Light Scattering Evidence for the Random Association of Flower Micelles of a Telechelic Hydrophobically Modified Poly(*N*-isopropylacrylamide) in Dilute Aqueous Solution

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The properties in water of amphiphilic telechelic polymers, consisting of a hydrophilic chain bearing a hydrophobic group on each end, exhibit a marked concentration dependence. In the dilute regime, low-viscosity solutions are formed as a result of the polymer self-assembly into flower micelles by association of the termini into a hydrophobic core stabilized in water by loops of the hydrophilic polymer chain, whereas in the concentrated regime, gelation takes place as a result of the formation of a network of flower micelles interconnected by bridging chains with termini entrapped in the core of two distinct micelles.[1−3] The situation in the intermediate concentration regime is not so clear. Repulsive forces between loops tend to prevent micellar association, whereas the loop−bridge transition favors association, since it relieves the entropic penalty associated with loop formation.[4,5] Whether the net interaction is repulsive or attractive for a given system is not a trivial question to answer.[6−9] Although Borisov and Halperin[7−9] proposed three different configurational scenarios (linear string, branched string, and close-packed globule) for the association of flower micelles, there has been no detailed experimental study on the association in solutions in the concentration range intermediate between the micellar and gel regimes.

Winnik and her co-workers[10−12] have investigated the properties of aqueous solutions of telechelic hydrophobically modified poly(*N*-isopropylacrylamide) (HM-PNIPAM) samples kept at room temperature where water is a good solvent for PNIPAM. They examined the effect of the polymer molecular weight (12 400 < M_n < 49 000) on the formation, and association, of flower micelles and demonstrated that micellization and gelation, respectively, occur in dilute and concentrated telechelic HM-PNIPAM solutions. In this study, we focus on one representative polymer, α,ω-di-(*n*-octadecyl)-PNIPAM, of M_n = 43 000 and investigate by light scattering the association behavior of this polymer in aqueous solutions of concentrations ranging from the dilute regime to the onset of the gel regime. The high molecular weight HM-PNIPAM sample selected has good solubility in water below the lower critical solution temperature and large enough radius of gyration to be determined by light scattering.

The telechelic HM-PNIPAM sample was prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization of *N*-isopropylacrylamide (NIPAM) in dioxane using azobisisobutyronitrile as the initiator and *S*-1-*n*-octadecyl-*S*′-(α,α′-dimethyl-α″-*N*-*n*-octadecylacetamide)trithiocarbonate as the chain transfer agent, following a protocol described previously.[10] The polymer was purified by three consecutive precipitations from tetrahydrofuran into diethylether. The weight-average molecular weight (M_w = 47 500) and the polydispersity index (M_w/M_n = 1.11) were measured by gel permeation chromatography[10] (see Supporting Information).

The polymer sample was mixed with deionized water (Millipore Milli-Q system) and stirred for ca. 12 h at room temperature (below 20 °C) to prepare a stock solution of concentration 7×10^{-3} g/cm^3. The stock solution was diluted with deionized water to a concentration range from 1×10^{-3} to 5×10^{-3} g/cm^3, and the resulting solutions were stirred for 12 h at room temperature. All solutions were filtered through a 0.20 μm cellulose acetate membrane filter directly into the light scattering cell.

Static light scattering measurements were carried out using a Fica-50 light scattering photometer in the angular range from 30 to 150° using vertically polarized light of 436 and 546 nm wavelengths at 25 °C. Experimental details of the light scattering instrumentation are described elsewhere.[13]

From static light scattering data, the apparent weight-average molar mass $M_{w,app}$ and the apparent *z*-average square radius of gyration $\langle S^2\rangle_{z,app}$ were estimated using the equation

$$\left(\frac{Kc}{R_\theta}\right)^{1/2} = \frac{1}{M_{w,app}{}^{1/2}}\left(1 + \frac{1}{6}\langle S^2\rangle_{z,app}\,k^2 + \cdots\right) \qquad (1)$$

where K is the optical constant, c is the polymer mass concentration, R_θ is the excess Rayleigh ratio, and k is the magnitude of the scattering vector. The refractive index increment included in K was measured to be 0.167 cm^3/g (436 nm) and 0.162 cm^3/g (546 nm), in agreement with literature data[14] for normal PNIPAM. The estimated $M_{w,app}$ and $\langle S^2\rangle_{z,app}$ are affected by virial terms and are related to the true weight-average molar mass M_w and true *z*-average square radius of gyration $\langle S^2\rangle_z$ by,[15,16]

$$M_w = \frac{M_{w,app}}{1 - 2A_2M_{w,app}c - 3A_3M_{w,app}c^2}$$
$$\langle S^2\rangle_z = \frac{\langle S^2\rangle_{z,app}}{1 - 2A_2M_{w,app}c - 3A_3M_{w,app}c^2} \qquad (2)$$

respectively, within the third virial approximation, where A_2 and A_3 are the second and third virial coefficients.

