Small-Angle Neutron Scattering Study of Micellization of Ionic Copolymers in Aqueous Solutions. The Effects of Side-Chain Length and Molecular Weight

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ABSTRACT: We have used small-angle neutron scattering (SANS) technique to study the micellization of a series of alternating comb-shaped copolymers, poly[1-alkene-*co*-(maleic anhydride)], in the fully neutralized state in water with the 1-alkenes ranging from 1-octene to 1-octadecene and weight-average molecular weights from 6000 to 20 000. The structural parameters of the amphiphilic aggregates are determined by analyzing the intraparticle structure factor of the SANS intensity data. The analysis has shown that the copolymer derived from 1-octadecene forms cylindrical-shaped micelles while the copolymers derived from lower 1-alkenes form ellipsoidal-shaped micelles with the transition occurring at the 1-hexadecene copolymer. Analysis of the absolute neutron scattering intensity at zero scattering angle has shown a strong dependence of the mass of the aggregates on the side-chain length, namely, there are approximately 200 monomer repeating units per aggregate for the 1-octadecene copolymer versus about 20 monomer repeating units per aggregate for the 1-octene copolymer. The effect of molecular weight on aggregation is not observed possibly due to the polydispersity in the copolymers.

Introduction

The formation of micelles by amphiphilic molecules in aqueous solution is dependent on the balance of hydrophobic and hydrophilic free energies of the amphiphiles in the aqueous environment. We have previously used small-angle neutron scattering (SANS) and small angle X-ray scattering (SAXS) techniques to study a comb-shaped, alternating copolymer, poly[1-octadecene-*co*-(maleic anhydride)] in the neutralized state in D_2O.[1-3] When hydrolyzed, this class of copolymers has an array of hydrophobic hydrocarbon side chains on one side and two hydrophilic carboxylic acid groups per repeating unit on the other side. Each repeating unit consists of one 1-alkene and one maleic anhydride monomer. The analysis of the SANS data has shown that this copolymer forms cylindrical micelles in water and that each micelle consists of approximately 200 repeating units as determined by the absolute neutron-scattering intensity at zero scattering angle. Analysis of large-angle data shows that the radius of the cylinder is approximately equal to the hydrocarbon side-chain length and the length of the cylinder equal to that of the copolymer backbone.

In this study, we have systematically varied the hydrophobicity of the amphiphilic copolymers by varying the length of the hydrocarbon side chains. Our objective is to study the effect of the hydrophobicity of the copolymer on the formation and on the structural parameters of the micelles. This study has covered 1-alkenes from 1-octene to 1-octadecene. Henceforth, we refer to the alternating copolymer derived from 1-octene as C_8 copolymer etc. We have also attempted to examine the effect of the molecular weight averages on the solution aggregational behavior.

A similar class of copolymers, poly[(alkyl vinyl ether)-*co*-(maleic anhydride)], has been studied extensively by Strauss, Dubin, and Hsu[4-8] using various techniques including potentiometry, viscometry, fluorescence, and luminescence quenching methods. They divided the class of copolymers into three groups according to the alkyl group size, small ($n < 3$), intermediate ($n = 4$–8), and large ($n > 10$), and proposed different conformations at different pHs for different groups of copolymers. The work of Strauss et al. has primarily focused on the copolymers with intermediate ($n = 4$–8) alkyl chains. They have suggested that the hydrolyzed copolymers at low pH assume a hypercoiled conformation and form intramolecular micelles. Recently Chu and Thomas[9] have employed steady-state and pulsed fluorescence spectroscopy to study micellar properties of poly[1-octadecene-*co*-(maleic anhydride)], or C_{18} copolymer, in water, fully neutralized with KOH and buffered at pH 8.0. They arrived at the conclusion that a single polymer molecule forms a polymer micelle.

Our present study represents the first systematic effort to correlate the micellar formation with the hydrocarbon side-chain length for this class of copolymers. We have covered the range of the large ($n > 10$) and part of the intermediate ($n = 4$–8) alkyl group sizes, as defined by Strauss and co-workers for *n*-alkyl vinyl ether–maleic anhydride copolymers. We have used the SANS technique to determine the structural parameters of this class of copolymers in the fully neutralized state and at high pH in D_2O. Results of our analysis have demonstrated a strong effect of the side-chain length on the mass of the aggregates. In a SANS experiment, the mass and shape of the aggregates can be accurately deduced from the scattering intensity distribution for two reasons: first, the absolute value of SANS intensity at zero scattering angle is easily determined for dilute solutions when there are no appreciable interparticle interactions and, second, the SANS cross-section formula at finite angles can be written without ambiguity once the structural model is chosen. The analysis has also shown that the C_{18} copolymer is cylindrically shaped while the lower 1-alkene copolymers, C_{14} and below, are ellipsoidal. The shape of micelles formed by the C_{16} copolymer can be either cylindrical or ellipsoidal within experimental errors, although the fit with the ellipsoidal model is slightly better than with the cylindrical model.

