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Polymer 47 (2006) 6202–6207

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Amphiphilic telechelics with polyhedral oligosilsesquioxane (POSS) end-groups: Dilute solution viscometry

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Received 15 March 2006; received in revised form 21 June 2006; accepted 21 June 2006
Available online 11 July 2006

Abstract

Using capillary viscometry, we have investigated the associative behavior of new amphiphilic telechelics incorporating polyhedral oligosilsesquioxane (POSS) as an end-group of poly(ethylene glycol) (PEG) chains of varying length. Solution viscosities were strongly affected by the solvent composition in THF/water mixtures. When water, a selective solvent for PEO segments but a selective non-solvent for POSS segments, was added to the THF solutions, behavior common to polyelectrolytes was observed. In particular, for relatively high concentrations the reduced viscosity remained nearly concentration-invariant for both POSS telechelics and pure PEG homopolymers, indicating a limiting molecular weight of aggregates. On the other hand, a dramatic increase in the reduced viscosity was observed with decreasing concentration for lower concentration values, suggesting aggregate formation and a concentration-dependent aggregate size.

Keywords: Polyhedral oligosilsesquioxane; Telechelics; Solution properties

1. Introduction

Self-assembly behavior of associative materials, such as block copolymers or hydrophobically modified polymers, is a phenomenon with widespread current interest and great utility as a building block approach to the preparation of nanostructured materials [1–5]. Associative polymers are polymers that contain small amounts of functional groups that are capable of forming multiplets in a selective solvent. These materials are industrially important since they can be tailored to exhibit specific rheological properties and have found wide applications in formulation of coatings, paper manufacture, oil production and transportation, water treatments, and thickeners for food and health care products [1,6–8]. For instance, water-soluble copolymers of poly(ethylene oxide) and poly(propylene oxide), often denoted PEO–PPO–PEO, are commercially available nonionic macromolecular surfactants commonly known as Poloxamers (manufactured by ICI) or Pluronics (manufactured by BASF). Tailoring the copolymer composition and molecular weight of such amphiphilic polymers allows for a wide range of solution phase behavior with optimum properties suitable for use in a variety of industrial applications. When one of the constituent blocks is water soluble, micelles can form in aqueous solution and this has important implications for drug delivery systems [9,10].

Telechelic polymers represent a simple architecture to yield association behavior. These polymers are linear chains containing associating ‘sticker’ groups only at the chain-ends and are analogous to triblock copolymers [1]. Telechelic polymers developed to date are most often based on poly(ethylene glycol) (PEG). Recently, we reported [11] new amphiphilic telechelics – the subject of our present investigation – incorporating polyhedral oligosilsesquioxane (POSS) with a quite narrow and unimodal molecular weight distribution ($M_w/M_n < 1.1$) and having close to 2.0 end-groups per PEG chain. For such materials, we anticipated that because of their hydrophobic, bulky, and well-defined end-groups,

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doi:10.1016/j.polymer.2006.06.050

self-assembly could occur in both the melt [12] and solution states.

POSS materials have attained much interest because of their well-defined nanostructure and versatile reactivity. Various types of POSS materials have been used as building blocks for precisely defined nanostructured functional materials, mainly with improved thermal and mechanical properties [13–19]. However, aqueous solution properties and aggregation behavior of the POSS-containing polymers have received less attention [20]. In the present paper, viscometric properties of well-defined amphiphilic POSS telechelics in salt-free solutions are explored by varying the polymer concentration and solvent polarity to indirectly observe formation of the molecular associations using viscometry. This sets the stage for future studies that examine self-assembly of this unique hybrid macromolecular building block.

