INTRODUCTION

In past few years, ionic polymers are being investigated for their applications in polyelectrolyte membranes, molecular separations and rheological modification. Sulfonated polymers such as sulfonated poly(ether ether ketone) (SPEEK) are considered as the potential candidates for electrolyte or proton exchange membrane in fuel cell. SPEEK is being investigated because it has high thermal stability, high mechanical strength and high oxidation resistance and good proton conductivity.¹ Chemical structure of SPEEK is shown in Figure 1. It contains repeating units of aryl ether ether ketone and sulfonated aryl ether ether ketone, and their relative numbers are quantified as the degree of sulfonation (DS). DS of an SPEEK macromolecule is the most important parameter in determining its properties.²

Most common investigations on the rheology of the polymers containing ionic groups along the chain, have been carried out on ionomers and polyelectrolytes. In a single chain of ionomer, <15% of the repeating units have ionic groups.³ In a polyelectrolyte, usually all the repeating units have ionic moieties. For sulfonated polymers, DS is 40–90%, implying 40–90% of the

repeating units contain ionic groups. For SPEEK, DS below 55 leads to very poor proton conductivity and DS above 80 leads to water solubility and poor mechanical stability. Given the flexible window of DS for SPEEK, solution rheology with varying concentrations of the polymer, is the focus of this work.

Rheology of ionomers and polyelectrolyte solutions are important to understand the clustering of ionic moieties and interaction between hydrophobic and hydrophilic parts, and the effect of these phenomena on the micro-structure. For example, Weiss and Yu found that in ionomer such as sulfonated poly(styrene), even as low as one sulfonate group per 1000 repeating units can have significant effect on the viscoelasticity.⁴ They suggested that interactions of the ionic groups shift the terminal flow region to low frequency and produce a new low-frequency relaxation. The low-frequency relaxation is believed to arise from long-lived pairwise ionic associations. Additional relaxations have been observed in various ionic polymers such as poly(styrene sulfonate)⁵ and poly(butylene succinate).³ In case of poly(ethylene methacrylic-acid) based ionic polymers, it was found that the presence of ions makes the relaxation time of polymeric chains longer.⁶

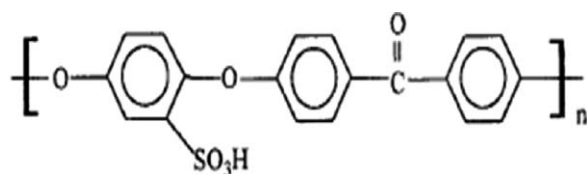


Figure 1. Repeating unit of SPEEK.

For polyelectrolytes as well, rheological properties were found to be different from that of neutral polymers because of the presence of electrostatic interactions between ionic groups. It is well known that the polyelectrolyte solution viscosity increases upon dilution for salt free solutions because of repulsion of charged groups.⁷ Scaling theories predict lower exponents for the variation of polyelectrolyte rheological properties with concentration, in comparison with non ionic polymers in the dilute and semi-dilute regime.⁸

Hydrophobically modified polyelectrolytes result in hydrophobic association which leads to unique rheological properties.⁹ Increase in charge density leads to increase in solution viscosity and modulus.¹⁰ However, a decrease in solution rheological properties has also been observed in associative system with increasing polymer charge density. This decrease has been attributed to a reduction in the number of association due to intermolecular repulsion and increase in polymer solubility.¹¹ Recently, it has been shown, by off-lattice Monte Carlo simulation that, gelation behavior of telechelic polyelectrolytes depends on the interplay between short range hydrophobic interaction and long range electrostatic repulsions.¹² The same group has also reported previously that for telechelic polyelectrolytes, increasing hydrophobic interactions may lead to sol–gel transition at fixed concentrations.¹³ It has also been found that aqueous solutions of hydrophobically modified poly(*N,N*-dimethylacrylamide-*co*-acrylic acid) show shear-induced thickening at critical shear rate due to gelation.¹⁴ There is a need for rheological characterization of SPEEK solutions as well as for investigating relation between microstructure and the rheology.

Processing and fabrication of fuel cell membranes from solutions always involves a liquid–solid transition. Properties of polymer solutions near this transition and the molecular associations near the transition are of great interest. For example, in a possible SPEEK membrane manufacturing process, the initial precursor material would be in a solution, with the ionic groups distributed based on polymer chain interactions, as shown in Figure 2(a). It is known that the final membrane in solid state, has clusters of ionic groups as shown in Figure 2(b).¹⁵ Thus, if we know how the clustering of ionic groups evolves from solution to the membrane, this would help in understanding process–structure–property relation in these polymers. When examining the liquid–solid transition, the concentration would be much larger than the overlap concentration. Therefore, it is of interest to carry out a detailed study of the rheology of sulfonated polymer solutions in concentrated regime and near the transition. Rheology around gelation, an important class of liquid–solid transition, are helpful for developing understanding the role of molecular associations, the microstructure, on gelation.¹⁶ One of the objectives of this work was to examine the

rheology of concentrated SPEEK solutions, approaching liquid–solid transition, and similarity/difference with respect to gelation. As mentioned earlier, SPEEK of a limited range of DS are of interest, and in this work SPEEK of DS 58–80 were investigated.

In this work, SPEEK of various DS were prepared, and the rheology was studied for SPEEK solutions of various combinations of DS and concentrations. The effects of different solvents on rheology of SPEEK solutions were also examined. Steady viscosity and linear viscoelastic oscillatory material functions are characterized, as they provide insights into material behavior under large and small deformations.