Experimental Section

1. Materials and Sample Preparations. The copolymers were synthesized, purified, and characterized by using the pro-

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Table I
Glass Transitions and Molecular Weights of Poly[1-alkene-*co*-(maleic anhydrides)], Determined by GPC Using Polystyrene Standards

copolymer sample	MW repeat unit	M_w	M_n	MWD	T_g, °C
C_{18}	350	6660	3960	1.68	57
C_{16}-1	322	11750	4200	2.80	85
C_{16}-2	322	10290	4100	2.50	72
C_{16}-3	322	8690	2600	3.36	66
C_{14}	294	8960	3130	2.86	81
C_{12}-1	266	10560	3650	2.89	90
C_{12}-2	266	7940	3760	2.11	81
C_{12}-3	266	5800	1570	3.69	60
C_{10}	238	11300	5000	2.26	107
C_8-1	210	20520	5980	3.55	120
C_8-2	210	14690	4400	3.34	112
C_8-3	210	9120	3770	2.42	102

cedures described in earlier publications.[1,2] The molecular weight distribution (MWD) of most of the original copolymers, especially those derived from lower 1-alkenes, was broad. Except for the C_{18} copolymer, the copolymers used in this study were fractionated by the super critical fluid fractionation (SCF) technique.[10] The polydispersity of the fractionated copolymers was slightly improved after fractionation. The fractionated copolymers were again characterized by known procedures of GPC, FTIR, and DSC. The stoichiometric amount of LiOH used to fully neutralize each copolymer was calculated from the elemental analysis of the oxygen content. The glass transition temperature, the molecular weight of the repeating unit, and the molecular weight averages for each copolymer are listed in Table I.

The concentration of the polymer solutions was maintained at 1% by weight for all samples. Each dry copolymer was weighed into a given amount of D_2O and the mixture was placed in an oil bath at a temperature range between 90 and 100 °C for about 5–10 h and the solution was occasionally vortexed. After heating and vortexing, the C_{16} and C_{14} copolymers formed milky dispersions, while the C_{12} and C_{10} copolymers formed partially translucent solutions. The three C_8 copolymers formed chunky gums and remained undispersed in D_2O. After heating, a stoichiometric amount of LiOH was then added to each solution to fully neutralize the copolymer. The solution was heated again for another short while until it became clear.

2. SANS Experiments. Except for a few data sets, which were taken at the Oak Ridge National Laboratory (ORNL) and Brookhaven National Laboratory (BNL) and described in earlier publications,[1,2] most of SANS measurements in this study were taken at the small-angle diffractometer (SAD) at the intense pulsed neutron source (IPNS) at Argonne National Laboratory. At the IPNS, high-energy neutrons were produced in pulses from a spallation source. The spallation reactions were induced by bombarding a natural uranium target with 450-MeV protons. The neutrons were then moderated by a solid methane moderator at 18 K. The wavelengths of the neutrons were determined by the method of time-of-flight and the wavelength distribution of the moderated neutron spectrum ranged from 0.5 to 14 Å. The thermal neutrons were then passed through a Soller collimator to reduce the angular divergence of the beam. At the sample position a cadmium aperture of 0.9 mm in diameter was used to define the circular beam.

Sample holders were disklike quartz cells with a diameter of 2 cm and a path length of 2 mm. The scattered neutrons were collected by a 17 × 17 cm^2 position-sensitive multidetector. The detected signals were corrected for the empty cell scattering, the sample thickness, and the sample transmission. The incoherent scattering from a 1-mm-thick H_2O sample was used to calibrate the relative sensitivity of each detector pixel. The corrected scattering intensity was then normalized by the total number of incident neutrons and converted into the absolute scale by using a scaling factor from the scattering of a secondary standard A14 sample with known cross section.[11] SANS intensity distribution was then presented as a function of the magnitude of the scattering vector $Q = (4\pi/\lambda) \sin(\theta/2)$, where λ is the neutron wavelength and θ is the scattering angle. The Q range in this study was from 0.005 to 0.35 $Å^{-1}$. The time required to collect one data set was highly dependent on the side-chain length and varied from 2 h for the C_{16} copolymer to about 12 h for the C_8 copolymer. Even with a very long accumulation time, the quality of the signal of some of the lower alkene copolymers was not as good.

