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ORIGINAL ARTICLE

Colloidal droplets of the concentrated phase in aqueous methanol solutions of a hydrophilically modified poly(dimethylsiloxane)

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Colloidal dispersions were prepared by adding water to methanol (MeOH) solutions of a hydrophilically modified poly-(dimethylsiloxane) (HPM-PDMS) up to weight fractions of water equal to or greater than 0.6, at which the ternary solution is in the biphasic region. Static light-scattering measurements of the colloidal dispersions demonstrated that the internal concentration of the colloidal droplets was remarkably higher than that of solutions of HPM-PDMS directly dissolved in MeOH–water mixtures of the same water contents, which were studied previously. This difference in the internal structure of the colloidal droplets affects the van der Waals attraction and also the stability of the colloidal particles.

INTRODUCTION

Ionomers are hydrophobic polymers that contain a small fraction of ionic groups. The ionic groups form multiplets or polar micro-domains in bulk, which confers the unique properties of crack and abrasion resistance, electric conductivity and adhesiveness to metals, among others.[1,2] If ionomers are casted or molded from solutions or dispersions, these unique properties should depend on the solution or dispersion state of ionomers. Thus, it is important to characterize and control the solution or dispersion state of ionomers.

In a previous study,[3] we observed the unique colloidal behavior of a hydrophilically modified poly(dimethylsiloxane) (HPM-PDMS; see for example, Scheme 1) dispersed in mixtures of methanol (MeOH) and water with 0.1 M sodium acetate (NaAc). When a bulk HPM-PDMS sample was mixed with a water–MeOH mixture with water content greater than ~ 50 wt% and with 0.1 M NaAc, the solution formed colloidal droplets a few hundred nanometers in size, even if the system was in the biphasic region. Subsequently, the droplets slowly coagulated to form a turbid solution. The uniqueness of this phenomenon is that the thermodynamically unstable colloidal droplets are formed before the more stable macroscopic phase separation. We attributed this unique colloidal behavior to the polar micro-domain structure formed by ammonium groups in the bulk HPM-PDMS sample before dissolution. That is, the micro-domains in the bulk sample can be swelled by the solvent component water, and the strong electrostatic repulsion among the swollen micro-domains disperses the colloidal droplets in the water–MeOH mixture.

Because of the unique dispersion process of HPM-PDMS, the colloidal particles in water–MeOH mixtures might display certain morphological differences compared with droplets comprising the uniform coexisting concentrated phase. In fact, the average polymer concentration c_{in} inside the colloidal droplet, as determined by light scattering and small-angle X-ray scattering, was not an increasing function of the water content in the solvent, which goes against the prediction of the Flory–Huggins theory for ternary systems consisting of a polymer, a solvent and a non-solvent.[3–5] Thus, the morphology of the colloidal particles of the HPM-PDMS is worthy of studying as an example of the characteristic dispersion state in ionomer solutions.

In the current study, we investigated colloidal droplets of the coexisting concentrated phase in the biphasic solution, which were prepared via a different procedure. The HPM-PDMS sample was first dissolved in the solvent MeOH (including 0.1 M NaAc), where HPM-PDMS was nearly molecularly dispersed,[3] and the non-solvent water (with 0.1 M NaAc) was added to the MeOH solution to bring the solution into the biphasic region. Colloidal droplets formed in the solution have been characterized by static light scattering, and the
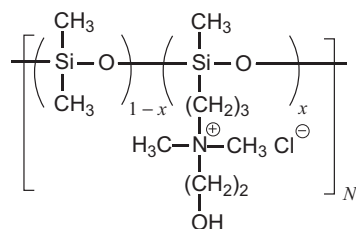
Scheme 1 Chemical structure of the studied hydrophilically modified poly (dimethylsiloxane).

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characteristics of the droplets have been compared with those in a solution of PHM-PDMS mixed directly with the water–MeOH mixture.[3] To distinguish the solutions prepared from the two different procedures, those used in the previous and current studies are referred to as the directly dissolved (DD) solution (that is, the bulk HPM-PDMS sample dissolved directly in water–MeOH mixtures) and water-added MeOH (WAM) solution, respectively, in the following sections. NaAc was added to the test solutions in the previous and current studies to reduce the strong electrostatic interaction among colloidal particles, which adds difficulty to the analysis of light-scattering data.

EXPERIMENTAL PROCEDURE

The HPM-PDMS sample used in this work was the same as that used in a previous study.[3] The degree of polymerization N_0 and the content x of the ionic side monomer units of the random copolymer sample were 1050 and 0.16, as determined by static light scattering and ^{1}H NMR, respectively.

