Star-Like Structure of Oligocarbonate-Fluorene End-Functionalized Poly(ethylene glycol) ABA Triblock Copolymers Below the Gel Point^{**}

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Summary: ABA-type oligocarbonate-fluorene end-functionalized poly(ethylene glycol) s form micelles with star-like correlations in dilute solutions where water solvates the middle (B) poly(ethylene oxide) block. Using small-angle neutron scattering (SANS), the star-arm aggregation number and arm radius of gyration were characterized by Benoit's star-polymer form factor under θ -solvent conditions and by Alessandrini and Cargnano's renormalization group theory in good solvent. Model-independent SANS Zimm plots provide the radius of gyration, micelle aggregation number, and second virial coefficient (A_2) as a function of temperature. In comparison to unfunctionalized poly(ethylene glycol) A_2 is consistent with predictions for self-assembling polymers below the gelation point with a theta temperature of \approx 75 °C.

Keywords: aggregation; cluster; neutron scattering; star-like micelle; triblock copolymer

Introduction

Current needs in accessing nanoscale biomaterials of controlled size, shape, and material properties have led to the design of novel and tailored-sequence of block polymers and block polyelectrolytes. These self-assembled polymer-based materials serve as platforms for tissue engineering^[1] and biodegradable drug delivery systems.^[2] The rich phase behavior and hierarchical structure exhibited by self-assembled polymer micelles and gels are controlled by the chemical dissimilarity, molecular mass and sequence structure of the constituent blocks. Hierarchical organization across multiple length scales can be designed with block copolymers in the solution state.^[3,4] Advances in the synthetic polymer chemistry have paved the way for facile access to well-defined block copolymer precursors, through which properties of self-assembled polymer micelles and gels can be tailored.

The properties of self-assembled gels, such as their elasticity, require an understanding and measurement of the local structure. Of particular interest is probing the local micelle and gel structure, which requires measurement methods sensitive to the sub 100 nm length scales. Small-angle neutron and X-ray scattering methods are able to provide high sensitivity to the local solution-dispersed particles and gel structure.^[5,6] The micelle structures often are modeled by core-corona form due to the presence of non-swollen and melt-like micro-phase separated domains.^[7–9] In contrast, with gels, the structure often requires understanding at multiple length scales arising from large-scale aggregate or cluster domains, local polymer chain fluctuations, and liquid-like ordering from the underlying microphase separation.

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The cluster formation is directly observed by small-angle scattering to provide a direct measurement of the Fourier transform of the pair-distribution function.^[10] One challenge is to provide a molecular description for the local micelle structure and origins of often-observed meso-scale clusters in solution. Recently, Hammouda et al. observed clustering in poly(ethylene oxide) (PEO, or poly(ethylene glycol), PEG) aqueous solutions with clustering extent sensitive to the PEG ends groups that included CH₃O-(CH₂CH₂O)_n-OH, CH₃O-(CH₂CH₂O)_n-OH, and HO-(CH₂CH₂O)_n-OH. A random phase approximation (RPA) theory was developed that separated contributions of PEG into hydrophobic ethylene $(-CH_2CH_2-)$ and hydrophilic ether (-O-) units. This mean field description provides a means to distinguish solvation effects from clustering effects. The thermodynamic origins of clustering were proposed via quantification of the interaction parameters by neutron scattering. This approach placed the origin to equilibrium clustering equally among all hydrophobic monomer groups, not only the end groups.^[11] However, as Hammouda experimentally showed, the propensity to cluster formation is sensitive to the end group functionality,^[12] but without regular micelle formation expected by block copolymers.

The present experimental work addresses the basic building-block structure by changing the end-groups in PEG where the middle hydrophilic block is preferentially dissolved and the hydrophobic end groups are specially synthesized aliphatic oligocarbonatefluorene (F-TMC) groups. In this case, the thermodynamic driving force for associations are increased via hydrophobicity and π - π stacking interactions.^[13] The strongly associating groups lead to micelles in dilute solution much like the self-assembly of diblock polymers.^[13] However, if both end groups are strongly associating, an entropic frustration may ensues for micelles with both chain ends co-located in the same core (flower-like micelle) due to the loop conformations. A star-like micelle formed with one free end group in solution suffers an enthalpic (hydrophobic) penalty, but may associate with other star-like micelles. We demonstrate using small-angle neutron scattering that star-like micelles form and the clustering of star-like micelles mediated by the associating ends are precursors for the gel-forming network at concentrations near and above the gel point.