EXPERIMENTAL

Materials

Poly(ether ether ketone) (PEEK) powder, grade 450PF with weight average molecular weight of 45000, was purchased from Victrex, UK. *N*-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO) of extrapure and extrapure AR grade were obtained from Sisco Research Laboratories, Mumbai, India. Sodium chloride of analytical grade was also purchased from Sisco Research Laboratories, Mumbai, India. Sodium hydroxide

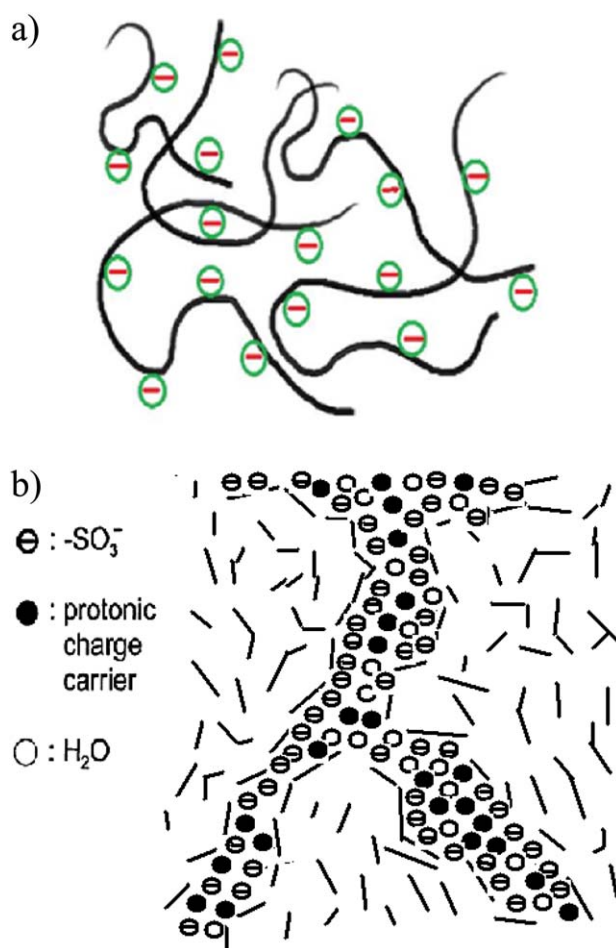


Figure 2. (a) SPEEK molecules in the solution state (b) SPEEK in solid state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was obtained from Ranbaxy Fine Chemicals, Mumbai, India. Hydrochloric acid (35 wt %), grade GR, and Sulfuric acid (98 wt %), grade GR, and dimethylformamide (DMF) were purchased from Merck Specialities, Mumbai, India.

Sulfonation of PEEK

Nearly 16 g of Victrex PEEK powder was dried in an oven for 8 h at 65°C. Then, it was dissolved in 300 mL of concentrated sulfuric acid at 46°C and vigorously stirred for the desired time. The reaction times were 4, 5.5, and 7 h to obtain DS of 58, 70, and 80, respectively. Subsequently, 5 L of ice-cold water were added to the reaction mixture, freezing the reaction. The SPEEK polymer, after filtering, was washed with distilled water 18 times to ensure that the pH of the washing solution was neutral. The SPEEK beads were kept under ambient conditions for 16 h and then dried in oven using a set temperature protocol (60°C for 16 h, 80°C for 16 h, 100°C for 24 h).

Determination of Ion Exchange Capacity (IEC) and Degree of Sulfonation (DS)

SPEEK was first dissolved in (NMP) to make a 10 wt % solution by stirring for 18 h. The solution was then cast in a flat glass Petri dish. The cast membranes were dried at 60°C for 12 h, and then at 80°C for 12 h and finally at 100°C for 24 h. The membranes were treated with 1M hydrochloric acid solution for 2 days at room temperature for protonation and subsequently rinsed with distilled water several times. This step is usually followed for all sulfonated polymers prior to characterization and application as fuel cell electrolyte.

The ion exchange capacity (IEC, meq g⁻¹) of sulfonated PEEK membranes was determined by acid–base titration. The SPEEK membrane (2 cm × 2 cm) was kept at 100°C the oven for 4 h for drying and then weighed (dry weight). The membrane was immersed into 100 mL of 2M NaCl and kept for 3 days for deprotonation, so that SPEEK-H was fully converted into its sodium salt form, SPEEK-Na. Each 100-mL beaker solution was titrated against 0.01M NaOH using phenolphthalein as an indicator. IEC is defined as the amount of ion exchange ($N_{\text{SPEEK-H}}$, referring to hydrogen ion of sulfonic acid groups) in SPEEK.

$$\text{IEC} = N_{\text{SPEEK-H}} / W_{\text{sample}} \times 100 (\text{meq/g}) \quad (1)$$

where W_{sample} is the weight of dry SPEEK-H after protonation. The degree of sulfonation (DS) can be calculated from IEC using

$$\text{DS} = [288 \times \text{IEC}] / [1000 - (80 \times \text{IEC})] \quad (2)$$

where 288 is the molecular weight of single PEEK monomer unit and 80 is the difference between molecular weight of SPEEK monomer and PEEK monomer unit.

Sample Preparation

SPEEK samples of three different DS, 58 ± 0.43 , 70 ± 3 , 80 ± 4 , were made. As mentioned earlier, SPEEK of DS lower than 55 is not soluble in any solvent, and DS of SPEEK higher than 80 is soluble in water (and is more difficult to recover after the sulfonation reaction is complete). SPEEK solutions of different concentrations (C_w), varying from 10 to 30 wt %, were prepared in NMP. For SPEEK of DS 70, solutions were prepared in all the three solvents: (dielectric constants, $\epsilon_r = 46.68$), DMF

Table I. Concentrations of SPEEK Solutions

Material	wt %	Molarity
SPEEK DS 58	10–30	0.342–1.320
SPEEK DS 70	10–30	0.332–1.283
SPEEK DS 80	10–30	0.325–1.254

($\epsilon_r = 36.71$), and NMP ($\epsilon_r = 32.2$). To prepare the solutions, an appropriate amount of SPEEK was dissolved in the solvent and kept for 17 days at room temperature to ensure that it is homogeneously mixed. Utmost care was taken during the preparation of the solution to make sure that it is free from any contamination. The concentrations of SPEEK solutions in terms of molarity have been summarized in Table I.

Rheology

The oscillatory shear and rotational shear tests were carried out using Anton Paar MCR-301 Rheometer. All the rheological experiments were done at 25°C unless otherwise stated. Cone and plate geometry (cone angle 1.010°, diameter 25 mm, and cone truncation gap of 0.047 mm) was used. Following is a description of the rheological tests:

- Determination of linear viscoelastic range: Strain was varied from 0.01 to 100%, at several frequencies, to evaluate the linear viscoelastic range.
- Oscillatory shear: Frequency was varied from 0.628 to 628 rad s⁻¹, at strain amplitudes in the linear viscoelastic range. For solutions of lower concentrations, results at frequencies lower frequencies may not be reliable due to the sensitivity of rheometer. Therefore, storage modulus (G'), loss modulus (G'') and $\tan \delta$ have been reported after ensuring reliability and repeatability.
- Steady shear: shear rate was varied from 1 s⁻¹ to 100 s⁻¹.