The sample was first mixed with MeOH (including 0.1 M NaAc) and stirred overnight at room temperature. Water with 0.1 M NaAc was added dropwise to the MeOH solution and stirred again by a magnetic stirrer for 24 h to prepare the water-added MeOH (WAM) solution with a polymer concentration c of ~0.01 g cm^{-3}. It was verified that the light-scattering intensity from the HPM-PDMS solution reached a constant value at 6 h after the water addition. To prepare test solutions with different c values, this original solution was diluted using the mixed solvent with the same water content. Light-scattering measurements were performed for the original and diluted solutions within 2 h
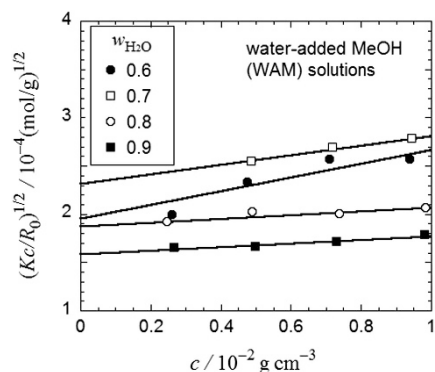
after the original solution was diluted. The light-scattering results for the WAM solutions were compared with those from previously studied DD solutions, which were prepared by mixing the HPM-PDMS sample directly with a water–MeOH mixture (including 0.1 M NaAc) and stirring with a magnetic stirrer for 24 h at room temperature. The solvent composition of the WAM and DD solutions is represented in terms of the weight fraction of water w_{H_2O} in the MeOH–water mixture in the following sections.

Static and dynamic light-scattering measurements were performed at 25 °C using an ALV/SLS/DLS-5000 light-scattering instrument (ALV, Langen, Germany) with an Nd:YAG laser operating at 532 nm. The scattered light intensity did not depend on time during the measurements.

The refractive index increment $\partial n/\partial c$ of HPM-PDMS required to analyze the light-scattering data was determined previously[3] by differential refractometry at 25 °C as 0.0531 ($w_{H_2O}=0.6$), 0.0579 (0.7), 0.0654 (0.8) and 0.0831 (0.9) cm^3 g^{-1}. These results were obtained for non-dialyzed solutions. Because the refractive indices of water and MeOH are highly similar and the composition dependence of the solvent refractive index is sufficiently weak ($n^{-1}\partial n/\partial w_{H_2O}$ is less than 4%), the preferential adsorption effect on the light-scattering results was neglected.[6]

RESULTS AND DISCUSSION

Figure 1 shows the polymer mass concentration dependence of $(Kc/R_0)^{1/2}$ for WAM solutions with $w_{H_2O}=0.6$–0.9 containing 0.1 M NaAc. Here, K is the optical constant, and R_0 is the excess Rayleigh ratio of the polymer solution over that of the solvent at the zero scattering angle. The data points almost follow a straight line for every w_{H_2O} from 0.6 to 0.9. As demonstrated in the previous study, at $w_{H_2O} \geqslant 0.6$, the polymer concentration in the coexisting dilute phase is much lower than the c range of the light-scattering measurements so that c can be identified with the mass concentration of the concentrated-phase particles in the solution. Thus, we can write

$$(Kc/R_0)^{1/2} = M_w^{-1/2} + A_2 M_w^{1/2} c \quad (1)$$

where M_w and A_2 are the weight average polymer molar mass and the second virial coefficient of the concentrated-phase droplet in the biphasic solution, respectively. From the lines indicated in Figure 1, we determined M_w and A_2 of the particles.

Table 1 lists the weight average polymer molar mass M_w, the weight average aggregation number m_w calculated by M_w/M_1 (M_1: the molar mass of the HPM-PDMS sample $= 1.04 \times 10^5$),[3] and A_2 for the concentrated-phase droplets at each w_{H_2O}. It can be observed that M_w and m_w for the WAM solutions are considerably smaller than those for the DD solutions obtained in the previous study, as also listed in Table 1. Because we have demonstrated that HPM-PDMS chains are nearly molecularly dispersed in MeOH with 0.1 M NaAc,[3]

Figure 1 Concentration dependence of $(Kc/R_0)^{1/2}$ for WAM solutions of HPM-PDMS at different w_{H_2O}. HPM-PDMS, hydrophilically modified poly (dimethylsiloxane); WAM, water-added MeOH.