These model materials provide tailored end groups for encapsulating hydrophobic drugs within micro-phase separated domains of the polymeric amphiphiles. The ability to design a local structure through the choice of polymer chemistry is essential to understand mechanisms of component loading and release, and formation of nanoparticles and gel delivery materials. The oligo endfunctionalization with novel hydrophobic groups provides a synthetic handle to control the self-assembly of biodegradable materials with reversible structure.

Experimental Section

Synthesis and Sample Preparation

Unless specifically mentioned, all materials were purchased from Sigma-Aldrich, TCI, or Merck. Solvents were of analytical grade, purchased from Fisher Scientific or J. T. Baker and used as received. Poly(ethylene glycol) macroinitiator, HO-PEG-OH was purchased from Sigma-Aldrich [BioUltra; product numbers 95172 - poly-(ethylene glycol) 20,000; LOT BCBF2828V]. The supplier provided molecular mass, as per certificate of analysis for the respective lots, was used without further cross verification. The macroinitiator lot-specific analysis had a number-average relative molecular mass (M_n) of 19600 g/mol, as calculated from hydroxyl value. Spiro[fluorene-9,5'-[1,3]-dioxan]-2'-one (F-TMC) was synthesized as reported earlier.^[13] 1,8-Diazabicyclo[5.4.0] undec-7-ene (DBU) was distilled from CaH2 under dry N₂ and transferred to a glove box. Before transferring into the glove box, monomers and other reagents (like HO-PEG-OH) were dried extensively by freezedrying under high vacuum.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The ¹H- and ¹³C-NMR spectra of monomers and polymers were recorded using a Bruker Avance 400 spectrometer, and operated at 400 MHz and 100 MHz respectively, with the solvent proton signal as the internal reference standard.

Molecular Mass Determination by Size Exclusion Chromatography (SEC)

SEC was conducted using tetrahydrofuran (THF) as the eluent for monitoring the polymer conversion and also for the determination of polystyrene equivalent relative molecular mass of polymers. THF-SEC was recorded on a Waters 2695D (Waters Corporation, U.S.A.) Separation Module equipped with an Optilab rEX differential refractometer (Wyatt Technology Corporation, U.S.A.) and Waters HR-4E as well as HR 1 columns with particle size of 5 µm and effective molecular mass ranges of 50 g/mol to 100 kg/mol and 100 g/mol to 5 kg/mol, respectively (Waters Corporation, U.S.A.). The system was equilibrated at 30 °C in THF, which served as the polymer solvent and eluent with a flow rate of 1.0 mL/min. Polymer solutions were prepared at a known concentration (ca. 3 mg/mL) with an injection volume of 100 µL. Data collection and analysis were performed using the Astra software (Wyatt Technology Corporation, U.S.A.; version 5.3.4.20). The columns were calibrated with series of polystyrene standards ranging from $M_p = 996 \text{ g/mol}$ to $M_p = 118 \text{ kg/mol}$ (Polymer Standards Service, U.S.A.).

Fluorescence Measurements

The critical micelle concentrations (CMCs) of the polymers in deionized water were

determined by fluorescence spectroscopy using pyrene as the probe.^[14] The fluorescence spectra were recorded by a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon) at 25 °C. The polymer samples were equilibrated for 10 min before taking measurements. Aliquots of pyrene in acetone solution $(6.16 \times 10^{-5} \text{ mol/L}, 10 \,\mu\text{L})$ were added to glass vials and air-dried to remove the acetone. All polymers were dissolved directly in HPLC grade water. HPLC grade water was then added to make up the volume to 1 mL with a polymer concentration of 500 mg/L. This solution was then transferred to a glass vial and water was then added to make up the volume to 2mL. Subsequently, polymer solutions of varying concentrations were then added to the pyrene at 1 mL each, and left to stand for 24 h. The final pyrene concentration in each vial is 6.16×10^{-7} mol/L. The excitation spectra were scanned at wavelength from 300 nm to 360 nm with an emission wavelength of 395 nm. Both the excitation and emission bandwidths were set at 1.0 nm. The intensity (peak height) ratio of I_{337}/I_{330} from the excitation spectra was analyzed as a function of polymer concentration. The CMC was determined based on the Boltzmann-type sigmoid fit approach^[15] and results are provided in Table 1.

ABA-F Triblock Copolymer Synthesis

ABA-F4

In a 7 mL vial containing a magnetic stir bar in the glove box, F-TMC (76 mg, 301 μ mol, 5.9 equiv.) and HO-PEG-OH (19610 g/mol, 1.002 g, 51.1 μ mol, 1.0 equiv.) were dissolved in dichloromethane (4.0 mL). To this solution, DBU (2.2 μ L, 2.2 mg, 14.7 μ mol, 0.3 equiv.)