Dynamic light scattering measurements were carried out on a DLS-7000 light scattering photometer (Photal Otsuka Electronics, Japan), using a He−Ne laser light source operating at 632.8 nm. The apparent hydrodynamic radius $R_{H,app}$ at each concentration c was determined using the semilogarithmic plot of $g^{(2)}(t) - 1$ vs t, where $g^{(2)}(t)$ is the intensity autocorrelation function and t is the delay time.[13]

Static light scattering results obtained for aqueous solutions of telechelic HM-PNIPAM of various concentrations c between 1×10^{-3} and 7×10^{-3} g/cm^3 at 25 °C were analyzed on the

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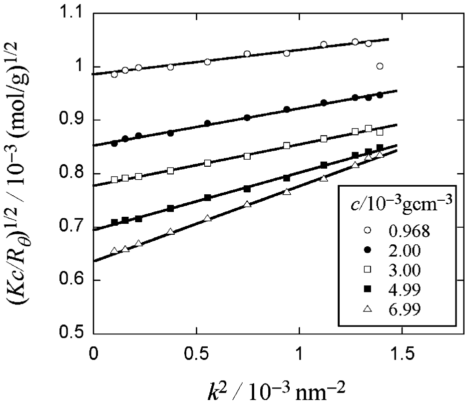

Figure 1. Static light scattering results for aqueous solutions of telechelic HM-PNIPAM at 25 °C.

Table 1. Light Scattering Results for Telechelic HM-PNIPAM in Water at 25 °C

c (10^{-3} g cm^{-3})	$M_{w,app}$ (10^6)	$\langle S^2\rangle_{z,app}^{1/2}$ (nm)	$R_{H,app}$ (nm)	$\langle S^2\rangle_{z,app}^{1/2}/R_{H,app}$
0.968	1.03	16.7	18.8	0.88
2.00	1.37	21.9		
3.00	1.66	24.8	23.8	1.04
5.00	2.08	30.8	30.7	1.00
6.99	2.44	36.2	38.7	0.94

basis of eq 1, yielding plots presented in Figure 1, and the values of $M_{w,app}$ and $\langle S^2\rangle_{z,app}$ are listed in Table 1 together with the apparent hydrodynamic radius $R_{H,app}$ values measured by dynamic light scattering. All values of $M_{w,app}$, $\langle S^2\rangle_{z,app}^{1/2}$, and $R_{H,app}$ definitely decrease upon dilution. The ratio of $\langle S^2\rangle_{z,app}^{1/2}$ to $R_{H,app}$ takes a value of ~1 in all cases except for the solution of lowest c, for which it is slightly less than unity.

The double logarithmic plot of $\langle S^2\rangle_{z,app}^{1/2}$ vs $M_{w,app}$ obtained is shown in Figure 2 by open circles. To obtain the true molar mass M_w and radius of gyration $\langle S^2\rangle_z^{1/2}$ from $M_{w,app}$ and $\langle S^2\rangle_{z,app}$, respectively, we have to consider the effects of the virial terms in eq 2. However, to estimate A_2 and A_3, we need structural information for the telechelic HM-PNIPAM. Thus, we must determine the structure and virial terms in an iterative way. For clarity, the virial term corrections are described as Supporting Information, and only the final results of M_w and $\langle S^2\rangle_z^{1/2}$ are shown in Figure 2 by full circles. The correction is only 3.4% for the highest c (7×10^{-3} g/cm^3) examined.

In Figure 2, the data represented by the full circles seem to obey a power law with an exponent of 0.87, which is higher than that expected for linear flexible polymers in good solvents. If telechelic HM-PNIPAM chains are assumed to form unicore flower micelles with an aggregation number m (and molar mass M), the radius of gyration may be approximated to that of a star polymer which consists of $2m$ arms of half PNIPAM chains. The radius of gyration $\langle S^2\rangle_{star}^{1/2}$ of this star polymer can be calculated by

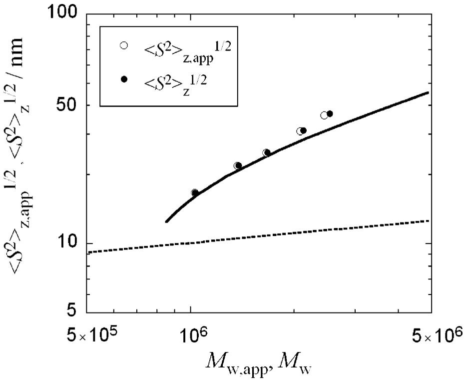

Figure 2. Molar mass dependence of the radius of gyration for telechelic HM-PNIPAM.

$$\langle S^2\rangle_{star}^{1/2} = [g_{star}(2m)\langle S^2\rangle_{linear}]^{1/2} \tag{3}$$

where $g_{star}(2m)$ is the g factor of the $2m$-arm star polymer and $\langle S^2\rangle_{linear}$ is the square radius of gyration of the linear PNIPAM chain with molar mass M, both of which are empirically expressed by[14,17]

$$g_{S,star}(2m) = 1.92(2m)^{-0.80}$$

$$\langle S^2\rangle_{linear}^{1/2} = 0.0188 \text{ nm} \times M^{0.54} \tag{4}$$

We can calculate m from M/47 500 and obtain the dotted line in Figure 2 for $\langle S^2\rangle_{star}^{1/2}$. The experimental data points remarkably deviate from $\langle S^2\rangle_{star}^{1/2}$ for all solutions and exhibit a much stronger molar mass dependence. This observation is a strong indication that association of flower micelles occurs in telechelic HM-PNIPAM solutions with c as low as 1×10^{-3} g/cm^3.