Table 1 Characteristics of colloidal droplets of the coexisting concentrated phase in biphasic solutions of HPM-PDMS in water–MeOH mixtures

w_{H_2O}	$M_w/10^8$ g cm^{-3} (m_w[a])		$A_2/10^{-6}$ [b]		c_{in}/g cm^{-3} [c]		M_w/M_n[c]		$<S^2>_z^{1/2}$/nm [d]	
	WAM	DD [e]	WAM	DD [e]	WAM	DD	WAM	DD	WAM	DD
0.6	0.26 (250)	2.0 (1900)	1.4	0.14	0.21	0.15	100	20	79	130
0.7	0.18 (180)	11 (11 000)	1.2	0.089	0.23	0.13	100	30	68	260
0.8	0.28 (270)	—	0.39	—	0.45	—	10	—	38	—
0.9	0.40 (380)	18 (18 000)	0.30	0.14	0.49	0.077	20	30	49	315
1	—	6.3 (6100)	—	0.25	—	0.070	—	30	—	260

Abbreviations: A_2, second virial coefficient; DD, directly dissolved solution; HPM-PDMS, hydrophilically modified poly(dimethylsiloxane); MeOH, methanol; M_n, number average molar mass; M_w, weight average molar mass; WAM, water-added MeOH solution.
[a]Weight average aggregation number estimated by M_w/M_1.
[b]In units of mol cm^3 g^{-2}.
[c]Estimated by fitting equations 2, 3, 4 and 5 to the light scattering results (Figure 2).
[d]Square root of the z-average mean square radius of gyration calculated by $<S^2>_z^{1/2} = \sqrt{\frac{3}{5}}\left(\frac{3M_w}{4\pi N_A c_{in}}\right)^{1/3}\left(\frac{M_w}{M_n}\right)^{2/9}$.
[e]Data taken from ref. 3.

the concentrated-phase droplets in the WAM solutions are formed by association of the molecularly dispersed HPM-PDMS chains, and the aggregation number m_w can be determined by the balance between the electrostatic repulsion and hydrophobic interaction, both of which become stronger with increasing w_{H_2O}. However, the colloidal droplets in the DD solutions should be formed through disentanglement of HPM-PDMS chains in the mixed solvent. The difficulty in this disentanglement process might enlarge the colloidal droplets in the DD solution.

Figure 2 shows the angular dependence of $(Kc/R_\theta)^{1/2}$ at infinite dilution for biphasic WAM solutions (left panel) and for biphasic DD solutions (right panel) at $w_{H_2O} \geqslant 0.6$. Here, k is the magnitude of the scattering vector. The angular dependences for the WAM solutions are much weaker than those for the DD solutions, indicating the existence of much smaller colloidal droplets in the WAM solutions. If the colloidal droplets of the concentrated phase in the biphasic solution are regarded as uniform-density spheres with a log-normal distribution of the polymer molar mass M, then $(Kc/R_\theta)^{1/2}$ at infinite dilution for the biphasic solutions can be expressed by[7,8]

$$\lim_{c \to 0} \frac{R_\theta}{Kc} = \int M \left[3 \frac{\sin(kR_M) - kR_m \cos(kR_M)}{(kR_M)^3} \right]^2 \cdot \frac{1}{\sqrt{\pi}} \exp(-x^2) dx \quad (2)$$

where R_M is the radius of the sphere with the polymer molar mass M, and x is defined by

$$x \equiv \sigma^{-1} \ln(M/\overline{M}) \quad (3)$$

with σ and $\overline{M}$ defined as

$$\sigma^2 \equiv 2 \ln(M_w/M_n), \overline{M} \equiv (M_w M_n)^{1/2} \quad (4)$$

Here, M_w and M_n are the weight average and number average polymer molar masses of the colloidal particles, respectively. The radius R_M is calculated as

$$R_M = \left(\frac{3M}{4\pi N_A c_{in}} \right)^{1/3} \quad (5)$$

using the polymer concentration c_{in} inside the spherical particles. In equation 2, the scattering from the polymer in the dilute phase was assumed to be negligibly weak. Because we have already determined M_w from Figure 1, the adjustable parameters in equations (2)–(5) are c_{in} and M_w/M_n.