Table 1.	
Polymer	characteristics

Sample	PEG M _n [g/mol] ^a	N _B , PEG ^b	N _A , F-TMC ^c	f _{f-tmc} N _A /N _B	C _{cmc} [g/cm ³] ^d
ABA-F3	19600	445	2.0	0.0045	5×10^{-5}
ABA-F4	19600	445	1.2	0.0027	$2.4 imes 10^{-4}$

^a Molecular mass data based on hydroxyl value, provided by the supplier. ^b Calculated from the supplier provided data. ^c Based on ¹H NMR spectroscopy. ^d By pyrene fluorescence.

was added to initiate polymerization. The reaction mixture was allowed to stir at room temperature. After 10 min, the reaction was quenched by the addition of $\approx 50 \text{ mg}$ of benzoic acid and was precipitated into ice-cold diethyl ether (2 × 50 mL). The polymer was dried in a tared vial for about 1 d to 2 d, until a constant sample mass was obtained as white powder (0.972 g). $M_n^{(\text{NMR})} = 20220 \text{ g/mol}; N_B = 445; N_A = 1.2;$ polydispersity index (PDI)^(SEC) = 1.22 based on uncorrected polystyrene equivalent molar mass.

ABA-F3

In a 7 mL vial containing a magnetic stir bar in the glove box, F-TMC (128 mg, 507 µmol, 9.9 equiv.) and HO-PEG-OH (19610 g/mol, 1.003 g, 51.1 µmol, 1.0 equiv.) were dissolved in dichloromethane (4.0 mL). To this solution, DBU (3.7 µL, 3.8 mg, 24.8 µmol, 0.5 equiv.) was added to initiate polymerization. The reaction mixture was allowed to stir at room temperature. After 10 min, the reaction was quenched by the addition of \approx 50 mg of benzoic acid and was precipitated into ice-cold diethyl ether $(2 \times 50 \text{ mL})$. The polymer was dried in a tared vial for 1 d to 2 d, until a constant sample mass was obtained as white powder (1.008 g). $M_n^{(NMR)} = 20620 \text{ g/mol}; N_B = 445;$ $N_{\rm A} = 2.0; \rm PDI^{(SEC)} = 1.23.$

Small-Angle Neutron Scattering

Samples of ABA-F3 and ABA-F4 polymers were pre-weighed into 1.5 mL plastic centrifuge tubes and dissolved in aliquots of deuterium oxide (Cambridge Isotopes 99.98 D atom%) to a final concentration of 0.010 g/cm³. Samples of lower concentration were prepared by successive dilutions with deuterium oxide. All sample preparation and handling took place in a LabConco Nano-Enclosure Class I BSC with HEPA filtration. Samples were placed into cleaned Hellma quartz cuvettes.

SANS measurements were performed at the National Institute of Standards and Technology Center for Neutron Research NGB 10m *n*SOFT beam line with cold

neutrons of 5.0 Å wavelength (λ) with spread $(\Delta\lambda\lambda)$ of 0.11. The scattered intensity I(O)was measured as a function of the wave vector (Q) defined by $Q = (4\pi/\lambda) \sin(\theta/2)$, where θ is the scattering angle. A sample-todetector configuration of 5.2 m was used. Data were placed on an absolute intensity scale via direct beam flux measurement, detector sensitivity and element size, transmission, sample-to-detector distance, and sample scattering volume considerations. Standard data reduction routines and scaling to absolute intensity measurements were applied.^[16] Background intensity due to incoherent scattering contributions from protons and deuterium oxide solvent scattering was experimentally estimated and subtracted using established methods.^[17]

In the limit of dilute solutions, a Zimm plot of SANS data may be performed where the absolute scattered intensity, I(Q), is plotted as a function of polymer concentration (C)by plotting H C/I(Q) versus $k C + Q^2$. H is a neutron optical constant $[b_v^2 N_a (v_m/M_m)^2]$ where b_v^2 is the square of the scattering length density difference between monomer repeat unit and solvent, $N_{\rm a}$ is Avogadro's number and, v_m and M_m are the molar volume and molecular mass of a monomer, respectively; k is a scaling factor that is independent of the extrapolated quantities. From the double extrapolation in concentration and scattering wave vector (Q), the z-average radius of gyration (R_{α}) , second virial coefficient (A_2) and mass-averaged relative molar mass (M_w) are obtained. Uncertainties are estimated as one standard deviation of the mean. Fits of the SANS data are made by a weighted least-squares minimization and error bars correspond to one standard deviation. Limits are left out for clarity when uncertainties are smaller than the plotted symbols.