2. Experimental section

2.1. Materials

Poly(ethylene glycol) (PEG) chains with varying molecular weight, $M_w = 1$, 2, 3.4, 8, and 10 kDa, designated as PEG1K, PEG2K, PEG3.4K, PEG8K, and PEG10K, respectively, were obtained from Aldrich. All PEG samples were purified by repeating twice the process of precipitation into *n*-hexane from chloroform solutions, followed by drying under vacuum overnight. Isocyanatopropyl-dimethylsilylcyclohexyl-POSS (POSS macromer) was provided by Air Force Research Lab, AFRL/PRSM. Dibutyl tin dilaurate (DBTDL; Aldrich, 95% purity) as a catalyst for urethane formation was used as received. Tetrahydrofuran (THF) was dried with CaH_2 and then distilled under nitrogen prior to use. Double distilled water was used for the preparation of all aqueous solutions.

2.2. Synthesis

Amphiphilic telechelics incorporating polyhedral oligosilsesquioxane (POSS) were prepared by direct urethane linkage between diol end-groups of PEG homopolymer and mono-isocyanate groups of POSS macromer using DBTDL as a catalyst and THF as the solvent according to our previous report [11]. Briefly, PEG solution was charged in a four-necked flask, equipped with a stirrer, a nitrogen inlet, an outlet, and a thermometer. A mixture of PEG and toluene was further predried by azeotropic distillation, and the concentration was controlled to approximately 10% (w/v). Subsequently, the mixture was cooled to 90 °C and POSS macromer solution (0.69 g, 0.60 mmol), containing 1.0 wt% of catalyst (DBTDL) based on the weight of the reactants, was added slowly (within 20 min) via a syringe into the flask containing a pre-weighed amount of PEG ($M_w = 10$ kDa, 3.00 g, 0.30 mmol). The reaction mixture was kept at 90 °C under a nitrogen atmosphere for about 12 h. Then, the reaction mixture was microfiltered (0.45 μm), precipitated in an excess amount of *n*-hexane, washed with fresh *n*-hexane several times and then carefully washed with deionized water to remove the unreacted POSS macromer and catalyst then PEG homopolymer, respectively. The resulting products, amphiphilic telechelics incorporating POSS (designated as POSS1K, POSS2K, POSS3.4K, POSS8K, and POSS10K which correspond to their PEG homopolymers), were dried under vacuum for at least 2 days. The structure of amphiphilic telechelics was confirmed by FTIR (Nicolet MAGNA-IR 560 spectrometer) and ^{1}H NMR (Bruker 500 MHz DMX500 high-resolution spectrometer). The chemical structure of amphiphilic POSS telechelic used in this work is shown in Scheme 1.

2.2.1. Viscometry

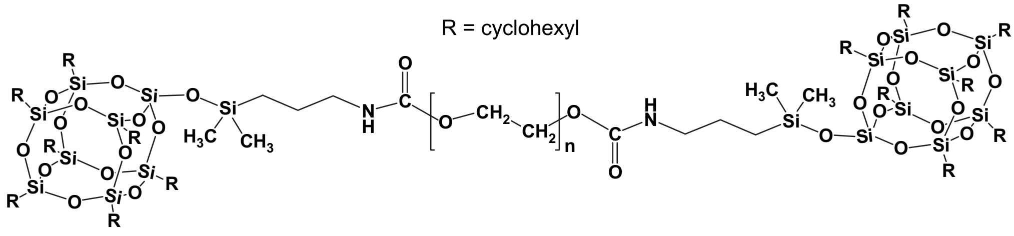
Solution viscosities were determined in THF/H_2O mixtures at 25 °C (±0.05 °C) using an Ubbelohde viscometer. Reduced viscosity (η_{sp}/c) data were obtained from flow time observations using the expression,

$$\eta_{red} = \frac{\eta_{sp}}{c} = \frac{1}{c}\left(\frac{t - t_o}{t_o}\right) \tag{1}$$

where η_{sp} is the dimensionless specific viscosity, and t and t_o are the outflow times for the solution and for the pure solvent, respectively. Using the well-known Huggins equation (Eq. (2)), the intrinsic viscosity ($[\eta]$) was obtained by plotting the resulting reduced viscosities against concentration and extrapolating to zero concentration:

$$\eta_{red} = [\eta] + k_H[\eta]^2 c \tag{2}$$

where k_H is the Huggins coefficient, and c is the polymer concentration in g/dL. The polymer solutions for viscometric analysis were prepared by dilution from a stock solution of 1.0 g/dL. The stock solutions of amphiphilic POSS telechelics in THF/H_2O mixtures were prepared by dissolving each sample in pure THF and then adding the desired amount of H_2O, resulting in solvents of varying polarity. As for THF polymer solutions, stock solutions of mixed solvent were also diluted



Scheme 1. The chemical structure of amphiphilic POSS–PEO telechelics used in this work.

with THF/H_2O mixtures of the same composition (e.g., 50/50) as the stock solution. In these cases of mixed solvents, the composition of these THF/H_2O mixtures is expressed as the mass fraction of water (φ_{H_2O}). Prior to viscosity measurements, all solutions were filtered using 0.45 μm filters to remove foreign particulate matter. Once charged into the Ubbelohde viscometer reservoir, solutions were equilibrated for about 30 min by immersion in a thermostated water bath at 25 °C. This was done to ensure that thermal equilibrium was achieved prior to the temperature-sensitive measurements. Viscosity was determined using the averaged flow-through time with a precision of ± 0.07 s for each and the observed reproducibility for five flow times being within 0.5%. The flow-through times for all THF and THF/H_2O mixed-solvent solutions were longer than 150 s so that the kinetic effects could be safely ignored.

We note that previous research from the 1950s [21–24] and more recently [25] on capillary viscometry of extremely dilute solutions revealed the potential for adsorption effects that can cause both upturns and downturns with decreasing concentration for measured reduced viscosities in the range $c < 10^{-3}$ g/mL ($<10^{-1}$ g/dL). As such, we have designed our experiments to feature a "control" set with pure THF as solvent, where adsorption effects *could* be detected, if they were to occur, without being masked by the complex formation in solution. Furthermore, we have purposefully chosen the range of concentration outside of the extremely dilute range: $c > 10^{-1}$ g/dL. Thus, we are confident that the trends we observe in reduced viscosity reflect solution behavior and not adsorption behavior.

3. Results and discussion

In order to investigate the effect of the incorporated POSS macromers on the associative behavior of PEO chains, the solution viscosities of the amphiphilic POSS telechelics (POSS1K–POSS10K) differing in chain length of PEO block, along with PEG homopolymers with the corresponding molecular weights (PEG1K–PEG10K), were measured. The obtained amphiphilic POSS telechelics were soluble in common organic solvents such as toluene, THF, and chloroform. In this work, THF was used as a typical good solvent for amphiphilic POSS telechelics. Water was used as a selective solvent for PEO blocks, but as a selective non-solvent for POSS blocks. Unlike PEG homopolymers, when the water composition was increased beyond 50% $(\varphi_{H_2O} = 0.5)$, the amphiphilic POSS telechelics became hazy and insoluble, indicating aggregate formation and phase separation, probably due to the enhanced hydrophobic interactions via an intra- and/or intermolecular associations of hydrophobic POSS moieties in poor solvent, such as water. (All POSS telechelics were insoluble in water.) Therefore, all viscosities of the solutions in THF/H_2O mixtures were investigated using mixed solvents with water fraction below $\varphi_{H_2O} = 0.5$.