The solid curves in Figure 2 indicate the fitting results from equations (2)–(5). Data points for the WAM solution at $w_{H_2O} = 0.6$ at low scattering angles were difficult to fit using the equations, which might be owing to the tail in the size distribution in the high M region, which is not represented by the log-normal distribution. Except for these data points, the fitting is satisfactory for both WAM and DD solutions. The parameters c_{in} and M_w/M_n selected in the fitting are listed in Table 1; values of M_w/M_n at $w_{H_2O} = 0.6$ and 0.7 were not as decisive because of insensitivity to the scattering function. The results of c_{in} for the DD solutions are slightly different from the previous results determined from M_w and the hydrodynamic radius obtained by dynamic light scattering (see for example, Table 2 and equation 5 in ref. 3). The particle size distribution might affect the value of c_{in} calculated in the two different methods.

In Table 1, c_{in} increases with w_{H_2O} for the WAM solutions. This dependence is consistent with the prediction from the Flory–Huggins theory for ternary systems consisting of a polymer (component 3), good solvent (component 2), and non-solvent (component 1),[4,5] where the interaction parameter $\chi_{23} = 0$, and χ_{12} and χ_{13} are large. By contrast, the w_{H_2O} dependence of c_{in} for the DD solutions is opposite, as noted previously.[3] The colloidal droplets in the DD solutions are formed through the swelling of polar micro-domains in the PHM-PDMS bulk sample owing to water and the subsequent disentanglement of HPM-PDMS chains in the mixed solvent. Thus, it is possible for the colloidal particle in the DD solutions to contain the coexisting dilute phase, which reduces the average concentration c_{in} inside the particle from the concentration c_c of the coexisting concentrated phase. If the colloidal droplet in the DD solutions contains the coexisting dilute phase of the volume fraction Φ_d, then c_{in} is given by

$$c_{in} = c_d \Phi_d + c_c(1 - \Phi_d) \quad (6)$$

where c_d is the concentration of the coexisting dilute phase. As demonstrated previously by small-angle X-ray scattering, c_d is sufficiently low at $w_{H_2O} = 0.7$ and 0.9 that we can approximate $c_d \sim 0$ in equation 6. Furthermore, if the colloidal droplet in the WAM solutions is assumed to consist of the pure coexisting concentrated phase, that is, $\Phi_d = 0$ for the WAM solutions, then Φ_d for the DD solutions can be estimated as 0.42 and 0.84 at $w_{H_2O} = 0.7$ and 0.9, respectively, from equation 6. The disentanglement of HPM-PDMS chains at higher w_{H_2O} might be more difficult such that a greater
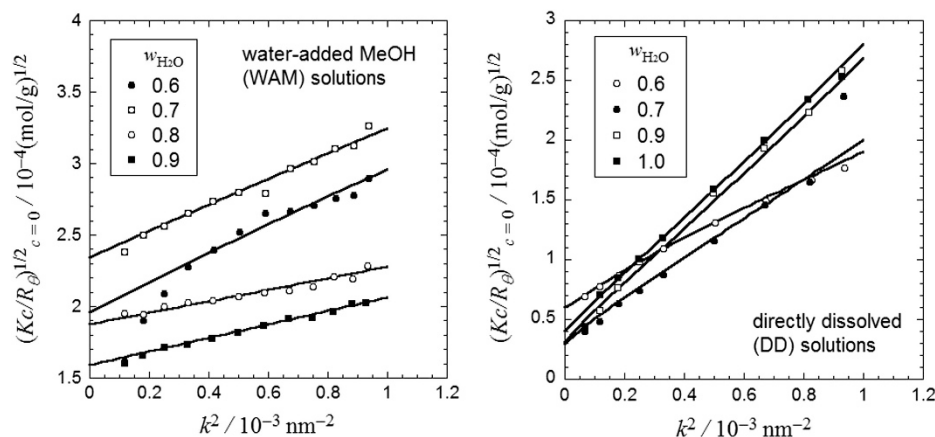

Figure 2 Angular dependences of $(Kc/R_\theta)^{1/2}$ at infinite dilution for WAM solutions (left panel) and DD solutions[3] (right panel) with different w_{H_2O}. Solid lines indicate fitting results calculated from equations 2,3,4 and 5. DD, directly dissolved; WAM, water-added MeOH.

