Scaling Behavior of the Viscosity of Poly(dimethylsiloxane) Ionomer Solutions

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ABSTRACT: We report solution viscosities of poly(dimethylsiloxane) (PDMS) sodium and zinc ionomers with tailored number of monomers between ions and number of ions per chain in good and in Θ solvent conditions over a broad range of concentrations. We analyze our data in terms of three concentration regimes of viscosity predicted for associating polymers. The first is a sticky Rouse semidilute unentangled regime with mostly intermolecular associations and renormalized association lifetimes. The second is a sticky reptation semidilute entangled regime also with mostly intermolecular associations and renormalized association lifetimes. The third regime is observed when strands between ions are entangled. For sodium ionomers with few ions per chain the power-law exponents observed experimentally in three predicted concentration regimes match the theoretical predictions. In the case of zinc ionomers with their divalent zinc ions, the power-law exponents do not match the exponents from theory. For ionomers with greater than 5−6 ions per chain, equilibration (dissolution) of dilute solutions is extremely slow and equilibration at higher polymer volume fractions to form physical networks is slow. At low polymer volume fractions, we find that zinc ionomers with fewer than three ions per chain behave as nonassociating polymers.

1. Introduction

Solutions of associating polymers have found an increasing number of applications.[1,2] Considerable theoretical[3−5] and experimental[6−16] effort has been devoted to understanding the rheology of these materials. Most associative polymer systems studied in the literature are hydrophobically modified water-soluble polymers.[6−16] As discussed in a previous paper,[17] we have developed a strategy to synthesize poly(dimethylsiloxane) (PDMS)-based ionomers with tailored number of monomers between ions, ions per chain, and cation. This allows us to synthesize ionomers with structures systematically varied to examine the viscosity vs polymer volume fraction for this highly flexible hydrophobic polysiloxane backbone. In this paper we discuss the solution viscosities of these model poly(dimethylsiloxane) zinc and sodium ionomers with low mol % of ions in Θ solvents and in good solvents by using inert polydimethysiloxane fluids of low molar mass as solvents.

We noted previously[17] that aggregates (assemblies of many cation−carboxyl pairs) are not expected with the zinc and sodium ionomers considered here, and the assumption of pairwise interactions may be applicable. It is therefore worthwhile to analyze our data in terms of models of associating polymers with stickers that have pairwise interactions. Recently, Rubinstein and Semenov[4] proposed scaling laws for the viscosity dependence on polymer volume fraction for associating polymers (i.e., $\eta \sim \phi^a$ where η is the zero-shear viscosity, ϕ is the polymer volume fraction, and a is the power-law scaling exponent) based on the sticky Rouse[5] and sticky reptation[4] models. The models are based on associating polymers with many stickers per chain, each with pairwise interactions. They predict a number of regimes of viscosity dependence on polymer volume fraction based on parameters linked to the solvent quality and associating polymer structure, i.e., the length between stickers, overall molar mass, strength of interactions, and entanglement molar mass of the polymer. From a technological standpoint, the existence of distinct regimes provides an opportunity to tailor polymer solutions for specific performance. From a fundamental science standpoint, it provides an opportunity to test our understanding of polymer solutions dynamics for diverse chain backbones. The different viscosity regimes provide further insights into the transformations in structure as a function of polymer volume fraction.

We review below the comparisons between the theoretical predictions of the scaling of viscosity with polymer volume fraction made by the Rubinstein and Semenov theory[4] and experiments for hydrophobically modified water-soluble polymers. All experiments to date have been conducted under good solvent conditions. The first application of the theory was with the poly(acrylamide) containing hydrophobic blocks of *N*,*N*-dihexylacrylamide (DiHexAM).[10,11] The number of hydrophobic stickers per chain, *S*, was tuned by adjusting either the molecular weight of the polymer, or the total hydrophobe content, or the length of the hydrophobic blocks. In the semidilute entangled regime, a scaling exponent of 4 (i.e., $\eta \sim c^4$, where c is the concentration of the polymer in the water and η is the zero-shear viscosity), which is comparable to the theoretical prediction of 3.75, is observed irrespective of the number of hydrophobes per micelle, the hydrophobic block length, and the hydrophobe content in the monomer feed. The authors also reported on the semidilute unentangled regime where viscosity grows strongly as a function of the above-mentioned variables. We note that the molar masses of polymers used in these studies (0.1−2.2 million g/mol) were higher than the molar masses considered here (less than 0.08 million g/mol).