Results and Discussion

Due to the relative ease in the introduction of a variety of functionalities, aliphatic cyclic carbonates have emerged as a versatile precursor for ring-opening polymerization (ROP) to synthesize functional degradable polymers.^[18] Recent advances in transitionmetal free organo-catalytic ROP allow controlled synthesis of well-defined aliphatic polycarbonates that are well suited for numerous biomedical applications.[19,20] Previous work on degradable cholesterol and fluorene-functionalized carbonate PEG diblock copolymers are extended here by starting from a PEG diol. We have synthesized ABA-triblock copolymer by polymerizing spiro[fluorene-9,5'-[1,3]-dioxan]-2'-one, a fluorene-functionalized cyclic carbonate monomer (F-TMC) by using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the organo-catalyst (Scheme 1).^[13] This monomer was specifically chosen because the strong associative interaction (hydrophobic and $\pi - \pi$ stacking interactions) of the fluorene units were expected to provide a "sticky" end to the PEG chain. Since we were primarily interested in studying short hydrophobic blocks, to this end, we synthesized two different polymers ABA-F4 and ABA-F3 with a relatively low degree of polymerization of F-TMC block (N_A) . N_A was determined by ¹H NMR spectroscopy by comparing the integral values of protons corresponding to PEG ($-CH_2CH_2O-4.0-$ 3.2 ppm) to that of F-TMC ($-CH_2OCOO$ CH_{2-} , 4.60–4.15 ppm). The degree of polymerization was found to be 1.2 and 2.0 (per hydroxyl initiating site), for ABA-F4 and ABA-F3, respectively (Table 1). These triblock copolymers have controlled composition and relatively low molar-mass polydispersity (PDI \leq 1.3). These triblocks can serve as model polymers to systematically probe the effect of end-groups on selfassembly.

The ABA-F4 and ABA-F3 systems are water-soluble (and deuterium oxide soluble) and form clear solutions under



Scheme 1. Chemical structure of the ABA polymers under study. ambient conditions below and above the gel point ($\approx 4 \text{ g/L}$). The concentrations studied here are restricted to below the gel point allowing one to characterize the structure and interactions via Zimm plot analysis of SANS data and the local intraparticle (micelle) correlations with modeldependent form factors. We develop insight into the structural length scales that are controlled by the F-TMC end-group molecular mass (Table 1). The local structure, interactions, and correlations in dilute solutions are necessary to develop an experimental framework of the structure, dynamics, and controlling parameters of the gel state and their coupling to phase separation.

Zimm Plot Analysis: Structure and Aggregation Number

SANS was measured for 5 concentrations $(0.000625 \text{ g/cm}^3 \text{ to } 0.01 \text{ g/cm}^3)$ as a function of 6 temperatures (25 °C to 75 °C) as shown in Figure 1 for block copolymers dissolved in deuterium oxide to maximize the scattering length density contrast between polymer and solvent. The SANS data show concentration and temperature-dependence in the ABA-F4 and ABA-F3 (shown). The temperature range remains within the homogeneous phase below the cloud-point temperature estimated by transmission measurements and single-angle dynamic light scattering for solutions dispersed in H₂O and below the overlap concentration $(C^* \approx 0.024 \text{ g/cm}^3)$. The second virial coefficient (A_2) , molecular mass (M_w) and the radius of gyration $\langle R_g \rangle$ of the structures are characterized by the classical Zimm plot.

Figure 2 shows the Zimm plots with double extrapolations as the open symbols (\circ , $Q \rightarrow 0$ and \Box , $C \rightarrow 0$). The extrapolations are made within the linear regions as deviations at higher Q are due to intra-particle correlations, as discussed later. The concentration-dependence of the inverse scattered intensity to zero angle ($Q \rightarrow 0$) provides the second virial coefficient through the relationship to the osmotic compressibility as shown in Equation 1, with higher-order virial terms.



Figure 1. SANS as a function of temperature for concentrations noted for the ABA-F3.

As observed in Figure 2, the concentration dependence has a positive slope initially at 25°C. However, the slope progressively decreases with increasing temperature

and reaches zero, within uncertainty. At each temperature the common intercept from the double extrapolation provides the inverse mass-average molecular mass



Figure 2.

Temperature-dependent SANS Zimm plots for the ABA-F3. Error bars correspond to one standard deviation.



Figure 3.

SANS Zimm Plot for ABA-F3 and ABA-F4 series (a) Radius of gyration (b) Aggregation number (M_w/M_1) . Uncertainties (error bars) are estimated by one standard deviation of the mean by least-squares minimization of fits to the SANS data.