Table II
Neutron Scattering Parameters of the Hydrolyzed Comb-Shaped Copolymers, Poly[1-alkene-*co*-(maleic anhydride)]

copolymers from 1-alkenes	b_m,[a] 10^{-12} cm	R (or b),[b] 10^{-8} cm	v_m,[c] 10^{-24} cm^3	C_m,[d] 10^{19} cm^{-3}
C_{18}	2.7340	24.21	637.5	1.7206
C_{16}	2.9008	21.67	583.7	1.8702
C_{14}	3.0676	19.14	529.9	2.0483
C_{12}	3.2344	16.61	476.1	2.2639
C_{10}	3.4012	14.08	422.3	2.5303
C_8	3.5680	11.55	368.5	2.8676

[a] b_m: scattering length of a repeating unit. [b] R (or b): the cross-sectional radius of the cylindrical micelle (or the minor axis of the ellipsoidal micelle). [c] v_m: dry volume of a repeating unit. [d] C_m: number density of the repeating unit of the polymer.

Data Analysis

Due to the weak interparticle interactions in dilute solutions, the value of the structure factor $S(Q)$ can generally be treated as unity above a certain value of Q, which is approximately equal to the position of the first diffraction peak. Since the intermicellar interactions for this particular polyelectrolyte system are very much reduced due to the considerable counterion condensations around the micelles,[3] the $S(Q)$ can thus be taken as unity for Q greater than 0.04 $Å^{-1}$. The neutron scattering cross section for the entire Q range can be expressed as

$$I(Q) = I_0\bar{P}(Q) \tag{1}$$

The factor I_0 is the scattering cross section at $Q = 0$ and can be calculated according to[1,2]

$$I_0 = C_m PN(b_m - v_m\rho_{D_2O})^2 \tag{2}$$

where C_m is the number density (number/centimeter cubed) of the repeating unit in solution, P the degree of polymerization in a copolymer, N the aggregation number defined as the number of polymer molecules per aggregate, b_m the scattering length of the repeating unit, v_m the dry volume of the repeating unit, and ρ_{D_2O} (=6.34 × 10^{10} cm^{-2}) the scattering length density of D_2O. Neutron scattering parameters used to calculate I_0 are listed in Table II.

The relationship between P, N, and the micellar size is given by the volume conservation condition

$$\pi R^2 L = PN(v_m + v_{D_2O}N_{D_2O}) \tag{3}$$

for a cylindrical micelle, or

$$\pi ab^2 = PN(v_m + v_{D_2O}N_{D_2O}) \tag{4}$$

for an ellipsoidal micelle, where R and L are the cross-sectional radius and the length of the cylinder respectively, a and b are the major and minor axes of the ellipsoid, v_{D_2O} is the volume of a D_2O molecule (=30.2 $Å^3$), and N_{D_2O} is the hydration number per repeating unit. The cross-sectional radius of the cylindrical micelle and the minor axis of the ellipsoidal micelle are calculated according to

$$R \text{ (or } b) = l_t + 3.725 \text{ Å} \tag{5}$$

where l_t = 1.5 Å + (N_c − 1) × 1.265 Å[12] is the length of a hydrocarbon tail with N_c the number of carbon atoms in the tail; for example, N_c is 16 for the C_{18} copolymer, and 3.725 Å is the length of the hydrophilic head.

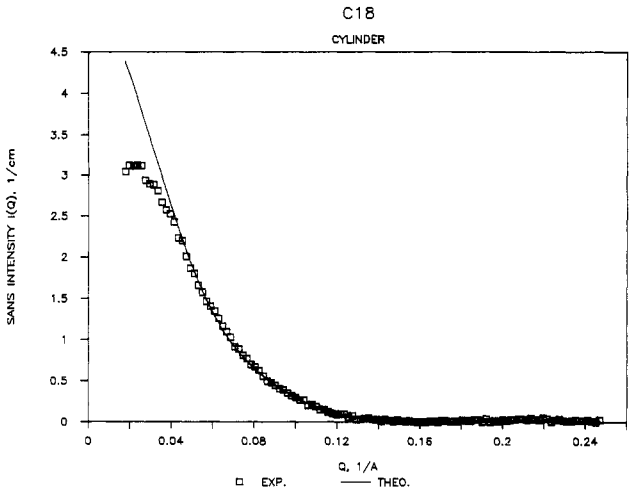

Figure 1. Fit between the experimental data (squares) and the cylindrical SANS cross section (solid line) for the C_{18} copolymer.