For dilute and semidilute solutions, the solution viscosity (η) is usually presented in terms of specific viscosity or intrinsic viscosity. Specific viscosity (η_s) is defined as the increase in the viscosity of solvent (η_0) when polymer is dissolved:

$$\eta_s = (\eta - \eta_0) / (\eta_0) \quad (3)$$

In the present work, the focus is on the semidilute and concentrated regimes, and viscosity is being used for presenting the steady shear results.

RESULTS AND DISCUSSION

In this section, the rheological behavior of sulfonated poly(ether ether ketone) (SPEEK) in *N*-methylpyrrolidone (NMP) is presented initially, followed by the behavior of SPEEK in different solvents.

SPEEK in NMP

SPEEK, of different degree of sulfonation (DS), in NMP were characterized in oscillatory and steady shear. The dynamic mechanical behavior of many polymer solutions follows viscous behavior at low concentrations,

$$G' \sim \omega^2; G'' \sim \omega; \text{ as } \omega \rightarrow 0. \quad (4)$$

For higher concentrations, oscillatory response of DS 58 SPEEK solutions in NMP, at three representative concentrations, is

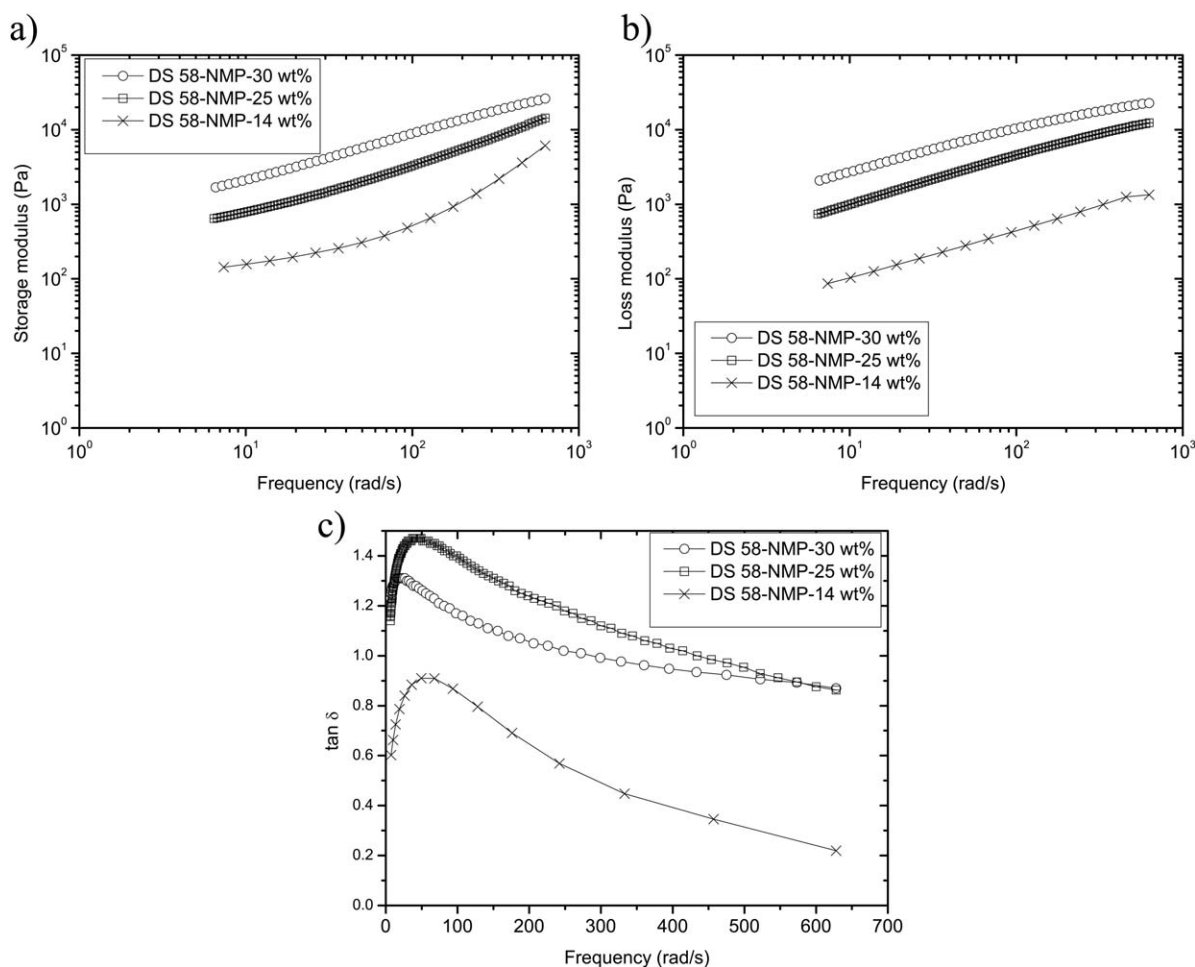


Figure 3. Oscillatory shear response of SPEEK DS 58 in NMP (a) storage modulus (b) loss modulus (c) $\tan \delta$.

shown in Figure 3. Both storage and loss moduli are increasing functions of frequencies. For 14% SPEEK solution, a low-frequency plateau in G' is apparent. Interestingly, this solution exhibits lower $\tan \delta$ compared to higher concentration solutions. This implies prevalence of associations, leading to stronger elastic response. However, the associations seem to be weak, and unlike at higher concentrations, do not lead to shear thinning behavior as described later.

In general, for higher concentrations of SPEEK solutions regardless of the DS, significant deviation from eq. (4) was observed. This deviation, usually observed with increasing concentration, is taken to be an indication of gelation transition, as is reported for poly(vinyl/dioctyle phthalate)/tetrahydrofuran¹⁷ and for poly(acrylonitrile) in DMSO.¹⁸ The quantitative nature of this deviation, as well as other indicators of gel-like response of SPEEK solutions at higher concentrations are discussed below.