 $(1/M_w)$ Similarly, the concentration extrapolation $(C \rightarrow 0)$ provides the z-average radius of gyration, $\langle R_g \rangle$.

$$\frac{H_n C}{I(0)} = \frac{1}{M_w} (1 + 2A_2 C + \cdots)$$
(1)

The Zimm plot results for $\langle R_g \rangle$ of ABA-F3 and ABA-F4 series are shown in Figure 3a. The mass-averaged molecular mass, normalized by the molecular mass (M_1) of the PEG middle-block (Table 1), estimates the aggregation number (N_{agg}) as shown in Figure 3b. $\langle R_g \rangle$ and N_{agg} demonstrate that the solutions are comprised of multi-chain assemblies, or micelles. The structures appear even in the presence of the F-TMC end-group mean degree of polymerization of 1.2 and 2.0 for ABA-F4 and ABA-F3, respectively. N_{agg} appears temperature-independent between 25°C and 75°C, while a small reduction in the $\langle R_{g} \rangle$ is observed between 55 °C to 75 °C. The micelle $\langle R_g \rangle$ appears similar between the two polymers, yet the aggregation numbers differ. If the $\langle R_g \rangle$ contraction with temperature were caused by an isotropic reduction via chain conformation, due to a change in solvent quality, then this may be reflected in the value of the second virial coefficient. This was observed upon quantifying A₂ shown in Figure 4 for ABA-F3 and ABA-F4.

Micelle Interactions (A₂) Below the Gel Point

Figure 4a shows the $Q \rightarrow 0$ extrapolation as a function of concentration with virial coefficient shown in Figure 4b, summarized for ABA-F3 and ABA-F4. A₂ is positive and decreases to zero at 75 °C for the ABA-F3 and similarly for ABA-F4. The crossing of A_2 to 0 equates to a θ -temperature (T_{θ}) between structured micelles indicating a weakening of hydrogen bonds^[21] with increasing temperature. These observations are made in the context on the known lower critical solution temperature in aqueous solutions of poly(ethylene glycol).^[22,23] At the observed θ -temperature the chain dimensions are reduced from their swollen, good solvent state at lower temperatures. The lack of a change in N_{agg} implies the overall micelle $\langle R_g \rangle$ changes are related to chain conformation, in particular at $T_{\theta} \approx 75 \,^{\circ}\text{C}$, rather than a change in average number of chains per micelle. In these relatively low molar mass polymers the coil-globule transition would not be sharp, but the trends are consistent with this expectation.

The value of A_2 (with parent PEG of $M_w = 19610 \text{ g/mol}$) may be compared to the linear, unfunctionalized PEG. Devanand and Selser^[24] experimentally determined the molecular mass dependence, $A_2 = 1.84 \times 10^{-2} M_w^{-0.20 \pm 0.06} \text{ mol} \cdot \text{cm}^3/\text{g}^2$,



Figure 4.

(a) Extrapolated inverse scattered intensity to zero-angle from Zimm plot as a function of concentration for ABA-F3. (b) Second virial coefficient between micelles determined for ABA-F3 and ABA-F4 series from linear C dependence. Uncertainties (error bars) are estimated by one standard deviation of the mean by least-squares minimization of fits to the SANS data.

yielding $A_2 = 2.55 \times 10^{-3} \text{ mol} \cdot \text{cm}^3/\text{g}^2$ using $M_w = 19,610 \text{ g/mol}$ for the parent polymer. A value of $A_2 = 2.4 \times 10^{-3} \text{ mol} \cdot \text{cm}^3/\text{g}^2$ at $30 \,^{\circ}\text{C}$ for $M_w = 16,000 \text{ g/mol}$ PEG was found by Venohr et al.^[25] with a temperature dependence of A_2 and extrapolation to 0 at $\approx 80 \,^{\circ}\text{C}$. The A_2 values determined by SANS are a factor of 10 smaller than those for the corresponding unfunctionalized PEG, yet the temperature at which $A_2 = 0$ is similar to that reported by Venohr et al.