$\bar{P}(Q)$ in eq 1 is the normalized orientational-averaged intraparticle structure factor. For a cylindrical micelle, $\bar{P}(Q)$ can be written as[13]

$$\bar{P}(Q) = \int_0^1 \left[\frac{\sin(Q\mu(L/2))}{Q\mu(L/2)}\right]^2 \left[\frac{2J_0(QR(1-\mu^2)^{1/2}}{QR(1-\mu^2)^{1/2}}\right]^2 d\mu \quad (6)$$

where μ is the direction cosine between Q and L and $J_0(x)$ is the zeroth-order Bessel function. For an ellipsoidal micelle, the formula is[14]

$$\bar{P}(Q) = \int_0^1 \left\{\frac{3j_1(Q[a^2\mu^2 + b^2(1-\mu^2)^{1/2}]^{1/2})}{Q[a^2\mu^2 + b^2(1-\mu^2)^{1/2}]^{1/2}}\right\}^2 d\mu \quad (7)$$

where $j_i(x)$ is the first-order spherical Bessel function.

Results and Discussion

For Q greater than 0.04 Å^{-1}, eq 1 is a good approximation for the intensity distribution function $I(Q)$ and is used for the analysis in this study. In our model, the four input parameters are PN, N_{D_2O}, R, and L for the cylindrical model and PN, N_{D_2O}, a, and b for the ellipsoidal model. Because R and b can be calculated from eq 5, the theory thus consists only three parameters, PN, N_{D_2O}, and L (or a).

The fitting of the experimental data to eq 6 and 7 is not sensitive to the variations of N_{D_2O}. In other words, the change of the value of N_{D_2O} does not affect significantly the values of PN and L (or a). For practical purposes, N_{D_2O} can thus be regarded as a fixed number. We have chosen N_{D_2O} to be 10 for the C_{12}–C_{18} data and 15 for the C_8 and C_{10} data. The criterion was such that the numbers are consistent with the values calculated from our previous measurements for the C_{18} copolymer[1,2] and that they produce the best fit between experimental data and theory. At a fixed value of N_{D_2O}, one may notice that the remaining two parameters, PN and L (or a), are functionally related to neutron intensity distribution in a very different way: PN is proportional to the overall amplitude of the intensity distribution (eq 1 and 2), while L (or a) dictates the shape of the intensity distribution through eq 6 and 7. These two parameters are further related to each other by a constraint of the volume conservation (eq 3 and 4). The data fitting is thus made by varying a single parameter for the entire curve, including its absolute intensity and the curve shape. The fit is thus unique. The parameters

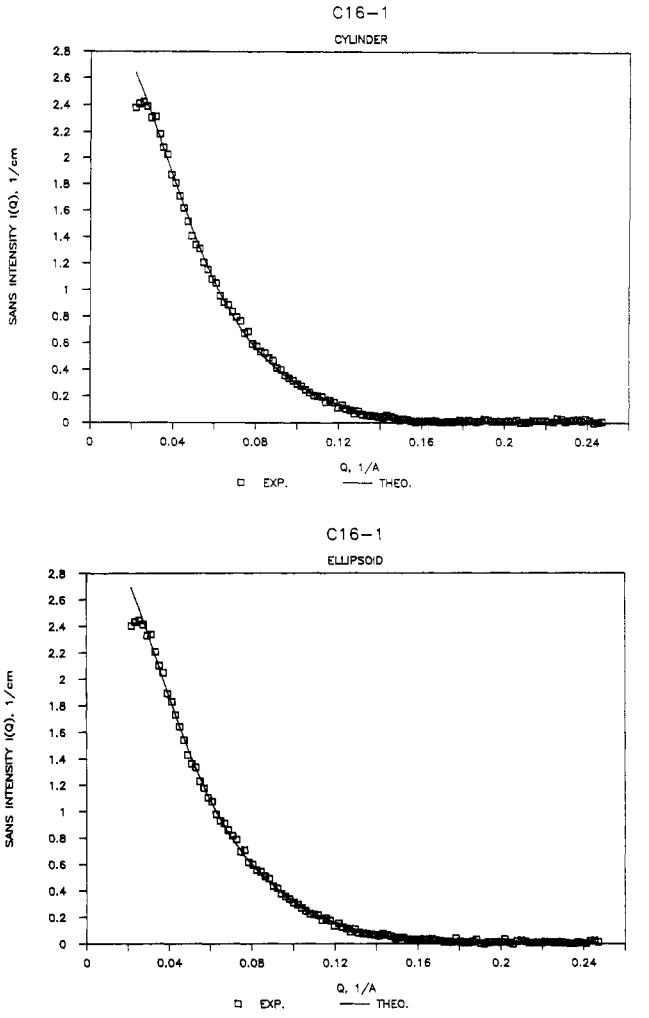

Figure 2. Fit between the experimental data (squares) and (a, top) the cylindrical SANS cross section (solid line) and (b, bottom) the ellipsoidal cross section (solid line) for the C_{16} copolymer.