Steady shear viscosity of SPEEK solutions of DS 58 in NMP (for the same concentrations as given in Figure 3) is shown in Figure 4. As expected, the viscosity is higher for the higher concentration. Shear thinning behavior is apparent for 25 and 30 wt % solutions. On the other hand, 14% SPEEK solution shows no shear thinning for the range in which data is presented. SPEEK solutions of DS 70 and DS 80 exhibited qualitatively

similar behavior, shear thinning at higher concentrations. Similar to the departure from frequency dependence of the moduli, shear thinning behavior is an indication of the complex nature of SPEEK solutions. Given that higher concentration solutions show shear thinning, while 14% SPEEK solution does not, we

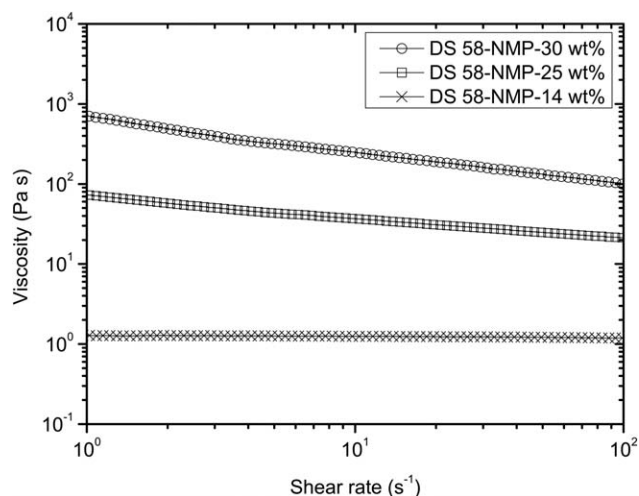


Figure 4. Steady shear viscosity of SPEEK solutions of DS 58 in NMP.

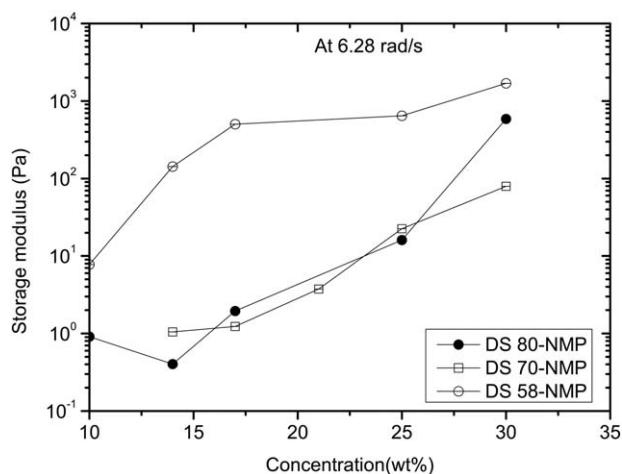


Figure 5. Storage modulus variation with concentration at 6.28 rad s^{-1} for DS 58, 70, and 80.

can infer that associations at lower concentrations are weak. These weaker associations lead to elastic contributions under small deformations of oscillatory shear, but viscous nature is obtained at larger deformations as in case of steady shear. Such behavior is observed only at lower DS, or with larger hydrophobic segments. Therefore, even at low concentrations, the larger number of hydrophobic segments would lead to weak associations.

The overall dependence of oscillatory and shear response for different DS and concentrations has been highlighted by focusing on storage modulus and viscosity in the following discussion. Not all solutions exhibited a low-frequency plateau. Therefore, to compare storage modulus of different solutions, we have used the value of storage modulus at 6.28 rad s^{-1} . Figure 5 shows variation of storage modulus (G' , at 6.28 rad/s) for different concentrations (C_w) of SPEEK solutions of different DS. As expected, the storage modulus of SPEEK solution of any DS increases with increase in concentration. It is also worth mentioning that storage modulus is found to be the highest for SPEEK solution with the lowest DS, i.e., SPEEK solution of DS 58 has the largest storage modulus value compared to SPEEK solutions of DS 70 and DS 80 at any given concentration. Power law dependency of plateau moduli on concentration is known for other systems such as associative telechelic polyelectrolytes, and is useful for the analysis of network structures.¹⁹ Such quantitative analysis on SPEEK solutions is not possible, as the plateau modulus was not observed in all the cases.

Similar to the increase in storage modulus, viscosity of SPEEK solutions is higher at a higher concentration. Variation of the viscosity for different DS and concentrations is shown in Figure 6. Many solutions investigated in this work did not exhibit the Newtonian plateau at lower shear rates, and hence to calculate viscosity, viscosity of the sample at shear rate of 1 s^{-1} was chosen. As with the case of storage modulus, the viscosity was found to be the highest for SPEEK solution with the lowest DS.

Storage modulus and viscosity are higher for lower degree of sulfonation or higher level of hydrophobicity in the polymer chains. It is anticipated that the hydrophobic groups are capable

of aggregating, forming larger structures. As the sulfonation content is increased, less hydrophobic character is present within the chain and a corresponding decrease in the inter-chain associations results.²⁰ SPEEK solution with the lowest DS 58, has the highest concentration dependency. We speculate that with the larger fraction of hydrophobic groups along the chain, the effectiveness of aggregation increases at higher concentration. Similar increase in viscosity with hydrophobic content of the chain, though for an entirely different system, has also been reported for aqueous solution of hydrophobically modified poly(*N,N'*-dimethylacrylamide-*co*-acrylic acid), above critical aggregation concentration.¹⁴ They suggested that intermolecular hydrophobic associations might be taking place thereby forming aggregates, which eventually percolate to form self-supporting gels with further increase in concentration.¹⁴ Similar observation has been made for associative telechelic polyelectrolyte, poly(sodium acrylate) end-capped with short poly(styrene) (PS) blocks, in aqueous media.¹⁹ In their case also, $\eta^* \sim C^{5.9}$. A weak gel due network formed by PS junctions bridged by stretched poly(sodium acrylate) long chains. It should be noted that concentrations of polymers are much lower in associative polyelectrolyte telechelic system. The average molecular weight of SPEEK is 45,000 compared to 107,400 of associative polyelectrolyte telechelic system. Therefore, these comparisons do not necessarily indicate associations in SPEEK which are similar to other systems. For flexible polyelectrolytes specific viscosity varies as $\sim C^{3.75}$ for concentrated solutions.²¹ The concentration dependence is much stronger for SPEEK solutions possibly due to semiflexible backbone of SPEEK.