The ABA triblock structure and micelle formation are the source of this difference as predicted by Tanaka's mean field theory for thermoreversible gels.^[26] Below the gel point, the dimensionless second virial coefficient has the form $A_2 = (1/2 - \chi) +$ $\kappa_1/2N$, where χ is the Flory-Huggins interaction parameter between the polymer and solvent, N is the degree of polymerization of the polymer with functional (sticky) groups and κ_1 is a negativedefinite leading order term in the expression for the osmotic pressure below the gel point. Therefore, the theory predicts that the second virial coefficient must always be lowered by the formation of clusters, association, or micelle formation. Such behavior is qualitatively consistent with the experimental observations for the ABA polymers with oligocarbonate-fluorene groups hwne compared to unfunctionalized linear homopolymer counterparts. The predicted change in A_2 is larger than that from calculating A_2 with the apparent micelle molecular mass. Hammouda et al. have developed a random phase approximation approach that treats PEG in water as a ternary system, whereby the pairwise interactions among ether oxygens, the saturated ethylene groups, and water are considered leading to three Flory–Huggins χ parameters. In the presence of the carbonate-fluorene end-groups, important specific $\pi - \pi$ interactions may dominate; however, the alternate RPA approach may prove valuable in the case where the clustering and possible exclusion of water occurs at higher concentrations.[11,12,27]

Correlations Within Micelles at T_{θ}

The Zimm plot considers the overall micelle structure without insight into the intra-micelle correlations that distinguish linear from branched structures, for example. A Kratky plot is often used to understand these correlations and branching.^[10] Deviations from the Kratky plateau that shows a transition to Gaussian chain scaling, or good-solvent scaling are directly

observable without reference to a particular model. Kratky plots of the data in Figure 1 show a peak at all concentrations and temperatures. Figure 5 shows the concentration dependence at 75°C for ABA-F3 on a log-scale for clarity. Considering limiting topologies, a Kratky plot peak is an exact analytic result for cyclic (ring) and regular star-branched polymer form factors.^[10] A more probable paircorrelation at the peak, or more compact structure, as compared to the equivalent linear chain, is formed by closing a linear Gaussian polymer to form a ring, or creating a point-origin with branches for a regular star.

We suggest that due to the ABA block structure and high degree of amphiphilicity caused by the hydrophobic F-TMC end groups, the end-groups drive the associations.^[13] In the present case, the end-group fraction in ABA-F3 and ABA-F4 systems is so small (0.045 and 0.027%, respectively) that the expected size of the junction would be in the nm scale. The hypothesis of endgroups self-assembling, driven by the π - π interactions of the oligocarbonate-fluorene from water and PEG, leads to a few trial structures. In star-like assembly, one end per chain aggregate forming a point-like core with chains emanating to form the arms. Another trial structure have both chain ends joining to form a hair-pin loop of stars, often referred to as flower-like micelles. These two limiting forms share a star-like structure at magnifications within the micelle as shown in Scheme 2. However, the flower-like micelle is not simply a star, but a looping star that would have twice as many arms for the same aggregation number. Further, the entropic penalty for forming the loop would lead to a smaller arm $R_{\rm g}$. The star form factor was exactly calculated by Benoit for Gaussian chain statistics.^[10] In order to provide insight to these monomer-monomer correlations, we use the evidence from the Zimm plot as to the solvent quality and the available exact form factors to understand the number of star arms and the radius of gyration of the arm from a model-dependent approach.

Figure 5 shows ABA-F3 at T_{θ} for 5 concentrations. The apparent Gaussian plateau above $Q = 0.05 \text{ Å}^{-1}$ appears between $C = (0.01 \text{ to } 0.0025) \text{ g/cm}^3$ with positive deviations appearing at the lower concentrations. The solid lines are the Benoit form factor fits to a prefactor, $\langle R_{\rm g} \rangle_{\rm arm}$, and number of arms per star ($f_{\rm arm}$) with fixed arm degree of polymerization N given by



Figure 5.

Kratky plot at the theta temperature (75 °C) for 5 ABA-F3 concentrations noted. Benoit form factor fits shown with fit results of the concentration-dependent (b) number of arms/star and (c) star arm radius of gyration. Uncertainties (error bars) are estimated by one standard deviation of the mean by least-squares minimization of fits to the SANS data.



Scheme 2.

Schematic of two limiting forms for structures for dilute micelles.

Table 1. The fits capture the Kratky peak region and decay. Within the theory, the peak position is a function of the arm radius of gyration and functionality of the star. The peak position does not change markedly across the concentrations. A logarithm scale was used to highlight the wide-range in concentration data without further scaling.