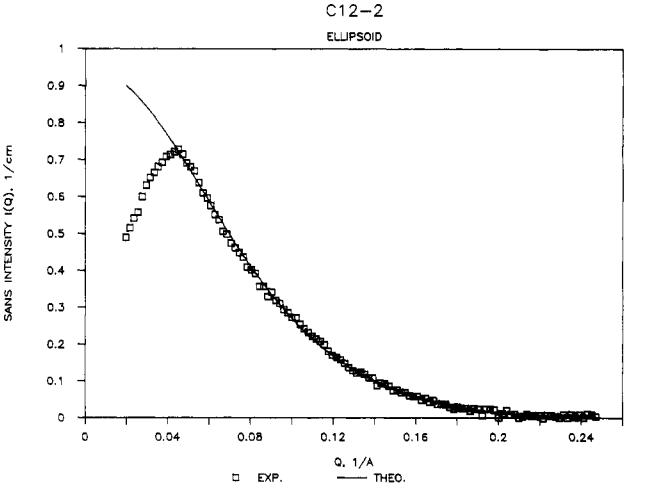

Figure 3. Fit between the experimental data (squares) and the ellipsoidal SANS cross section (solid line) for the C_{12}-2 copolymer.

resulting from the analysis are tabulated in Table III. Examples of experimental data and theoretical fits are shown in Figures 1–5. Notice that the neutron intensity, or the S/N of the data, becomes progressively poorer as the side-chain length decreases, which is a further evidence that the mass of the aggregates has become smaller.

The most accurately estimated parameter in Table III is PN which is the average total number of repeating units per aggregate. The uncertainty of this parameter is es-

Table III
Conformational Parameters from SANS Measurements of Comb-Shaped Copolymers, Poly[1-alkene-*co*-(maleic anhydride)], in the Ionized State in Water

sample ID 1-alkenes	shape[a]	I_0[d]	R[b] or b	PN[e]	L[c] or a	P	N	N_{D_2O}[f]	N_p[g]	ζ[h]
C_{18}	cyl	5.234	24	214	109	21.6	9.9	10	8	28
C_{16}-1	cyl	3.398	22	156	94	18.6	8.4	10	12	16
	ell	3.203	22	147	66	26.1	5.6	10	12	16
C_{16}-2	cyl	3.471	22	160	96	19.0	8.4	10	12	16
	ell	3.366	22	155	70	27.5	5.6	10	12	16
C_{16}-3	cyl	3.862	22	178	107	21.1	8.4	10	12	16
	ell	3.795	22	174	79	31.0	5.6	10	12	16
C_{14}	ell	1.655	19	87	47	18.6	4.6	10	24	13
C_{12}-1	ell	0.940	17	57	38	15.2	3.8	10	37	11
C_{12}-2	ell	0.950	17	58	39	15.4	3.8	10	37	11
C_{12}-3	ell	1.144	17	70	47	18.5	3.8	10	37	11
C_{10}	ell	0.396	14	29	31	12.3	2.3	15	87	7
C_8-1	ell	0.206	12	18	27	10.7	1.7	15	159	5
C_8-2	ell	0.199	12	18	26	10.3	1.7	15	159	5
C_8-3	ell	0.192	12	17	25	9.9	1.7	15	159	5

[a] Cyl, cylinder; ell, ellipsoid. [b] R: the cross-sectional radius of the cylindical micelle (Å). [c] L: the length of the cylindrical micelle (Å). [d] I_0: scattering cross section at $Q = 0$ (cm^{-1}). [e] PN: degree of polymerization times aggregation number. [f] N_{D_2O}: hydration number of a repeating unit of the polymer. [g] N_P: number of micelles per cm^3 ($10^{16}/cm^3$). [h] ζ: dimensionless linear charge density parameter ($\approx 7.15 \times 2P(N/L)$ (or a)).

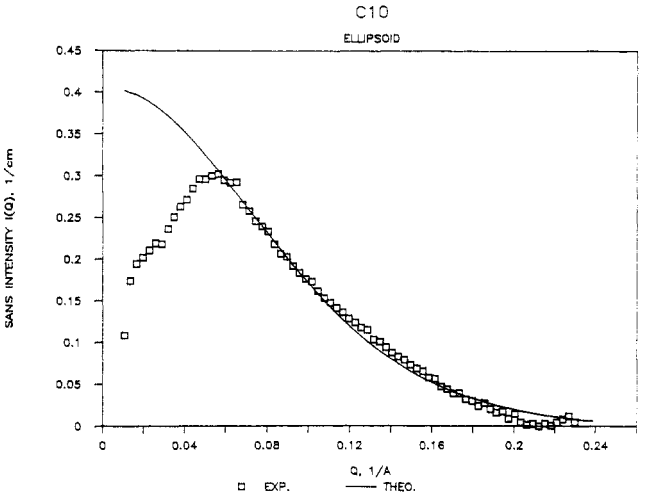

Figure 4. Fit between the experimental data (squares) and the ellipsoidal SANS cross section (solid line) for the C_{10} copolymer.