Polyacrylamides hydrophobically modified with small amounts of *N*,*N*-dialkylacrylamides (*N*,*N*-dihexylacrylamide and *N*,*N*-dioctylacrylamide) were prepared as telechelic, as multisticker, and as associative polymers having hydrophobic groups along the chain as well as at the chain ends by Jimenez-Regalado et al.[14] These authors found that, irrespective of the size and location of the hydrophobic groups, a scaling exponent of 4 in the semidilute entangled regime was observed experimentally, which compared well with a theoretical prediction of 3.75 in a

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Table 1. Molar Mass and Polydispersity of OH-Terminated PDMS Precursors Used in the Synthesis of Ionomers

precursor chains	M_n (kg/mol)	M_{peak} (kg/mol)	PDI
6K	6.0	5.6	1.28
11K	12.5	11.2	1.32
15K	16.4	14.7	1.37
18Ka	17.8	18.0	1.32
18Kb	19.6	18.1	1.40
27K	29.5	27.2	1.32

good solvent. Finally, Cram et al.[16] have studied the scaling behavior of copolymers based on *N*,*N′*-dimethylacrylamide (DMAM) containing dodecyl or octadecyl groups. They observed exponents that correlate well with two predicted cases of sticky Rouse dynamics at very low polymer volume fractions in a good solvent.

The second class of hydrophobically modified polymers whose viscosities have been interpreted in terms of this scaling theory are hydrophobically modified alkali soluble emulsion (HASE) polymers.[8,9,12] These polymers usually consist of hydrophilic methacryclic acid (MAA) and ethyl acrylate (EA) segments with hydrophobic side chains attached to the backbone via urethane linkages to unsaturated alkyl or aryl groups that are separated from the backbone by 5−100 ethylene oxide units. Abdala et al.[8,9] have found three concentration regimes of viscosity in these polymers. In regime one, they find a scaling exponent of 1.2 for low MAA content HASE polymers and a scaling exponent of 0.6 for high MAA content polymers, which implies predominantly intramolecular interactions. In regime two, where interactions convert from intramolecular to intermolecular, they observe a very high exponent of 9 for low MAA content and 5.4 for high MAA content (comparable to the theoretical prediction of 4.2). In regime three, hydrophobes are primarily engaged in intermolecular interactions, and they observe a scaling of 2.6, much lower than 3.75 predicted by theory. In the third regime they also observe that this exponent depends on whether a water-rich solvent or a propylene glycol (PG)-rich solvent is used. In a PG-rich solvent they observe an exponent of 1.4, similar to that of a polymer without any hydrophobes.

In summary, a number of predictions seem to hold in a good solvent system. The samples considered above have high polydispersity, complex structures, and generally weak hydrophobic interactions. Given these conditions, it is indeed remarkable that experimental observations come close to the predictions of a theory that requires pairwise interactions between strongly interacting groups. We present in this paper solution viscosity measurements from our tailored moderate-polydispersity ionomer systems with strong interacting groups in both good solvent and in theta conditions to provide further insights into the applicability of the models.

2. Experimental Procedures

2.1. Synthesis of Tailored Polydimethysiloxane with Interacting Groups. The synthesis involves a polycondensation reaction of hydroxyl-terminated PDMS of low polydispersity with a dichlorosilane compound containing a *tert*-butyl-protected carboxylic acid group, which incorporates the carboxyl group at fixed intervals. These intervals are determined by the molar mass of the precursors OH−PDMS−OH. These precursor chains were characterized using gel permeation chromatography (GPC) to measure the polystyrene-equivalent number-average molar mass and polydispersity index (PDI). A correction to the molar masses based on an established calibration curve for PDMS[18] was only 5% for the lowest molar mass precursor chain (6K) and much smaller for the higher molar mass ionomers. Toluene was used as the solvent. Table 1 shows the polystyrene-equivalent molar mass (M_n), the molar mass corresponding to the peak position of the gel permeation chromatograph (M_{peak}), and PDI of the OH−PDMS−OH precursors. The precursor names are rounded-off values of M_{peak}. Cleavage of the *tert*-butyl group with ppm concentrations of triflic acid as a catalyst yields the acid form (hereafter called PDMS−COOH samples). To make ionomers, PDMS−COOH solutions are neutralized with 100% excess of zinc(II) or sodium acetylacetonate. The final step is a fractionation in a good/bad solvent mixture to yield fractions with moderate polydispersity. The details of the synthesis scheme are reported elsewhere.[17]

Table 2. Molar Mass and Polydispersity of Polymers Used in This Study

polymer chains	M_n (kg/mol)	M_{peak} (kg/mol)	PDI	avg. no. of COOH sites/chain
		Zinc Samples		
6K-f1-Zn	80.7	122.0	1.48	19
6K-f2-Zn	46.4	61.7	1.41	9
11K-f2-Zn	37.9	48.6	1.38	3
18Ka-f1-Zn	72.0	122	1.53	6
18Ka-f2b-Zn	52.3	96.1	1.45	4
18Ka-f3-Zn	45.0	63.8	1.32	3
27K-f1-Zn	57.6	75.7	1.43	2
		Sodium Samples		
11K-f2-Na	29.1	41	1.48	3
18Kb-f1-Na	56.0	61.7	1.4	2
		COOH Samples		
11K-f1-H	60	81.0	1.58	6
27K-f1-H	61.7	86.7	1.51	2
		Unmodified PDMS		
reference	55.5	89.7	1.56	