One important thing to notice from Figures 5 and 6 is that the dependence of viscosity and storage modulus on concentration for both DS 70 and DS 80 are comparable. It appears that when the DS reaches 70, viscoelastic properties do not change much with the number of sulfonic groups on the repeating unit. In other words, when the DS is more than 70, rheology of the SPEEK solutions is probably not much affected by the number of charged groups. We speculate that, when the DS is on the lower side, viscoelastic responses of SPEEK solutions, for a given concentration, increases with a decrease in DS. In other

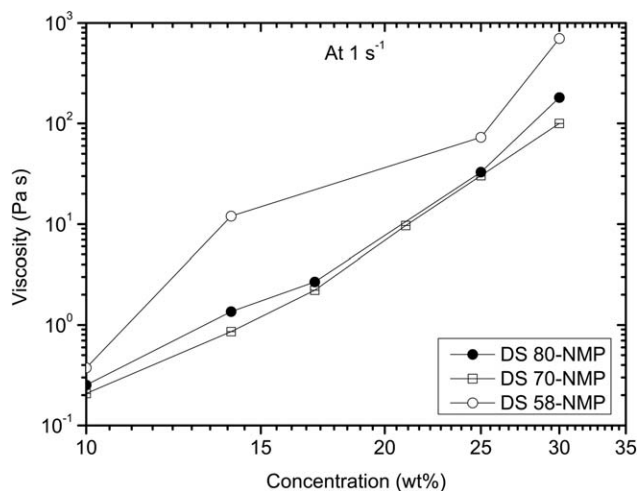


Figure 6. Viscosity variation with concentration for DS 58, 70, and 80.

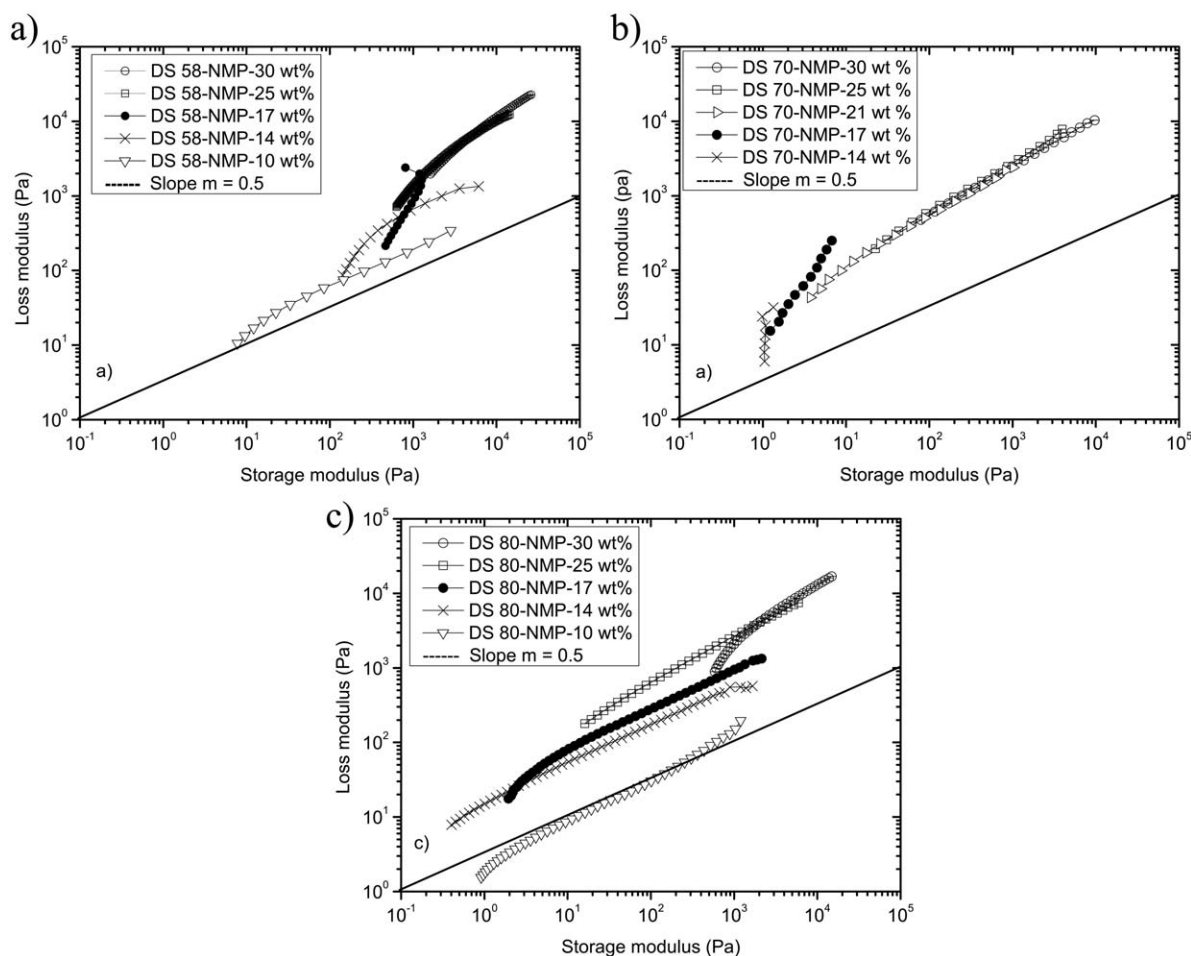


Figure 7. Cole–Cole plots of SPEEK solutions in NMP with (a) DS 58 (b) DS 70, and (c) DS 80 for the concentrations as indicated in the figure.

words, there is an inverse relationship between elasticity and DS, for SPEEK below DS 70. On the contrary, when the number of ionic groups are on the higher side, i.e., greater than in case of DS 70, viscoelastic properties of the SPEEK solutions do not change significantly with a change in number of ionic groups.