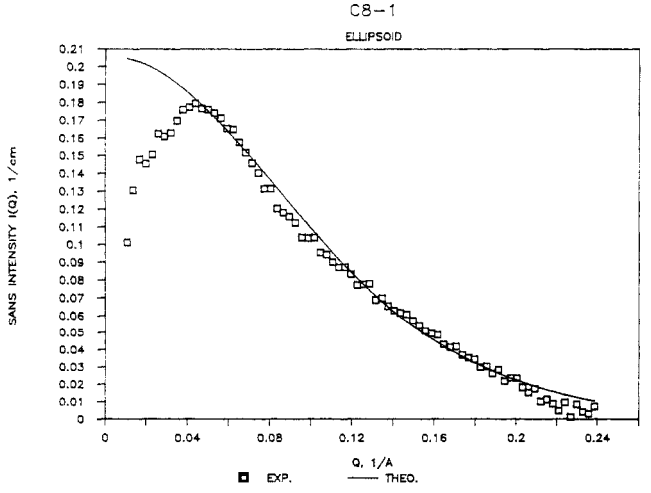

Figure 5. Fit between the experimental data (squares) and the ellipsoidal SANS cross section (solid line) for the C_8-1 copolymer.

timated to be 10%. The number of repeating units per aggregate decreases rapidly from 214 for the C_{18} copolymer to about 18 for the C_8 copolymer, which corresponds to molecular mass of 80 000 and 4500 per aggregate, respectively. In other words, the micelles gradually change from

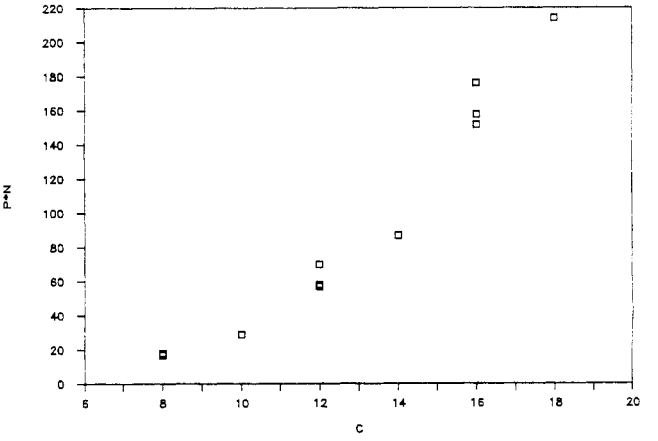

Figure 6. Number of repeating units per aggregate as a function of the number of carbon atoms in the 1-alkenes.

an intermolecular association for the C_{18} copolymer to an intramolecular association for the C_8 copolymer. The transition occurs at the C_{10} copolymer with 30 repeating units per micelle. The plot of the average number of repeating units per micelle versus the number of carbon atoms in the 1-alkenes is shown in Figure 6.

The length of the cylinder, L, or the major axis of the ellipsoid, a, is also listed in Table III. The accuracy of these parameters is limited by the polydispersity of the copolymers and estimated to be 10%. At this moment, there is no convenient thermodynamic theory that would allow us to take the polydispersity into account in calculating the $S(Q)$ factor in eq 1 for this type of amphiphilic copolymer. Our simple fitting procedures have shown that the average size of the aggregates decreases progressively with decreasing side-chain length (Table III). In our earlier work with the C_{18} copolymer, which has the narrowest MW polydispersity, we have attempted to deduce the weight-average molecular weight from the length of the cylinder by dividing L by 5.06 Å, the length of a repeating unit in the backbone direction; the result was in good agreement with the GPC data.[2] However, in this study, the calculations of P have only produced a qualitative correlation. The effect of molecular weight on aggregation is not observed, possibly due to the polydispersity in the copolymers. After allowing for the estimated error limit, the value of P falls somewhere between M_w and M_n as deter-

mined by the GPC. In other words, the current analysis is not sufficiently sensitive to differentiate aggregates of different molecular weight averages given the broad polydispersity of these samples. In Table III, we also list the average aggregation number N, the number of polymer molecules per aggregate obtained from PN and P. The value of N is far less accurately determined than the product PN, because the former is dependent on the estimation of the P value while the latter is determined from the absolute neutron intensity without ambiguity. The model-independent (cylinder versus ellipsoid) nature of the PN values is further demonstrated by the C_{16} copolymer in Table III. However, it is important to note the qualitative trends in N and draw conclusions from the correlation between the aggregation behavior and the amphiphilic characteristics of this class of copolymers.