3.1. Solution dilutions in THF

Fig. 1 shows plots of reduced viscosity, η_{red} vs c for various PEG homopolymers (PEG1K–PEG10K, Fig. 1(a)) and amphiphilic POSS telechelics (POSS1K–POSS10K, Fig. 1(b)), each dissolved in pure THF. Linear dependences of η_{red} on c for both polymers at lower concentration $(\leq 1.0 \text{ g/dL})$ were observed at 25 ± 0.05 °C, indicating a lack of self-association behavior of the constituent polymer chains in pure THF. Surprisingly, reduced viscosities and intrinsic viscosities for POSS8K and POSS10K were *lower* than those of PEG8K and PEG10K, whereas POSS3.4K showed higher values of η_{red} than PEG3.4K. Reduced viscosity values for POSS2K and POSS1K were higher than PEG1K, but slightly lower than PEG2K. From the dilute solution theory, it is expected that the intrinsic viscosity $[\eta]$ measurements relate to the hydrodynamic volume of the polymer chains in solution, with any large differences upon parameter variation reflecting

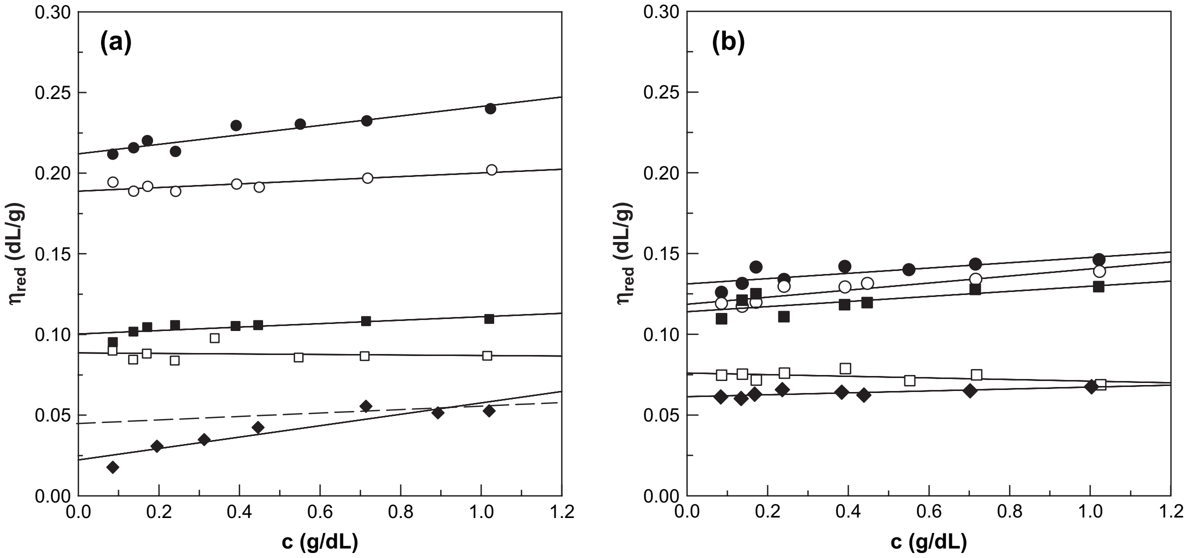


Fig. 1. Concentration dependence of the reduced viscosity η_{red} for various (a) PEG homopolymers: PEG10K (●); PEG8K (○); PEG3.4K (■); PEG2K (□); PEG1K (◆) and (b) amphiphilic POSS telechelics: POSS10K (●); POSS8K (○); POSS3.4K (■); POSS2K (□); POSS1K (◆) dissolved in pure THF at 25 °C.

Table 1
The composition, intrinsic viscosity, and hydrodynamic radius for the studied samples

Amphiphilic POSS telechelics	POSS[a] (wt%)	M_w[b] (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})	R_V (nm)	PEG homopolymers	M_w (g mol^{-1})	$[\eta]$[c] (cm^3 g^{-1})	R_V[c] (nm)
POSS1K	68.1	3470	6.1	1.1	PEG1K	1000	2.0 (4.6)	0.1 (0.24)
POSS2K	52.7	4480	8.4	2.0	PEG2K	2000	8.7	0.9
POSS3.4K	40.7	5730	11.4	3.4	PEG3.4K	3400	9.8	1.8
POSS8K	23.6	10,230	11.8	6.4	PEG8K	8000	18.8	8.0
POSS10K	19.8	12,140	13.1	8.4	PEG10K	10,000	21.2	11.2