Table 2 lists the ionomers used in this study with their M_n, M_{peak}, PDI, and the average number of COO$^-$ groups. The values of M_{peak} listed in Tables 1 and 2 give additional information on the molar mass distribution. (For example, the percent difference between M_n and M_{peak} is small for the precursor chains but larger for the fractionated ionomer chains despite comparable PDIs.) We also found it more convenient to define the number of ions per chain based on the peak molar mass (see below) so that an ionomer that leads to a physically cross-linked network would have an average of at least two ions per chain based on this definition. The average number of COO$^-$ groups is calculated as $\{(M_{peak}/M_n$ of precursor PDMS$) - 1\}$ with the assumption that there are no COO$^-$ groups at the ends. However, there will be a fraction of chains with COO$^-$ groups at the ends in which case the average number of COO$^-$ groups would be $\{(M_{peak}/M_n$ of precursor PDMS$) + 1\}$. For consistency, we assumed there are no COO$^-$ end groups to characterize the ionomers used here. As an example of the nomenclature used here, 6K-f1-Zn indicates 6K precursor chains, fraction 1, and counterion Zn.

2.2. Viscosity Measurements. Steady shear rate sweeps were carried out with a Rheometrics RDA II rheometer in parallel plate geometry with 10, 15, or 25 mm diameter plates to obtain the zero-shear viscosity. For all samples, the zero-shear viscosity was estimated as the average of all viscosity data points in the Newtonian regime where the viscosity does not change with shear rate. For samples with very low viscosity, the lower shear rate data points were noisy due to instrument sensitivity, and we excluded such points from the averaging.

3. Results and Discussion

We have reported the viscosities of melts of the samples used in this study.[17] Melts of low ion concentration (0.3−1.3 mol %) zinc ionomers and their unneutralized COOH precursors were found to precipitate as polymers that flow and exhibit a zero-shear viscosity. But these freshly prepared samples are in a nonequilibrium state; 2 days after precipitation the viscosity increases 2−3-fold for samples with a moderate number of ions per chain (between 3 and 5). The viscosity increases thereafter, and the samples equilibrate to physically cross-linked networks. The gel time follows an Arrhenius relationship which is used to predict and verify physical gel formation at room temperature over a time scale from several months to years. Sodium ionomers with a few ions per chain exhibit similar behavior but have stronger interactions due to the more ionic nature of sodium. The rate of increase of viscosity depends on the ion concentration and the number of ions per chain.

When ionomer melts are dissolved in nonpolar solvents, two aspects of sample preparation are important. First, the slow dissolution kinetics (as has also been reported by others[19]) necessitates waiting a few months before conducting any rheological experiments. Second, as discussed above, because the viscosities of all melts increase with time and the equilibrium states of all samples are physically cross-linked networks, the equilibrium states of samples at high polymer fractions are also expected to be networks. Thus, as will be discussed in section 3.6, samples with a large number of ions per chain (greater than 5−6) and with high polymer volume fractions are nonequilibrated, and results from such samples cannot be considered for zero-shear viscosity scaling. The polymer volume fraction beyond which the equilibrium state would be a network could be estimated by carrying out high-temperature gelation studies similar to the estimates we reported elsewhere for melts.[17] However, because of limited sample volumes, we could not conduct these experiments. Instead, we measured the viscosity a few months after solution preparation and repeated the measurement on the same samples 6 months later. If indeed the solution samples are equilibrated a few months after preparation, viscosity will be unchanged 6 months later.

3.1. Predictions Based on Sticky Rouse and Sticky Reptation Models. In the semidilute unentangled regime of nonassociating polymers, the viscosity scales with the polymer volume fraction as[20]

$$\eta \sim \phi^{1.3} \qquad \text{for a good solvent} \qquad \phi^* < \phi < \phi_e \tag{1}$$

and

$$\eta \sim \phi^{2.0} \qquad \text{for a } \Theta \text{ solvent} \qquad \phi^* < \phi < \phi_e \tag{2}$$

where ϕ^* is the overlap polymer volume fraction and ϕ_e is the entanglement polymer volume fraction. In a good solvent $\phi^* \approx N^{-0.77}$, while in a Θ solvent $\phi^* \approx N^{-0.5}$, where N is the number of Kuhn monomers of the polymer. In a good solvent $\phi_e \approx (N_{e0}/N)^{0.77}$, while in a Θ solvent $\phi_e \approx (N_{e0}/N)^{0.75}$, where N_{e0} is the number of Kuhn monomers in an entanglement strand in the melt.