Our results of the conformational transition of the copolymer aggregations occurring at the C_{10} copolymer are consistent with earlier work by Strauss and co-workers[4-8] for alkyl vinyl ether–maleic anhydride copolymers. They have concluded that when the hydrocarbon side-chain length is less than eight carbon atoms, which is equivalent to our C_{10} copolymer, the conformation is different from that of higher alkyl side chains, $n > 8$, given the same solution conditions. Although, due to the differences in molecular structures and pH conditions, our present study cannot be directly compared with the data of Strauss and co-workers, we believe that the common observation of conformational transition at $n = 8$ is significant. As mentioned in the Introduction, on the basis of the photochemical measurements at neutral pH, Chu and Thomas[9] have concluded that one molecule of the C_{18} copolymer forms one intramolecular micelle. This is quite a different conclusion from ours based on the absolute neutron intensity measurement at $Q = 0$ at alkaline pH. In view of the facts that much experimental data by viscometry[4] and spectroscopy[15] have suggested that the conformation and aggregation of this class of polyelectrolytes are strongly influenced by the solution pH (pH 8 in Chu and Thomas' work[9] and pH 11 in our study), it is not possible to draw direct comparisons between these two systems because of the difference in pH.

The formation of micelles by amphiphiles is determined by the balance between the hydrophobic effect of the hydrocarbon side chains and the interactions between the hydrophilic head groups.[12] With decreasing side-chain lengths, the free energy due to the head-group repulsions becomes more predominant compared to the hydrophobic free energy. As a result, the size and the mass of the aggregates decrease and the micelle changes from intermolecular to intramolecular associations. Our SANS result is also consistent with SANS results on monomeric surfactant systems. It is well-known that the average aggregation number $\bar{N}$, the number of surfactant molecules per micelle, is strongly dependent on the hydrocarbon chain length. For example, $\bar{N}$ is 53 for sodium dodecyl sulfate and 16 for sodium octanoate.[16] Light scattering work by Swarbrick and Daruwala[17] on *N*-alkylbetaines, an alkyl-substituted *N,N,N*-trimethylglycine, in water at low pH has also shown that the weight-average aggregation number decreases from 120 to 20 as the number of carbon atoms in the alkyl chain decreases from 16 to 8. Our results are comparable to these numbers. Due to the more pronounced repulsive energy between the head groups for shorter side-chain amphiphiles, the size and the aggregation number of the micelles, formed by either monomeric or polymeric amphiphiles, must become smaller to accommodate the intricate balance between the hydrophobic effect and the ionic repulsive energies.

There is another physical consequence of the precipitous decrease of PN as the side-chain carbon number decreases. Since the number of micelles per unit volume N_p/cm^3 is $N_p = C_m/PN$, we can compute N_p as a function of the chain length. The results of the number density of micelles as a function of the side-chain length are tabulated in Table III. We can then estimate the center-to-center distance between micelles according to $d \sim N_p^{-(1/3)}$. The results show that d decreases steadily from 232 Å down to 86 Å as the chain length changes from 16 to 6 carbons. Furthermore, according to Manning's counterion condensation theory,[18] the fractional surface charge of the cylindrical micelles is given by the inverse of the linear charge parameter ξ. In our case,

$$\xi = 7.15(2PN/L) \tag{8}$$

The parameter can be estimated from the values given in Table III. We obtain $\xi = 28$ for the C_{18} copolymer and 5 for the C_8 copolymer as listed in Table III. In other words, the effective fractional charge becomes bigger for lower 1-alkene copolymers. The combination of these two effects, (1) a decrease in the intermicellar spacing and (2) an increase in the effective fractional charge, gives rise to more pronounced interactions peaks for shorter side-chain copolymers as seen in Figures 1–5.