Semenov et al.[6] and also Borisov and Halperin[7-9] theoretically predicted that flower micelles formed by telechelic chains strongly attract each other in dilute solution. The attraction arises from the bridging telechelic chain between two micelle cores. Although Semenov et al.[6] speculated a macroscopic phase separation into a dilute micellar phase and a concentrated liquid phase of closely packed flower micelles, we observed no macroscopic phase separation in aqueous telechelic HM-PNIPAM solutions; all our test solutions were transparent and the light scattering intensity did not diverge even at the highest concentration examined.

Instead of the closely packed micellar phase, we assume here a random association of flower micelles and calculate the radius of gyration according to Dobson and Gordon,[18] who developed a cascade theory for random f-functional polycondensates. They formulated the (unperturbed) z-average square radius of gyration $\langle S^2\rangle^\circ_z$ for the polycondensates as well as the weight-average molar mass M_w as a function of the reacted fraction α of the functional groups on f-functional monomer units:

$$\langle S^2\rangle^\circ_z = \frac{b^2 f\alpha}{2(1+\alpha)[1-\alpha(f-1)]}$$

$$M_w = \frac{1+\alpha}{1-(f-1)\alpha} M_u \tag{5}$$

where b is the bond length of the polycondensates and M_u is the molar mass of the unimer. When the unimer flower micelle has a finite size, the z-average radius of gyration $\langle S^2\rangle_z^{1/2}$ obtained by scattering experiments is given by

$$\langle S^2\rangle_z = \langle S^2\rangle^\circ_z + \langle S^2\rangle_u \tag{6}$$

where $\langle S^2\rangle_u$ is the square radius of gyration of unimer. If the unimer behaves as a hard sphere, the bond length b may be equal to $2[(5/3)\langle S^2\rangle_u]^{1/2}$.

Extrapolating M_w and $\langle S^2\rangle_z^{1/2}$ to the zero concentration, we estimated $M_u = 8.5 \times 10^5$ g/mol and $\langle S^2\rangle_u^{1/2} = 12.4$ nm for the unimer flower micelle, and inserting the results into eqs 5 and 6, we calculated M_w and $\langle S^2\rangle_z^{1/2}$ for different values of α. The relationship between M_w and $\langle S^2\rangle_z^{1/2}$ thus obtained was not very much dependent on the f value. The solid curve in Figure 2, indicating the relation at $f = 4$, successfully reproduces the strong molar mass dependence of the radius of gyration for telechelic HM-PNIPAM. The theory seems to slightly underestimate the radius of gyration at high molar masses, which may come from the intracluster excluded volume effect.

We have chosen $\alpha = 0.224$ at $c = 0.007$ g/cm^3, where the weight-average aggregation number[19] of unit flower micelles in a cluster is only 3.7 and is still considerably smaller than the critical α at the gel point ($^1/_3$ for $f = 4$). It should be noted that the power-law exponent (0.87) of the M_w dependence of $\langle S^2 \rangle_z^{1/2}$ must not be an asymptotic one at such a small aggregation number. Kujawa et al.[12] reported the threshold concentration of gelation for a telechelic HM-PNIPAM with $M_w = 37\,000$ to be 0.02 g/cm^3. We have observed the gelation in aqueous solution of our HM-PNIPAM sample at a similar concentration. Thus, we conclude that the random association of flower micelles formed by the telechelic HM-PNIPAM takes place in aqueous solution at concentrations ($\sim 1 \times 10^{-3}$ g/cm^3) much lower than the gelation threshold. Furthermore, we observed dissociation of the aggregates upon dilution (Figure 1), indicating that the flower micelles are in the association−dissociation equilibrium.

This association may be induced by the bridging attraction between micelles as predicted theoretically.[6−9] The theories predicted that the strength of the bridging attraction depends on the aggregation number of the unimer flower micelle. Because the aggregation number may increase with decreasing molecular weight of the loop chain, we expect a pronounced trend of association for lower molecular weight HM-PNIPAM. We are now investigating the molecular weight dependence of the association behavior of the HM-PNIPAM flower micelle.

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Supporting Information Available: Synthesis and characterization of the telechelic HM-PNIPAM sample and virial term correction. This material is available free of charge via the Internet at http://pubs.acs.org.

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