In entangled semidilute solutions the viscosity scales with polymer volume fraction as

$$\eta \sim \phi^{3.9} \qquad \text{for a good solvent} \qquad \phi_e < \phi < 1 \tag{3}$$

and

$$\eta \sim \phi^{4.7} \qquad \text{for a } \Theta \text{ solvent} \qquad \phi_e < \phi < 1 \tag{4}$$

Rubinstein and Semenov[4,5] used a sticky Rouse model to describe the dynamics of unentangled solutions of associating polymers below the entanglement polymer volume fraction ϕ_e and a sticky reptation model[4] to describe the dynamics of the entangled solutions above ϕ_e. The volume fraction ϕ_e is the same as described for nonassociating polymers. Two important concepts are introduced in these models. One concept is the transformation of intramolecular associations into intermolecular associations that occurs at volume fraction ϕ_s defined as

$$\phi_s \approx l^{-1/2} \qquad \text{for } \Theta \text{ solvent} \tag{5}$$

and

$$\phi_s \approx l^{-0.77} \qquad \text{for a good solvent} \tag{6}$$

where l is the number of Kuhn monomers between stickers. The polymer volume fraction ϕ_s represents the overlap volume fraction of strands between stickers. In Θ solvents $\phi < \phi_s$ corresponds to a phase-separated state. The other concept is the renormalization of the lifetime of an association. At a high degree of association, it is improbable that an unassociated sticker finds another unassociated sticker, and multiple reassociations with its previous sticker increase the effective lifetime of the association. The renormalized lifetime of an association is given by $\tau_b^* \approx \kappa t_b/\phi_{\text{unassoc}}$, where τ_b is the lifetime of an association, κ is the a priori probability of contact between an unassociated sticker and its previous partner, and ϕ_{unassoc} is the volume fraction of unassociated stickers (not involved in either an interchain or intrachain association and referred to as ϕ_{open} in the model).

For all our samples, the sticky Rouse regime between ϕ_s and ϕ_e can be observed. In this regime

$$\eta \sim \phi^{1.15} \qquad \text{for a good solvent} \qquad \phi_s < \phi < \phi_e \tag{7}$$

and

$$\eta \sim \phi^{0.5} \qquad \text{for a } \Theta \text{ solvent} \qquad \phi_s < \phi < \phi_e \tag{8}$$

Most of the bonds in this regime are intermolecular, and the lifetime of associations must be renormalized.

Under the sticky reptation condition for which $\phi > \phi_e$, four regimes are predicted. Two of these regimes require $\phi < \phi_s$ and thus are not relevant here because $\phi_s < \phi_e$ for all samples considered in this study. Two regimes of the sticky reptation model apply to our samples. In the first regime, the solution has a structure of mostly intermolecular bonds with renormalized bond lifetimes. In this regime the viscosity is predicted to follow the relations:

$$\eta \sim \phi^{3.75} \qquad \text{in a good solvent} \qquad \phi_e < \phi < \phi_{le} \tag{9}$$

and

$$\eta \sim \phi^{3.17} \qquad \text{in a } \Theta \text{ solvent} \qquad \phi_e < \phi < \phi_{le} \tag{10}$$

where ϕ_{le} represents the entanglement volume fraction of the strands between stickers and hence is calculated similar to ϕ_e but with l Kuhn monomers rather than the total number N of Kuhn monomers of the chain. In the second regime, the structure of the solution is that of entangled strands between stickers with renormalized bond lifetimes. In this regime, the viscosity is predicted to follow the relations

$$\eta \sim \phi^{4.72} \qquad \text{for a good solvent} \qquad \phi_{le} < \phi < 1 \tag{11}$$

and

$$\eta \sim \phi^{4.17} \qquad \text{for a } \Theta \text{ solvent} \qquad \phi_{le} < \phi < 1 \tag{12}$$

Two solvents were used in our study: a 700 g/mol inert PDMS polymer and a 4000 g/mol inert PDMS polymer. A PDMS solvent acts as a Θ solvent for a PDMS backbone at