$$P(Q) = \frac{2N}{w^4} \\ \times \left\{ w^2 - \left[1 - e^{-w^2} \right] + \frac{f_{\rm arm} - 1}{2} \left[1 - e^{-w^2} \right]^2 \right\}$$
(2)

$$w = QR_{g,arm}$$

The ABA-F3 $\langle R_{g} \rangle_{arm}$ and star functionality, f_{arm} , are shown in Figure 5b. Firstly, the $\langle R_g \rangle_{arm}$ does not vary with concentration at T_{θ} with average (6.9 ± 0.3) nm. Secondly, above $C = 0.00125 \text{ g/cm}^3 f_{\text{arm}}$ is constant with an average (17 ± 2) arms. The value of $\langle R_{g} \rangle_{arm}$ compares to experimental data for linear (unfunctionalized) PEG that yield z-averaged $\langle R_{o} \rangle \approx 7 \,\mathrm{nm}$. The exact value for a ring polymer of the same degree of polymerization with Gaussian chain statistics is $1/\sqrt{2}$ that of the linear chain.^[10] These comparisons favor the starlike branching topology. Further refinement would need to consider modeling with mixed star and loop or flower-like micelles and perhaps inter-micelle bridging leading to stretched chains. An average chain dimension could be determined with deuterium-labeled chains by contrast variant SANS.[10,28]

The most dilute solutions have a smaller functionality for the star-like micelles at the lowest concentration at T_{θ} . However, the estimate provided by the Benoit form factor and the noted deviations imply fewer

arms at which there is less screening of the excluded volume within the star-like micelles, whereas at higher functionality, more screening of the excluded volume interactions occurs.

Correlations Within Micelles in Good Solvent

In order to go one step further with the star-like micelle local structure we apply the form factor as calculated using renormalization group methods applied to star polymers by Alessandrini and Cargnano.^[29] These calculations recover the results from Miyake and Freed for the arm radius of gyration within the first-order theory.^[30,31] The theory was developed for lower functionality of arm stars (or lightlybranched), since at high functionality local monomer-monomer hard-core details are not considered. In such as case, the scaling theory of Daoud and Cotton^[32] capture this limit for stars^[33] with f_{arm} up to 128 and dendrimer-star polymers^[34] with f_{arm} reaching \approx 750. Using a fixed number of arms $(f_{arm}=5)$ estimated from Benoit's form factor and fitting for $\langle R_{g} \rangle_{arm}$ the presence of excluded volume appears to represent the experimental data in Figure 6 for the lowest concentration ABA-F3.

The continuous decrease in $\langle R_{g} \rangle_{arm}$ (with fixed f_{arm}) as T_{θ} is approached is predicted by the star-like self-assembled polymer model. The renormalization group calculations, using the available coefficients, captures the correlations in the presence of excluded volume interactions. A quantitative comparison between the Gaussian star and excluded volume star is beyond the scope here as the theory is applied to help provide insight into the local chain structure of these self-assembling polymers. Further characterization of the star-like micelles would require consideration of (a) clustered end-group scattering and (b) junction fluctuations that smear the interface between end groups and chain. Both are expected to contribute in the high-Q region due to the nm to Å sizes of the F-TMC end group with average degree of polymerization of $n \approx 1.2$ and ≈ 2 .



Figure 6.

Temperature dependent fits of ABA-F3 scattering data to renormalization group theory at concentration 0.000625 g/cm³. Arm radius of gyration determined with fixed number of arms ($f_{arm} = 5$) for polymer concentration 0.000625 g/cm³. The estimated single chain radius of gyration from the good solvent scaling determined by Devanand and Selser is shown (\Box , 7 nm). Uncertainties (error bars) are estimated by one standard deviation of the mean by least-squares minimization of fits to the SANS data.

ABA Micelle Structure and Functionality

The micellization of amphiphilic diblock and triblock polymers in solution, or as blends with a corresponding homopolymer was considered by numerous theoretical treatments. In many cases for highlyasymmetric block molecular weights $(N_{\rm A} \ll N_{\rm B})$, the structure is spherically symmetric with a defined core and corona region. A minimization in the free energy per chain with contributions of the interface, core and corona predicts the scaling of the aggregation number and radius of the micelle. In dilute solution, when the solvent quality for AB block copolymers with poor solvent for the A-block, micelles of size (R)are formed with the aggregation number (f) was determined by the molecular mass of the insoluble A-block, predicted by the star model of Halperin^[35] as $f \sim N_{\rm B}^{4/5}$ and $R \sim N_{\rm B}^{4/25} N_{\rm A}^{3/5}$. The mean field treatment of Nagarajan and Ganesh^[36] found the aggregation number depends on both $N_{\rm A}$ and $N_{\rm B}$ when considering spherical domains formed by diblocks with a uniform density segregated core and solvent swollen shell as $f \sim N_{\rm A}^{1.19} N_{\rm B}^{-0.51}$ and $R \sim N_{\rm A}^{0.73} N_{\rm B}^{-0.17}$. The role of loops with ABA triblock were treated by ten Brinke and Hadziioannou who found that loops reduced the fraction of micelles and shifted the CMC to higher concentrations.^[37]