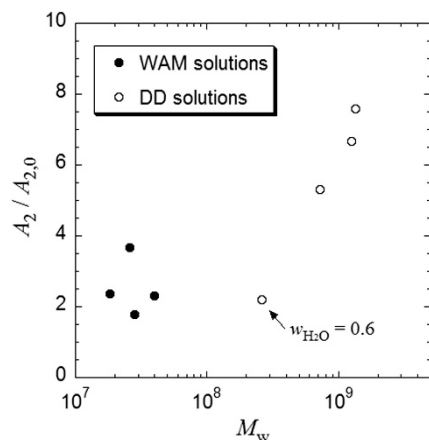**Figure 3** $A_2/A_{2,0}$ plotted against M_w for WAM and DD solutions of HPM-PDMS at values of w_{H_2O} from 0.6 to 1. DD, directly dissolved; HPM-PDMS, hydrophilically modified poly(dimethylsiloxane); WAM, water-added MeOH.

amount of dilute phase is contained in the colloidal particles at higher w_{H_2O} and trapped owing to high viscosity in the concentrated phase.

Because the angular dependences of the light-scattering profiles for the DD solutions shown in Figure 3 are smooth and nicely fitted by the scattering function for the uniform-density sphere given by equation 2, the dilute phase included in the colloidal droplets in the DD solutions should be much smaller than the wavelength of the light or take on irregular shapes. Moreover, the small-angle X-ray scattering profiles for DD solutions with $w_{H_2O} = 0.7$ and 0.9 obtained in the previous study (see for example, Figure 4 of ref. 3) decayed rapidly at high k, indicating that the colloidal droplets in the DD solutions have no definite regular micro-domain structure but contain the dilute phase of irregular shape and diffused interface.

The second virial coefficient $A_{2,0}$ for polydisperse hard spheres with a weight average molar mass M_w and dispersity index M_w/M_n or σ in equation 4 can be calculated as[6]

$$A_{2,0} = \frac{1 + 3e^{-\sigma^2/9}}{M_w c_{in}} \quad (7)$$

using equations (2)–(5). Figure 3 shows $A_2/A_{2,0}$ calculated from experimental A_2, M_w and c_{in} (listed in Table 1) and plotted against M_w (although the M_w/M_n values at $w_{H_2O} = 0.6$ and 0.7 in Table 1 were not as decisive, they were also not sensitive to $A_{2,0}$). For WAM solutions (filled circles), the $A_2/A_{2,0}$ values are within 2.7 ± 0.9, and the ratios for DD solutions are larger than those for the WAM solutions except at $w_{H_2O} = 0.6$. The discrepancies between A_2 and $A_{2,0}$ stem from the electrostatic repulsion between spherical particles, which stabilizes the colloidal particles, but this effect was not taken into account by equation 7. Because c_{in} of the spherical particle is higher in the WAM solution than in the DD solution, the van der Waals attraction between spherical particles in the former solution should be stronger,[9] and the electrostatic repulsion might be partially canceled out by the van der Waals attraction (it is noted that the ionic strength and the strength of the electrostatic repulsion are identical in the WAM and DD solutions). This observation explains why the experimental A_2 is closer to the theoretical $A_{2,0}$ for the WAM solutions.

As reported previously,[3] colloidal droplets in DD solutions are flocculated, and the solutions slowly became turbid. For WAM solutions, colloidal droplets were more stable, and the solutions

remained transparent for a longer period. This observation appears to contradict the above argument for A_2 that the van der Waals attraction between spherical particles is stronger in the WAM solution. However, we occasionally observe moving droplet phases or mesoglobules in aqueous polymer solutions and can explain these observations by the viscoelastic effect of concentrated-phase droplets.[7,8,10–17] The internal concentration of the droplets is higher and the coalescence of the droplets might be more difficult in the WAM than in the DD solution owing to the viscoelastic effect.

CONCLUSION

We have investigated colloidal droplets of the coexisting concentrated phase in dilute solutions of HPM-PDMS dissolved in MeOH–water mixtures (including 0.1 M NaAc) with water weight fractions $w_{H_2O} \geqslant 0.6$. When dilute MeOH solutions of HPM-PDMS enter the two-phase region by the addition of water (the WAM solution), molecularly dispersed HPM-PDMS chains associate to form colloidal droplets of the coexisting concentrated phase, which take the form of charged spheres of uniform density with a radius of gyration $\langle S^2 \rangle_z^{1/2}$ of less than 100 nm (Table 1). These droplets are remarkably different from those in solutions of HPM-PDMS directly dissolved in MeOH–water mixtures (including 0.1 M NaAc) with $w_{H_2O} \geqslant 0.5$ (the DD solution), which were studied previously.[3] In the DD solutions, colloidal droplets of the concentrated phase could be formed by dissociation of entangled HPM-PDMS chains in the bulk sample, which might contain the coexisting dilute phase. Because of the higher internal concentration, the colloidal droplets in the WAM solution have slightly stronger attractive interactions but are more stable against coalescence than the droplets in the DD solution.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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