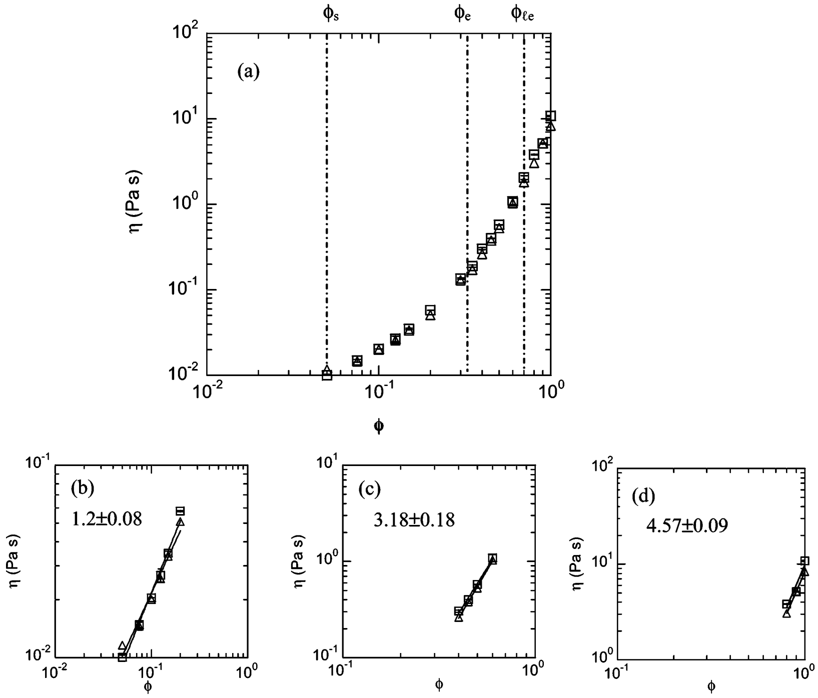

Figure 1. Zero-shear viscosity (η) vs polymer volume fraction (ϕ) in inert PDMS solvent (700 g/mol) for 18Kb-f1-Na samples a few months after preparation (△) and for 18Kb-f1-Na samples 6 months later (□). (b) Power law behavior for ϕ between ϕ_s (0.05) and ϕ_e (0.32). (c) Power law behavior for ϕ between ϕ_e (0.32) and ϕ_{le} (0.7). (d) Power law behavior for ϕ between ϕ_{le} (0.7) and 1.0.

high polymer volume fractions. However, at low polymer volume fractions, if the number of Kuhn monomers of the polymer chain N_a is greater than N_b^2 (where N_b is the number of Kuhn monomers of the solvent), then the solvent acts as a good solvent.[21] Thus, in this study both good solvent and Θ solvent scaling results will be obtained in appropriate regimes provided $N_a > N_b^2$.

3.2. Sodium Ionomers with Very Few Ions (2) per Chain. Figure 1a shows η vs ϕ for 18Kb-f1-Na in 700 g/mol PDMS solvent a few months after solution preparation and 6 months later. The overlap of all data points suggests samples were equilibrated after a few months. The accuracy of the viscosity measurements was estimated by repeating these measurements three times. The error bars are within the symbol size. For 18Kb-f1-Na in 700 g/mol PDMS,[22] $N_a = 147$ ($=$56000/381) and $N_b^2 = 3.5$ ($=(700/381)^2$). As can be seen in Figure 1a, the data over the entire concentration regime examined appear fairly continuous. The vertical lines indicate the theoretical predictions of three concentration regimes covered by the data on this system. Because $N_a \gg N_b^2$, scaling predictions of good solvent behavior apply at low polymer volume fractions, whereas Θ solvent predictions should apply at high polymer volume fractions. For this sample, the number of Kuhn monomers between ions $l = 51$ ($=$19600/381) and ϕ_s is calculated from eq 6 because good solvent behavior is expected. The polymer volume fraction ϕ_e is calculated[23] with $N_{e0} = 31.5$ and $N = 147$ using $\phi_e \approx (N_{e0}/N)^{0.75}$ for Θ solvent behavior whereas ϕ_{le} is calculated with $N_{e0} = 31.5$ and $l = 51$ using $\phi_{le} \approx (N_{e0}/l)^{0.75}$. Figure 1b shows the power law behavior for ϕ between $\phi = 0.05$ (corresponding to ϕ_s) and $\phi = 0.32$ (corresponding to ϕ_e). An exponent of 1.2 ± 0.08 is observed which corresponds to the sticky Rouse regime with mostly intermolecular association between ions and renormalization of the lifetime of these associations. Figure 1c shows the power law behavior for ϕ between ϕ_e (0.32) and ϕ_{le} (0.7) with an exponent of 3.18 and standard deviation of ±0.18. This is surprisingly close to the theoretical prediction of 3.17 despite the polydispersity in the samples considered. For samples with polymer volume fraction greater than 0.7, the viscosity change is less than 30% after 6 months. Even though these concentrated samples of the 18Kb-f1-Na are not truly equilibrated, they might be considered to be in a quasi-equilibrated state at any one time. Figure 1d shows the power law behavior between ϕ_{le} (0.7) and 1.0. An exponent of 4.5 is observed, which is close to the theoretical prediction of 4.17 in a Θ solvent. If one accepts this last result, then our experimental results match the theoretical predictions of both the sticky Rouse and sticky reptation models for these sodium ionomers with few ions per chain, over a wide range of polymer volume fraction.

We note that in fitting the data in any interval we ignored data points near the regime borders of the intervals because these points are likely in a transition regime. For the first regime ($\phi = 0.05$ to 0.32) data are fitted for polymer volume fractions 0.05−0.2, for the second regime ($\phi = 0.32$ to 0.7) data are fitted for polymer volume fractions 0.4−0.6, and for the third regime ($\phi = 0.7$ to 1.0) data are fitted between 0.8 and 1.0, thereby ignoring the data points in the extremes of the transitions. Similar data fitting procedure is used for all subsequent samples.