[a] Determined by ^{1}H NMR.
[b] Weight-average molecular weight obtained by GPC.
[c] Parenthetic quantities were obtained using the dashed line and unfilled circle of Figs. 1(a) and 2, respectively.

a conformational change of the polymer chains. In the dilute limit, assuming hard spheres and Rouse approximation, the value of $[\eta]$ can be expressed as [26,27]:

$$[\eta] = 2.5\frac{\phi}{\rho} = 2.5\frac{4}{3}\pi\frac{R_V^3 N_A}{M} \tag{3}$$

where $[\eta]$ is the intrinsic viscosity, ϕ is the volume fraction occupied by the spheres in the solution, ρ is the density of spheres, R_V is the viscometric hydrodynamic radius, N_A is the Avogadro's number, and M is the polymer chain's molecular weight. Assuming that this relationship holds for our telechelic polymers, we computed the hydrodynamic radii from $[\eta]$ observations and these values are summarized in Table 1 along with composition and intrinsic viscosity values. The data are discussed further below.

Fig. 2 shows log–log plots of $[\eta]$ vs molecular weight (as obtained by GPC for POSS telechelics or using manufacturers' specification for PEG) for various amphiphilic POSS telechelics and PEG homopolymers. As expected, $[\eta]$ increases monotonically with increasing molecular weight of the polymers; however, in neither case is a single slope (or Mark–Houwink exponent) indicated. For the PEG homopolymer, deviation from a simple Mark–Houwink relation (Fig. 2, filled circles) appears to be due to the lowest molecular weight sample, which witnesses negative deviation from a linear trend in Fig. 1(a). However, if higher concentration data are weighted more heavily for that sample (Fig. 1(a), dashed line) agreement with other samples can be achieved (Fig. 2, open circle) and a Mark–Houwink exponent (α) of 0.636 is achieved. Given that α values relate to polymer structure, the obtained value is a little higher or close to that of aqueous poly(ethylene oxide) solution, but much smaller than those of ionized polyelectrolytes and rod-like molecules, indicating that PEG homopolymer behaves like a flexible chain polymer in pure THF [28–30].

By comparison, the amphiphilic POSS telechelics feature a clear bi-linear trend on the log–log graph, suggesting a conformational transition at a molecular weight ca. 6 kDa. It can be further seen that $[\eta]$ values for the amphiphilic POSS telechelics are always lower than those of the PEG homopolymers of corresponding molecular weight; i.e., the molecular weight of the PEG end-capped to yield the derivative telechelic. This suggests that the telechelic coil volume R_V^3 (numerator, Eq. (3)) increases more slowly than molar mass (denominator) as POSS is incorporated into the telechelics [27]. Indeed, Fig. 3 shows that the calculated hydrodynamic radii (R_V; Eq. (3)) for the amphiphilic POSS telechelics are always smaller than those of the PEG homopolymers, increasingly so with increasing molecular weight. Apparently, POSS chain-ends

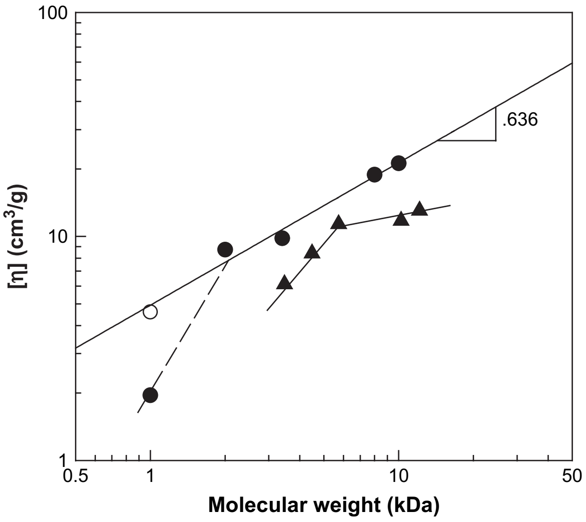


Fig. 2. Molecular weight dependence of the intrinsic viscosity ($[\eta]$) for amphiphilic POSS telechelics (▲) and PEG homopolymers (●) dissolved in pure THF at 25 °C.