Summary

The small-angle neutron scattering technique is uniquely suited to determine the structures of amphiphilic aggregates in water. In this study, we have investigated the aggregation properties of a class of comb-shaped alternating copolymers, poly[1-alkene-*co*-(maleic anhydride)] in D_2O. The copolymer molecules consist of hydrophobic hydrocarbon side chains on one side and hydrophilic carboxylate groups on the other side of the backbone. The analysis of the absolute neutron intensity at zero angle has shown that the mass of aggregates is strongly dependent on the side-chain length and that the nature of aggregation changes from intermolecular associations for higher alkene copolymers to intramolecular associations for the sid chains with eight carbon atoms or less. This is consisten with the observations by Strauss and co-workers on alkyl vinyl ether type copolymers that the conformational transition occurs at $n = 8$. Analysis of the large Q data has also shown that the aggregates formed by copolymers with long hydrocarbon side chains are cylindrical, while those formed by lower alkene copolymers are ellipsoidal. The deduction of other physical parameters such as the aggregation number N and the degree of polymerization P is complicated by the broad molecular weight polydispersity of these copolymers and only qualitative inference can be made from these results. We believe that this class of highly charged copolymers can serve as a good model for further quantitative understanding of the aggregation behavior of polymeric amphiphiles in water. It would be especially interesting if monodispersed copolymers are made available through synthesis or fractionation.

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Registry No. (C_{18})(maleic anhydride) (alternating copolymer, lithium salt), 113109-85-6; (C_{16})(maleic anhydride) (alternating copolymer, lithium salt), 115678-69-8; (C_{14})(maleic anhydride) (alternating copolymer, lithium salt), 115678-71-2; (C_{12})(maleic anhydride) (alternating copolymer, lithium salt), 115678-73-4; (C_{10})(maleic anhydride) (alternating copolymer, lithium salt), 115792-89-7; (C_8)(maleic anhydride) (alternating copolymer, lithium salt), 115678-74-5.

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A Statistical Theory of Weakly Charged Polyelectrolytes: Fluctuations, Equation of State, and Microphase Separation

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ABSTRACT: A microscopic statistical theory of polyelectrolyte solutions (PES) with polyions of low linear charge density is developed in the random phase approximation (RPA). Correlation functions of a multicomponent PES and the fluctuational electrostatic contribution to the free energy of the system are calculated. Owing to the high-polymer nature of the system these expressions differ essentially from those of Debye–Huckel (DH) type. It is shown that under certain conditions a microphase separation into oppositely charged domains takes place in PES. The phase diagram is given. The expressions for the screened Coulomb potential of a test charge are obtained. In some cases the potential oscillates. The RPA is shown to be valid for intermediate monomer or salt concentrations and is violated at very low or very high concentrations.

I. Introduction

Great attention has been paid recently to the theoretical study of weakly charged polyelectrolyte solutions (PES).[1-6] The first theoretical consideration of a single weakly charged macromolecule in a solution was to our knowledge performed by de Gennes et al.[1] Then Pfeuty[2] took into account excluded-volume effects. The behavior of a single weakly charged macromolecule in a poor solvent, where counterion condensation of the avalanche type occurs, was studied by Khokhlov;[4] Khokhlov and Khachaturian[5] considered different fluctuation regimes of a weakly charged PES and constructed the diagram of states with variables: polymer concentration in the solution and concentration of the low molecular weight salt. In their paper the problem of the Debye–Huckel (DH) screening by nonlocal objects was also considered. However, in ref 5 the effects of the solvent quality on the properties of PES were discussed only briefly. In this paper we shall develop the statistical theory of the DH type for a sufficiently concentrated weakly charged PES. This will enable us not only to consider the properties of PES in Θ and in poor solvents and to construct a diagram of states with variables (low molecular weight salt concentration and solvent quality) but also to calculate correlation functions of PES and moreover to obtain the contribution of the electrostatic interaction to the free energy of PES. Our investigation reveals some interesting effects, which seem to be common for all PES. These include an oscillating regime of the screening of a test charge, the possibility of microphase separation of the PES into oppositely charged domains in a poor solvent, and the possibility of regions within the diagram of states, where electrostatic and van der Waals contributions to the free energy are of the same order of magnitude. The last result is used in ref 7 for the development of the statistical theory of polyelectrolyte complexes, consisting of oppositely charged polyions. The expression for the electrostatic contribution to the free energy can be also important in considering a collapse of charged polymer networks, properties of charged macromolecules with extermal constraints (in pores, tubes, etc.), and in other cases, where the free energy of charged macromolecules should be minimized.

In section II we discuss some general physical properties of weakly charged PES, which are essential for the further treatment and which show the necessity of understanding the fluctuational behavior of such systems. In section III the random phase approximation (RPA) for PES is developed, and the expressions for correlation functions, the screening potential of the test charge and electrostatic contribution to the free energy, are obtained. In section IV we consider properties of polymer systems, when all the electric charges of PES are turned off. This system is called the basic polymer system. Analysis of the basic polymer system will enable us to introduce the notion of

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