3.3. Zinc Ionomers with Moderate Number (3−4) of Ions per Chain. Figure 2a shows the zero-shear viscosity vs polymer volume fraction in 700 g/mol PDMS solvent for 18Ka-f2b-Zn measured on samples a few months after preparation and one year later. Zero-shear viscosity data for all samples with a polymer volume fraction less than 0.7 are the same or within 5−10% a year later. Thus, these samples can be considered to be equilibrated. Comparison of the molar masses of the ionomers in these samples to that of the solvent show that the 700 g/mol solvent acts again as a good solvent below ϕ_e. For this sample $\phi_s \approx 0.05$ whereas $\phi_{le} \approx 0.74$ and and $\phi_e \approx 0.33$. Figure 2b shows the power law behavior for ϕ between ϕ_s and ϕ_e for 18Ka-f2b-Zn. A scaling exponent close to the theoretical prediction of 1.1 for an associating polymer in a good solvent is observed. On the other hand, power law behavior for ϕ between ϕ_e and ϕ_{le} in Figure 2c deviates from the theoretical prediction of 3.17

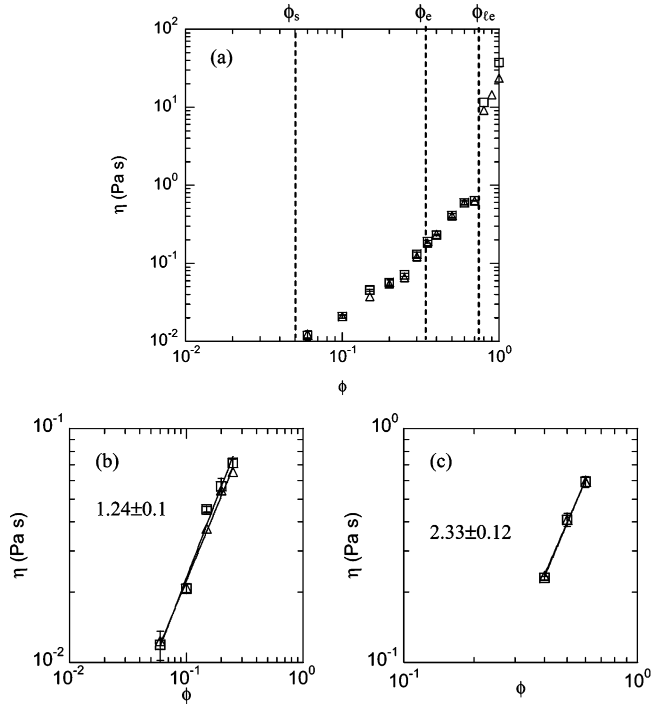

Figure 2. Zero-shear viscosity (η) vs polymer volume fraction (ϕ) in inert PDMS solvent (700 g/mol) for 18Ka-f2b-Zn samples a few months after preparation (△) and for 18Ka-f2b-Zn samples one year later (□). (b) Power law behavior for ϕ between ϕ_s (0.05) and ϕ_e (0.33). (c) Power law behavior for ϕ between ϕ_e (0.33) and ϕ_{le} (0.74).

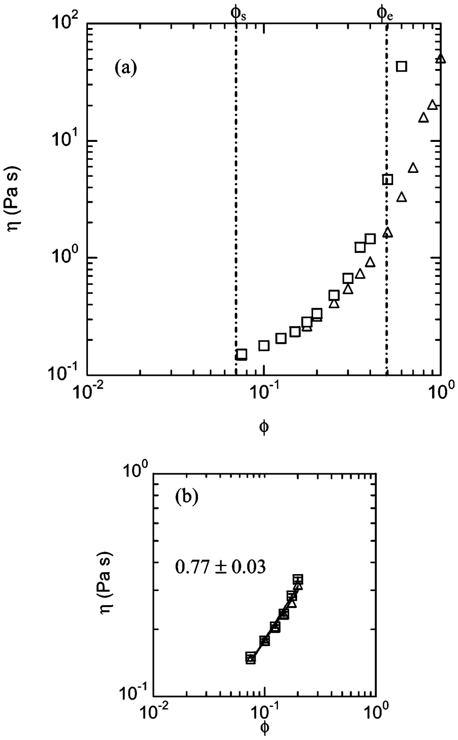

Figure 3. Zero-shear viscosity (η) vs polymer volume fraction (ϕ) in inert PDMS solvent (4000 g/mol) for 11K-f2-Na samples a few months after preparation (△) and for 11K-f2-Na samples 6 months later (□). (b) Power law behavior for ϕ between ϕ_s (0.07) and 0.3 for 11K-f2-Na.

in a Θ solvent. A plausible explanation for this result is that the weak interactions in zinc ionomers and the zinc divalent character do not satisfy two main assumptions of the model. The sticky Rouse and sticky reptation models assume a strongly interacting system and pairwise interactions, which is not the case for zinc ionomers. Although there are only a few data points in this regime, it can be argued that the experimental finding of an exponent 2.33 ± 0.12 does not match the theoretical prediction. The reason for the deviation could be a fundamental difference in the valence and strength of the ionic interactions considered.