The aggregation number from the Zimm plot for ABA-F3 was $f=23\pm 2$ with $N_{\rm A}=2.0$ and in ABA-F4 $f=6.0\pm 1.0$ with $N_{\rm A}=1.2$. Taking the aggregation number to depend only on the F-TMC degree of polymerization such that $f \sim N_{\rm A}^{\alpha}$, the data suggest $f \sim N_{\rm A}^{2.7\pm0.5}$, two systems cannot establish a scaling law, but it shows a dependence stronger than mean field predictions. The estimated scaling based upon the Benoit model fits to the number of star arms $f_{\rm arms} \sim N_{\rm A}^{3.0\pm0.5}$ averaging

across temperature and the highest 3 concentrations. The F-TMC end-group degree of polymerization controls the aggregation with a stronger than mean field dependence provided by available scaling models for unswollen spherical core and swollen corona chains. The F-TMC end-functionalized PEG polymers deviations are compared to ABA polymers $(\alpha \approx 1.5 \text{ to } 2)$ by M. Antonietti et al.^[38] and ($\alpha \approx 1.6$ to 1.9) Oin et al.^[39] for diblock copolymer micelles. The aggregation number will be influenced by the number of sticky-ends per micelle, such that a star-like micelle may form a stable clusters through bridging.

Scaling approaches for single micelles do not consider inter-micelle interactions and bridging. Such effects fall into the theory of thermoreversible gelation in which clustering and associations occur simultaneously.^[26,40] While the primary structures are micellar, larger-scale structures may form due to exposed associating functional groups. Under good solvent conditions for PEG, the chain is highly swollen and increases the probability for inter-micelle bridging through exposed end groups. This would increase the apparent aggregation number through bridging interactions among micelles. Under poorer solvent conditions for PEG a more compact chain conformation may be expected, thereby favoring flower-like micelles and reducing the probability of inter-connected micelles (Scheme 2).

This connectivity among micelles is considered in Figure 7 where the number of arms from Benoit form factor fits for Gaussian star-like micelles is shown along with the aggregation number from the molecular mass via Zimm plot as a function of temperature. At the theta temperature, the two are nearly equal within uncertainty. The systematic deviation from lower to higher temperature suggests aggregates estimated by the Zimm plot are composed of a few inter-connected star-like micelles, whereas at the theta temperature the micelle inter-connectivity is reduced as the aggregation number reaches the single



Figure 7.

Plot of the aggregation numbers estimated by Zimm plot and Gaussian star arm as a function of temperature for ABA-F3. Uncertainties (error bars) are estimated by one standard deviation of the mean by least-squares minimization of fits to the SANS data.

micelle value from the star-like form factor. At the micelle level, the number of star arms increases with temperature, consistent with the poorer solvent quality (R_g decreases in Figure 6b) for the PEG that increases the probability of loop conformations and buries the end groups within the same micelle. Note that in Figure 7 the star arms nearly doubles, which supports a case where star-like micelles completely reverted to flower-like micelles (Scheme 2).

Conclusion

Small-angle neutron scattering measurements were quantified as star-like structures at length scales larger than the free polymer chain. While a star-like trial structure is one of many variants, such as flower-like or a mixed flower and star-like micelle, this approach appears to be selfconsistent in two respects. The magnitude of the radius of gyration of the star arm over one decade in concentration at the estimated theta temperature is near that of the PEG polymer of the same molecular mass. Secondly, at fixed concentration, the

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magnitude and trend in the chain conformation decrease near the theta temperature using the renormalization group theory. The Zimm analysis recovers the second virial coefficient with expected sign and decreased magnitude when compared to similar PEG polymers. The theta condition appears consistent with the literature along with corresponding changes in chain dimensions, below the cloud point temperature. These star-like micelles further assemble into clusters enabled by stickyends that are not buried. These larger-scale structures will be reported elsewhere, but the primary structures and end-group functionalization provides guidance as a fundamental building block of the gels and the associated temperature versus concentration phase diagram. The structural hierarchy exhibited shows that the chain conformation, micelle structure and further self-assembly of micelles into aggregates or clusters are coupled. This coupling at the micelle level of star-like versus flower-like micelles that in turn influences the assembly or clustering is crucial to understand gelation behavior and rheological properties. An analytical form factor of the loopstar or flower-like motif and the mixtures would be useful to understand further local structure details.

Acknowledgements: Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology (NIST) nor does it imply that the material or equipment identified is necessarily the best available for this purpose. S.V. and Y.Y.Y acknowledge funding support from the Institute of Bioengineering and Nanotechnology (Biomedical Research Council, Agency for Science, Technology and Research, Singapore). V.M.P. thanks the support of the NIST Materials Genome Initiative.

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