The presence of physical structures in SPEEK solutions can be elucidated by examining Cole–Cole plots of SPEEK for DS 58, DS 70, and DS 80 in NMP as shown in Figure 7(a–c). In these log-log plots of G'' Vs G' a slope of m can be defined as,

$$G'' \sim G'^m \quad (5)$$

A value of 0.5 for m would follow from eq. (4) for terminal viscous response. It has also been used to infer isotropic and homogeneous nature of the polymer solutions or polymer melt.²² The slope is higher when the melt or solution contains physical structure, which dissipates energy by collapse under shear.²²

The presence of strong hydrophobic aggregations is apparent in Cole–Cole plots of SPEEK solutions of DS 58 in NMP, as $m > 0.5$ for all of them. In Figure 7(a), as the concentration increases the slope also increases indicating increasing presence of the aggregation, network or heterogeneity in the sample. The nature of these could be possibly be elucidated by exam-

ining scattering response of concentrated solutions of sulfonated polymers. Similar rheological observation has been reported for poly(vinyl alcohol) solutions due to increase in hydroxyl group interactions.²³ For 10 wt % solution, slope was observed to be 0.5 due to the viscous and homogeneous nature of solution, but at higher concentration of 30 wt %, slope increased due to increasing interactions among hydroxyl groups.

In contrast, in Figure 7(b,c), the slopes remain 0.5 for many concentrations for both DS 70 and DS 80. The exceptions were observed to be the higher concentration solutions (>25 wt %) for DS 80. Another important point to note from Figure 7(b) is the collapse of storage and loss moduli on a single master curve. Although storage modulus and viscosity variation with concentration are comparable for DS 70 and DS 80 solutions (Figures 5 and 6), significant difference is observed through these Cole–Cole plots.

Another way to examine the structural features of a polymer solution is to examine the variation of G' at low frequencies.

$$G' \sim \omega^n \quad \text{as } \omega \rightarrow 0. \quad (6)$$

Slope of $n=2$ would be an indication of terminal viscous behavior, with a structure-less fluid, while the slope near to 0

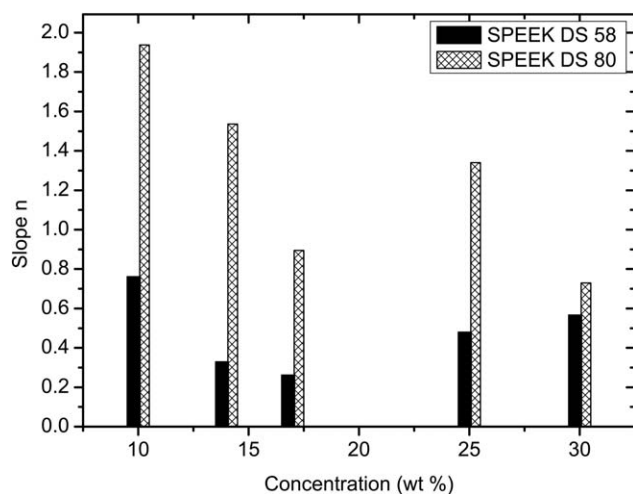


Figure 8. Variation of slope of storage modulus at lower frequency with concentration for DS 58 and DS 80. Slope has been calculated from linear fit of the curve from frequency values lower than 20 rad s⁻¹.

would indicate gel like behavior with a percolated network due to molecular associations.

Variation of n , calculated at lower frequency, with respect to concentration is presented in Figure 8 for DS 58 and DS 80 SPEEK solutions. The variation of slopes with the repeated trials with the same material was within 10%. It is interesting to note that for every concentration, slope of SPEEK solutions of DS 58 is lower compared to that of SPEEK solutions with DS 80. This would be due to the larger amount of hydrophobic content in the sample leading to stronger hydrophobic aggregations.

The complex viscosity (η^*) is a useful variable in describing the viscoelastic behavior near gelation. Figure 9 shows the dependency of complex viscosity on frequency for 30 wt % SPEEK solutions in NMP of different DS. For all the three samples, viscosity decreases with increase in frequency. At lower frequencies, for DS 58 and DS 80, the viscosity decreases with an increase in frequency. However, SPEEK of DS 70 has almost a constant viscosity in the low frequency region, which indicates even till 30 wt % there may not be a percolated network to lead to gel-like behavior. It should be noted that the formation of critical gel in SPEEK solutions (DS 58 and DS 80) could not be established. However, all the results presented, taken together indicate molecular organizations. This overall conclusion is substantiated further by examining the results based on Cox–Merz rule and Winter–Chambon criterion.

The presence of microstructure, and it being sensitive to shearing, can also be inferred from comparing steady shear and complex viscosities based on Cox–Merz rule.^{24,25} As can be seen in Figure 9, Cox–Merz rule is not obeyed for 30% DS 58 and DS 80 SPEEK solutions. The interesting behavior of 14% DS 58 SPEEK solution was described earlier, and as expected the Cox–Merz rule was not observed for this solution as well. On the other hand, the Cox–Merz rule was observed for other DS at lower concentrations.

Based on the results presented so far, it is evident that SPEEK solutions become generally more viscoelastic at higher concen-

trations. Exception was observed at lower concentrations at DS 58, for which a weak gel-like behavior was observed. The quantitative variations in the rheological behavior as functions of concentration as well as DS are complex. In the next section, the effect of dielectric medium or solvent on the rheological behavior of SPEEK solutions is presented.

Gelation in polymer solutions has also been analyzed by observing variation of $\tan \delta$ Vs concentration at different frequencies.¹⁷ Based on the Winter Chambon criterion, $\tan \delta$ is independent of frequency at the gel point.¹⁶ This criterion has been observed for crosslinking polymers, even in the presence of fillers due to polymer network²⁶ and for polymers with a percolating filler network.²⁷ In the first case, gelation is observed due to increase in the extent of reaction with time, while in the second case, gelation is observed with an increase in concentration of the filler. In all the above cases, observation of Winter Chambon criterion implies the presence of self-similar percolated network at the gel point. A similar analysis was carried out for SPEEK solutions with different concentrations. For example, such behavior is shown in Figure 10 for SPEEK solution of DS 80. $\tan \delta$ increases and decreases with concentration at a particular frequency. It can be observed that $\tan \delta$ is less and less dependent on frequency at higher concentrations. Additionally, it can be observed that $G''/G' \sim 1$ at higher concentrations. Therefore, it appears that the gel point indicating $\tan \delta$ being independent of frequency and $G'' = G'$, if at all, would be observed at a concentration higher than 30 wt %. It was not feasible to investigate such higher concentrations (higher than 30%) due to sample heterogeneities and miscibility limits.