3.4. Ionomers with Moderate Number (3−4) of Ions per Chain in 4000 g/mol PDMS Solvent. Figure 3a shows η vs ϕ in 4000 g/mol PDMS for 11K-f2-Na samples tested a few months after their preparation and tested 6 months later. The data taken 6 months later reveal equilibrated solution behavior only up to a polymer volume fraction around 0.3. Beyond 0.3 the viscosity increase 6 months later indicates movement toward a network state. Thus, we can test the theoretical predictions only for the low polymer volume fraction sticky Rouse regime in this case. The number of Kuhn monomers of this ionomer is $N_a = 76$ and is of the same order as the square of the number of Kuhn monomers on the solvent, $N_b^2 = 110$. Figure 3b shows a power law behavior between a polymer volume fraction of 0.07 (corresponding to ϕ_s) and 0.3 for this sample. The power law exponent is 0.77, which is intermediate between a prediction for the sticky Rouse in good solvent (1.1) and that for the sticky Rouse in a Θ solvent (0.5). Note that ϕ_s based on a Θ solvent prediction would be 0.17.

Figure 4a shows η vs ϕ in the 4000 g/mol PDMS solvent for 18Ka-f2b-Zn and 18Ka-f3-Zn, both measured a few months after preparation and 6 months later. The data after 6 months verifies equilibration of these samples, which allows comparison with theory in both the sticky Rouse and sticky reptation regimes. The number of Kuhn monomers for 18Ka-f2b-Zn and 18Ka-f3-Zn (≈120−140) is again comparable to the square of the Kuhn monomers of the solvent ($(4000/381)^2 = 110$), implying scaling behavior intermediate between a good solvent and a Θ solvent. Figure 4b shows the power law behavior for ϕ between ϕ_s and ϕ_e for 18Ka-f2b-Zn and 18Ka-f3-Zn with an exponent of 0.82. Note that ϕ_s based on a Θ solvent prediction would be 0.15. Figure 4c shows power law behavior for ϕ between ϕ_e and ϕ_{le} for 18Ka-f2b-Zn and 18Ka-f3-Zn, and a scaling exponent of 2.65 ± 0.29 is observed. Within experimental error this exponent is the same as observed for 18Ka-f2b-Zn in the 700 g/mol PDMS, verifying that above ϕ_e both solvents act as Θ solvents.

3.5. Zinc Ionomers and Carboxyl Polymers with Very Few (2) Ions per Chain. Figure 5a shows η vs ϕ in 700 g/mol PDMS for 27K-f1-Zn. Also shown for comparison are the data for the corresponding carboxylic sample (27K-f1-H) and a reference PDMS sample of comparable molar mass and polydispersity. Here $N_a \approx 145$ and $N_b^2 \approx 3.5$ for all three samples. Thus, at low polymer volume fractions, scaling predictions of good solvent behavior should apply, whereas at high polymer volume fractions, theta conditions are expected.

Figure 5b shows that between ϕ_s (0.036) and ϕ_e (0.3) the viscosity scales as $\eta \sim \phi^{1.3}$ for 27K-f1-Zn, 27K-f1-H, and the reference PDMS sample. This implies that in this concentration regime the Zn or −COOH samples with a few stickers behave essentially like nonassociating polymers (reference PDMS). Figure 5c shows that beyond ϕ_e a scaling exponent close to 4.7 predicted for nonassociating polymers in a Θ solvent is observed for all three samples.

We note that melts of 27K-f1-H and 27K-f1-Zn immediately after precipitation from good/bad solvent mixtures have viscosities very similar to the reference PDMS sample of similar molar mass.[17] The rheological properties are similar because the ionomers have very few ions (2) per chain. The above scaling