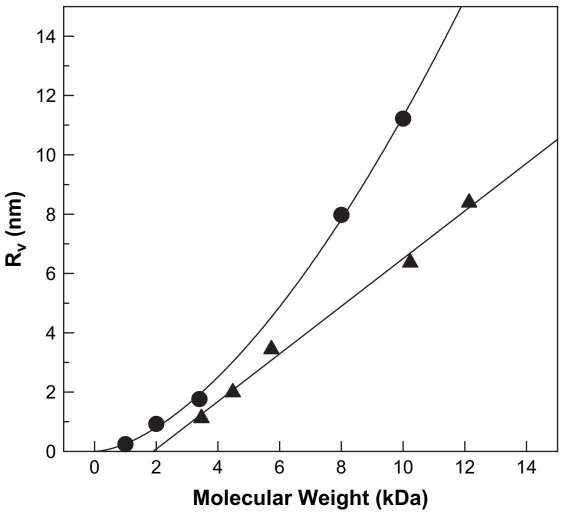


Fig. 3. Molecular weight dependence of the hydrodynamic radii (R_V) for amphiphilic POSS telechelics (▲) and PEG homopolymers (●) dissolved in pure THF at 25 °C.

lead to more compact coils in THF when compared to the hydroxyl end-groups of the parent PEG chains. Direct measurement of polymer chain dimensions using light scattering is needed to confirm the indicated trends and conclusions.

Still considering the THF-solution data, we also inspected the trends in $[\eta]$ and R_V vs POSS wt% (Fig. 4), although this architectural parameter is inversely related to molecular weight of the telechelics through the expression:

$$\mathrm{POSS(wt\%)} = \left(\frac{2M_{\mathrm{POSS}}}{\overline{M}_{\mathrm{n}}}\right) \times 100\% \tag{4}$$

That being said, we observed that $[\eta]$ values of the amphiphilic POSS telechelics decrease linearly with POSS wt%, while R_V decreases more rapidly, following the form $R_V \sim P^{-1.4}$, where P is the POSS wt%.

3.2. Effect of solvent polarity

We expect that any conformational transitions of amphiphilic POSS telechelic chains would be different for solvents of varying polarity. Therefore, we investigated the solution viscosity in various THF/H_2O mixtures. For the polymers under study, water serves as a good solvent for the PEO bridge of the telechelics, but as a poor solvent for POSS end-groups. Fig. 5 shows the trends of η_{red} for PEG10K and POSS10K with concentration for various THF/H_2O mixtures as solvent. POSS10K telechelic solutions with as low as 5% water $(\varphi_{H_2O} = 0.05)$, featured a dramatic upturn in reduced viscosity in the very dilute regime (below 0.2 g/dL), akin to what is observed for solutions of charged polymers [26,27]. By comparison, a more water-rich solvent (30% or higher) is required to yield a similar response in a PEG solution. We note that, commonly, salt is added to PEG and PEO aqueous solutions to eliminate this dilute solution effect [31].