SPEEK in Different Solvents

There have been several reports of differences in properties of SPEEK films prepared from different solvents. The differences have been attributed to residual solvent content and/or morphological features that arise during film casting due to solvent/polymer interactions.^{28,29} SPEEK solutions have also been

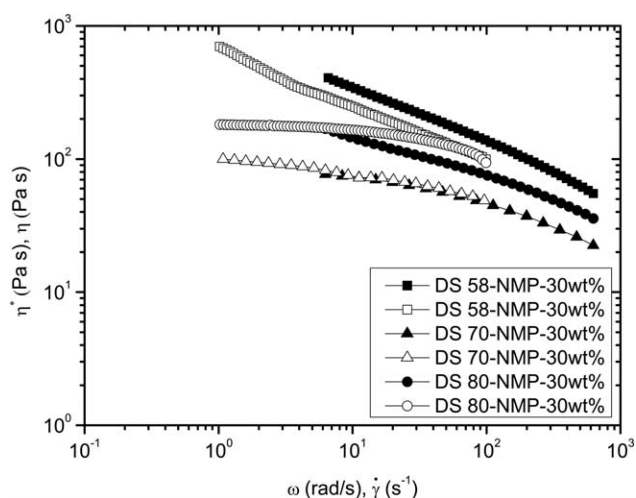


Figure 9. Complex viscosity (filled symbols) as a function of frequency for SPEEK solutions with DS 58, 70, and 80 in NMP for 30 wt % concentration. For observing Cox–Merz rule, steady viscosity (open symbols) with strain rate is also shown.

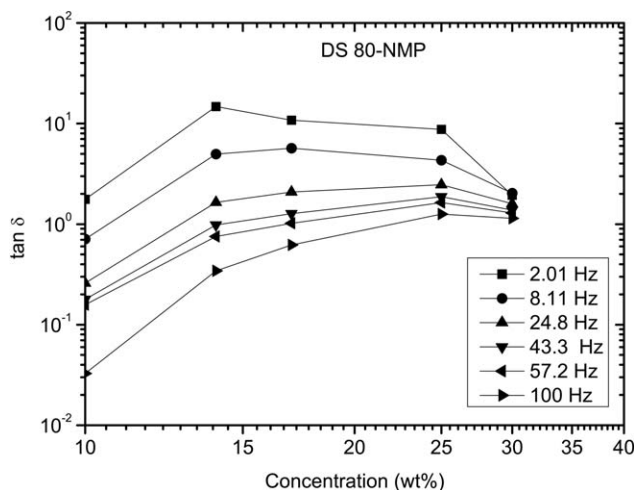


Figure 10. $\tan \delta$ as a function of concentration at different frequencies for SPEEK solution of DS 80.

reported to have different viscosities based on the solvent due to differing solvent/polymer interactions.³⁰

Steady shear and oscillatory shear behavior was examined for SPEEK solutions of DS 70 in all the three solvents; DMF ($\epsilon_r = 36.71$), DMSO ($\epsilon_r = 46.68$) and NMP ($\epsilon_r = 32.2$). Shear thinning begins from 25 wt % with all the solvents. However, the extent of shear thinning is marginally higher for SPEEK in DMSO solution for 30 wt % solution, compared to SPEEK in NMP and SPEEK in DMF for the same concentration. When expressed in terms of a power law model (viscosity \sim shear rate^{*index*}) leads to a power law index for DMSO is 0.45 while that for NMP and DMF are 0.38 and 0.36, respectively. As discussed earlier, for the SPEEK solution of DS 70 in NMP, a low frequency plateau in complex viscosity was observed. This plateau and the onset of plateau (in terms of critical shear rate above which shear thinning behavior is exhibited) are not affected by the solvent.

The dependence of the storage modulus, measured at 6.28 rad s^{-1} , on concentration is shown in Figure 11. Though quantitative

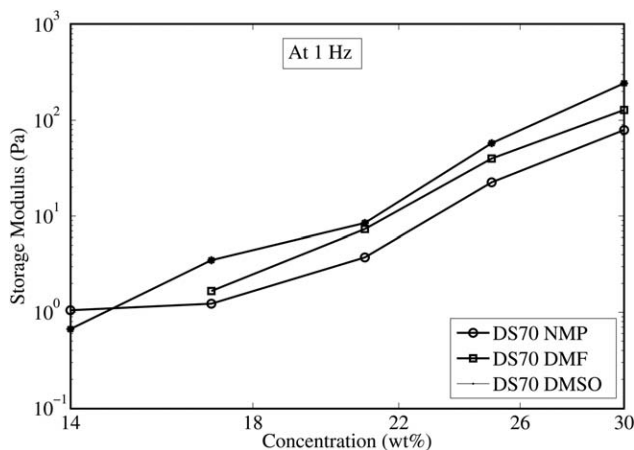


Figure 11. Behavior of storage modulus at 6.28 rad s^{-1} with concentration for DS 70 in different solvents.

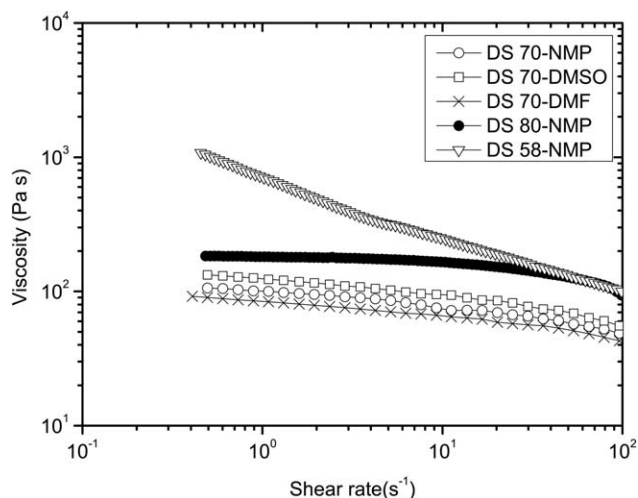


Figure 12. Steady shear viscosity comparison for all 30 wt % solutions for all the samples as indicated in the figure.

tively different, the qualitative variation with respect to concentration is similar with SPEEK solutions of all solvents. When behavior is observed with Cole–Cole plots, for all the three solvents, higher concentration solutions exhibited slopes ($m > 0.5$). In addition, there is superimposition of all the curves in all the three solvents, as mentioned earlier for SPEEK (DS 70) solutions in NMP. SPEEK film properties are influenced quantitatively, though not qualitatively, when prepared from different solvents. Similarly, the rheological behavior of concentrated SPEEK solutions with different solvents, though not qualitatively different, was observed to depend marginally on the solvent.