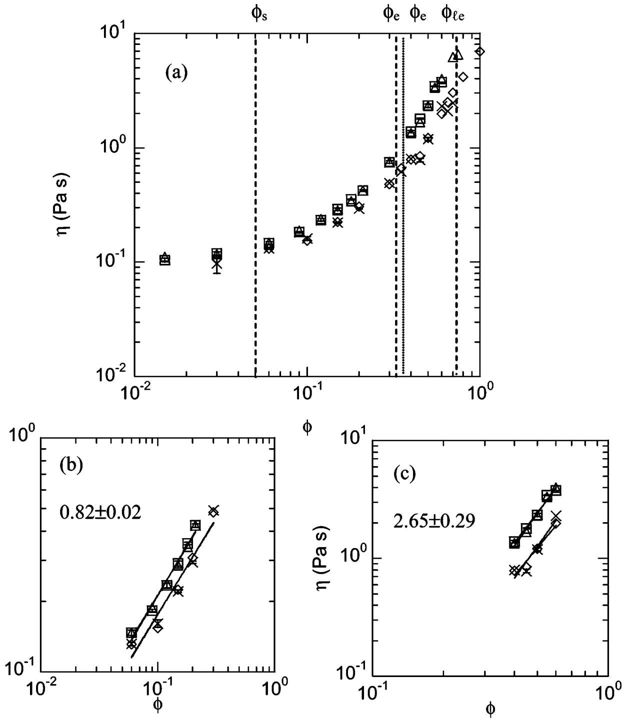

Figure 4. Zero-shear viscosity (η) vs polymer volume fraction (ϕ) in inert PDMS solvent (4000 g/mol) for 18Ka-f2b-Zn samples a few months after preparation (△), 18Ka-f2b-Zn samples 6 months later (□), 18Ka-f3-Zn samples a few months after preparation (◇), and 18Ka-f3-Zn 6 months later (×). (b) Power law behavior for ϕ between ϕ_s and ϕ_e for 18Ka-f2b-Zn and 18Ka-f3-Zn. (c) Power law behavior for ϕ between ϕ_e and ϕ_{le} for 18Ka-f2b-Zn and 18Ka-f3-Zn. For both samples $\phi_s \approx 0.05$ and $\phi_{le} \approx 0.74$. For 18Ka-f2b-Zn $\phi_e \approx 0.33$ and for 18Ka-f3-Zn $\phi_e \approx 0.37$.

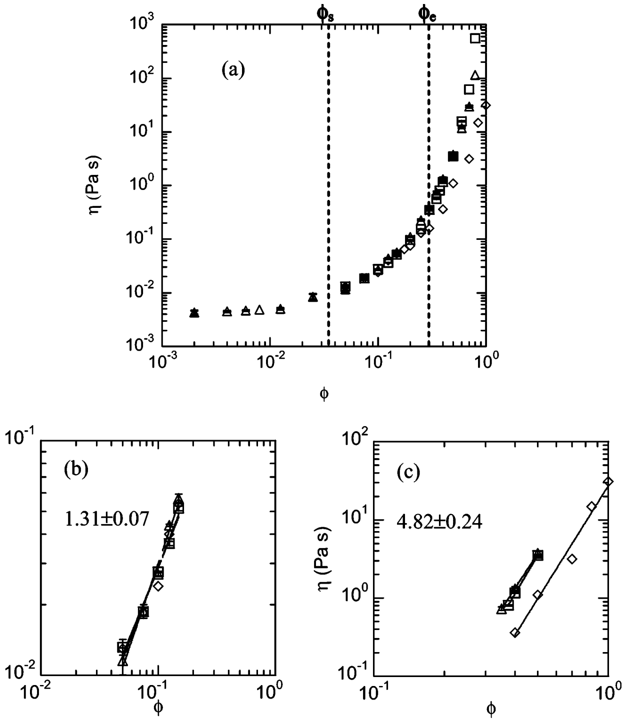

Figure 5. Zero-shear viscosity (η) vs polymer volume fraction (ϕ) in inert PDMS solvent (700 g/mol) for 27K-f1-Zn (△), 27K-f1-H (□), and reference (◇). (b) Power law behavior for ϕ between ϕ_s and ϕ_e. (c) Power law behavior for ϕ above ϕ_e. For both 27K-f1-H and 27K-f1-Zn, $\phi_s \approx 0.035$, and for all three samples $\phi_e \approx 0.3$.

results for the solution viscosities of these polymers are consistent with the previous results for freshly precipitated melts. Similar to the melts, we note that solutions of 27K-f1-H and 27K-f1-Zn at polymer volume fractions above 0.5 show a sharp increase in viscosity with time. These solutions appear to be equilibrating to a network state, and data points for these concentrations were excluded from any viscosity scaling discussion.

3.6. Polymers with a Large Number of Ions per Chain (Greater Than 5). Solutions of different polymer volume fractions of 6K-f1-Zn, which has an average of 19 ions per chain, in 700 g/mol PDMS solvent remained nonequilibrated 6 months after preparation as the zero-shear viscosity of these solutions continued to change.[24] Similar observations were also made with 18Ka-f1-Zn, which has 6 ions per chain. No meaningful quantitative results could be obtained from these nonequilibrated series.

4. Conclusions

We have synthesized tailored poly(dimethylsiloxane) ionomers to test the recent scaling predictions of viscosity with polymer volume fraction derived via sticky Rouse and sticky reptation models. We show very good agreement with the predictions of these models for sodium ionomers over a very wide range of polymer volume fractions in both the good-solvent sticky Rouse regime and in the theta-solvent sticky reptation regimes. For these PDMS ionomers, the dynamics in both the entangled and unentangled semidilute regimes can therefore be modeled by intermolecular bonds with renormalized lifetimes. Zinc ionomers show regimes similar to those observed for the sodium ionomers with scaling exponents that do not match the exponents from theory but are close. We speculate that the divalent character of zinc and its weak ionic character when complexed with COO^- ions cause this difference. Zinc ionomers with very few ions per chain (2) are found to obey the scaling laws for nonassociating polymers. Solutions of ionomers with a large number of ions per chain (greater than 5−6) did not reach equilibrium even a year after preparation.

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