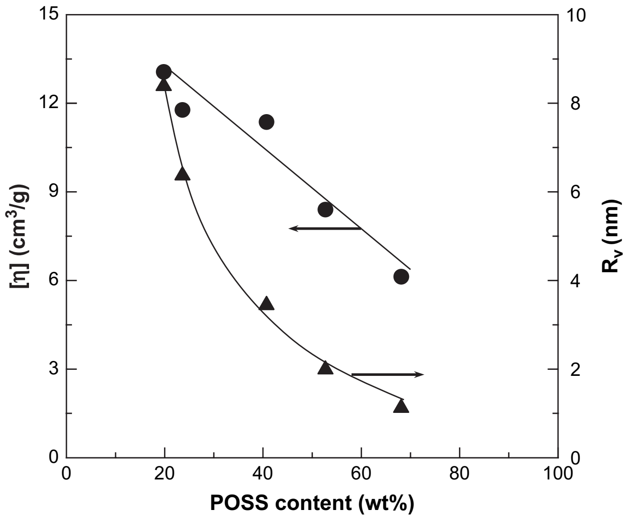


Fig. 4. POSS content dependence of the intrinsic viscosity (●, $[\eta]$) and hydrodynamic radii (▲, R_V) for amphiphilic POSS telechelics dissolved in pure THF at 25 °C.

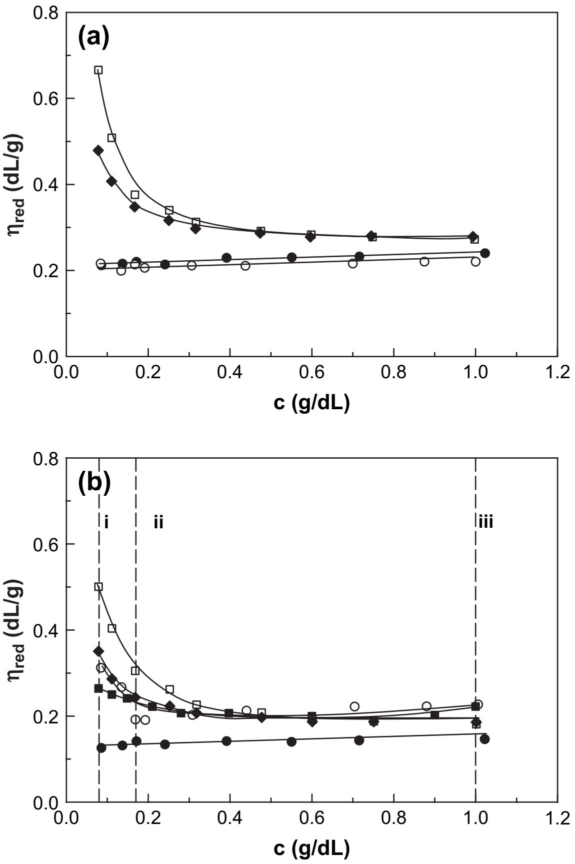


Fig. 5. Concentration dependence of the reduced viscosity, η_{red} for a PEG homopolymer (PEG10K) ((a): $\varphi_{H_2O} = 0$ (●); $\varphi_{H_2O} = 0.05$ (○); $\varphi_{H_2O} = 0.3$ (□); $\varphi_{H_2O} = 0.4$ (◆)) and an amphiphilic POSS telechelic (POSS10K) ((b): $\varphi_{H_2O} = 0$ (●); $\varphi_{H_2O} = 0.05$ (○); $\varphi_{H_2O} = 0.2$ (■); $\varphi_{H_2O} = 0.3$ (□); $\varphi_{H_2O} = 0.4$ (◆)) dissolved in mixed THF/H_2O mixtures at 25 °C.

Fig. 6 shows the dependence of η_{red} on the water mass fraction (φ_{H_2O}) for several polymer concentrations (vertical reference lines in Fig. 5) of POSS10K in THF/H_2O mixtures. As