Overall Comparison Amongst Different Solutions

Steady shear and oscillatory shear rheology of 30 wt% SPEEK solutions with different DS, and SPEEK of DS 70 in different solvents are illustrated in Figures 12 and 13. Stronger shear thinning is observed in SPEEK, of DS 58, in NMP solution compared to all the other samples. As we discussed, this would

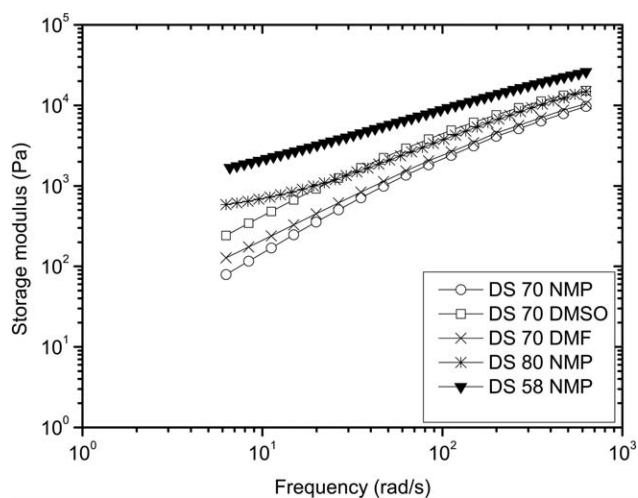


Figure 13. Storage modulus with respect to frequency for 30 wt % solutions.

be due to the presence of strong hydrophobic aggregation at lower DS, and the break-up of these aggregations at higher shear rates. For SPEEK solutions with DS 70 and 80, Newtonian plateau at low shear rates is observed, followed by slight shear thinning at higher shear rates.

Storage modulus as a function of frequency is shown in Figure 13 for 30 wt % SPEEK. SPEEK solutions with DS 80 and DS 58 exhibit a weak gel-like behavior with plateau at lower frequency range. Plateau modulus for SPEEK solution with DS 58 is larger than that of DS 80 owing to more hydrophobic aggregation. Another consequence of this aggregation is that the scaling of G' with frequency is less for the DS 58 solution, compared to that of the DS 80 solution. For SPEEK solutions with DS 70 in all the solvents, scaling of G' in the terminal region, is more than that for both DS 58 and DS 80 SPEEK solutions.

The overall rheology is very different for DS 70 solutions, as compared to DS 58 and DS 80 solutions. Therefore, we speculate that when the DS is low, hydrophobic interactions dominate. On the other hand, for DS 80 solutions, hydrophobic groups are fewer in number and the ionic groups' interactions dominate. SPEEK of DS 70 appears to be in crossover region, and therefore exhibits rheological behavior which is different compared to DS 58 and DS 80. It is interesting to note, that a DS of around 70 is usually claimed to be the optimum for fuel cell membrane applications.

As discussion along with Figure 2 highlighted, with an optimum DS, SPEEK membranes in solid state contain hydrophobic/hydrophilic molecular segregation to allow interconnected hydrophilic clusters and channels as conducting pathways. At less than optimum DS (such as DS 58), the larger number of hydrophobic groups leads to stronger associations amongst the groups. Similarly, at more than the optimum DS (such as DS 80), the larger number of hydrophilic groups leads to stronger associations amongst the groups. Consequently nonpercolating cluster-channel morphology exists at less DS, while very large clusters exist at more DS. Our results with the concentrated solutions also seem to suggest this crossover behavior when SPEEK solutions of different DS are observed.

The scaling of steady shear viscosity with concentration, and the observation of Cox–Merz rule depends on the microstructure of the polymer solutions.^{31,32} The effect of concentration is determined mainly by molecular weight, inter-molecular interactions, type of solvent and presence of additives such as salts. A rich variety of microstructure based on molecular associations and phase separations have been reported based on relative influence of these factors. The indications of microstructure and the crossover behavior reported in this work demonstrate the need for examining microstructure of the concentrated sulfonated polymer solutions. Furthermore, whether the microstructure of the solution of DS 70, as surmised in this work, leads to the optimum structure in the solid state membranes, needs to be investigated.

CONCLUSIONS

Sulfonated poly(ether ether ketone) (SPEEK), an important material being investigated for fuel cell membrane applications,

is an interesting model system to study the rheology of concentrated solutions of ionic polymers. In this work, SPEEK solutions of varying degrees of sulfonation (DS), concentrations, and in different solvents, were investigated for their rheological behavior. Based on the oscillatory and steady shear measurements, linear viscoelastic properties and viscosity were characterized for all the solutions. Moduli as well as viscosity increased several orders of magnitude with concentration, pointing to strong associative behavior. A gel-like rheological response could be ascertained based on scaling of G' , G'' , complex viscosity and variations of $\tan \delta$ with concentration. The failure of Cox–Merz rule for several SPEEK solutions may also be due to the complex microstructure of these solutions. The rheological response is influenced by DS, since changing DS leads to different fractions of hydrophobic and hydrophilic groups. Among the DS investigated, rheological properties of DS 70 SPEEK solutions were shown to be different (compared to the other DS), and it is surmised that this is due to an apparent balance of hydrophobic and hydrophilic groups. The rheology of SPEEK solutions with lower and higher DS appears to be dominated by either hydrophobic or hydrophilic groups, respectively. The microstructure of ionic polymer solutions, and its relation to rheology, should be explored further to investigate the nature of associations in these systems.

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