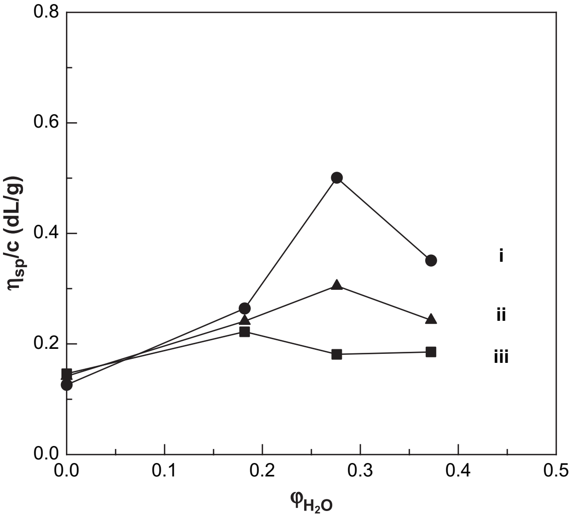


Fig. 6. Dependence of η_{red} on water weight fraction (φ_{H_2O}) at various concentrations of amphiphilic POSS telechelics (●), 0.08 g/dL; (▲), 0.17 g/dL; (■), 1.0 g/dL) dissolved in THF/H_2O mixtures at 25 °C.

seen in Fig. 6, η_{red} initially increases dramatically, then goes through a maximum at $\varphi_{\mathrm{H_2O}} = 0.3$, and finally decreases. The lower the polymer concentration, the more significant the change in η_{red} occurs. As a result, the change in solution viscosity caused by the change in the hydrodynamic radius of the polymer coils may be the result of the solvent power for the polymer as a whole. Therefore, intra- or/and intermolecular interactions of the hydroxyl end-groups of PEG homopolymers (via a hydrogen bonding) as well as of POSS macromers of amphiphilic POSS telechelics (via a hydrophobic interaction) may need to be accounted for with respect to their dependence on solvent polarity and polymer concentration.

An upturn in η_{red} at low concentrations implies unambiguously that the relative viscosity, η/η_{s} grows with concentration less strongly than that predicted by Eq. (2), at least for concentrations lower than the semidilute regime:

$$\frac{\eta}{\eta_{\mathrm{s}}} \propto c^{\alpha};\ \ \alpha < 1 \tag{5}$$

Here, η_{s} is the solvent viscosity. Inspection of Eqs. (2) and (3) reveals that for Eq. (5) to hold, then the ratio R_{V}^3/M (volume/mass) for flow units — unimolecular or not — must weakly *decrease* with concentration as,

$$R_{\mathrm{V}}^3/M \propto c^{-\beta};\ \ 0 < \beta < 1 \tag{6}$$

so that the product $[\eta]c$ has a net concentration dependence as indicated in Eq. (5). Thus, we are left needing to explain Eq. (6). One possible explanation, at least for the POSS telechelics, is the formation of micelles in dilute solution of the mixed water/THF solutions. In such a scenario, increasing concentration may decrease the ratio R_{V}^3/M due to the compact structure of the micelles. At higher concentrations, where we observe η_{red} to increase with concentration in all cases, the compactness of flow units becomes disrupted and R_{V}^3/M begins to increase with concentration. To confirm this interpretation, measurements of the critical micelle concentration (CMC) are needed.

4. Conclusions

Dilute solution viscosity data were examined for new POSS–PEO telechelics in order to reveal the influences of polymer architecture and solvent polarity on associative behaviors of the polymers in dilute solutions. Solution viscosities were strongly affected by the solvent (THF/water) composition. It was found that the more polar solvent (H_2O) caused a polyelectrolyte-like effect to occur, manifested as an upturn in η_{red} at low concentration. It is postulated that the formation of micelles in the solutions may explain the observed behavior. We further revealed the dependence of hydrodynamic radius (as inferred from viscometric data) on molecular weight, POSS content, and solvent polarity. We conclude that the associative behavior of the amphiphilic POSS telechelics could vary depending on the POSS content and the length of PEO blocks affording a significant variation in hydrophobic/hydrophilic balance as well as on solvent polarity. Future work is needed both on the experimental front, especially scattering data to directly measure coil or aggregate sizes, and on the theoretical front in the area of analytical modeling that might allow quantitative explanation of our observations.

Acknowledgements

We gratefully acknowledge the support of AFOSR/NL through grant FA9550-05-1-0142.

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