Conformation and dynamics of colloidal aggregates in detergent and copolymer systems*

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The conformation and dynamics of colloidal aggregates, from small detergent molecules to copolymers in solution may be investigated by combining laser light scattering and (synchrotron) small angle X-ray scattering with measurements of rheological properties of the supramolecules. The inter- and intramolecular interactions may be complex in nature involving, in addition to hydrophobic–hydrophilic interactions, solvent–non-solvent considerations and metal coordination type complexation. Nevertheless, scattering techniques can provide useful information on the size, size distribution and conformation of the aggregates. Studies of microstructures of the colloidal aggregates at dilute concentrations become feasible with intense synchrotron X-rays. Recent investigations of detergent molecules, such as cobalt monooleate in apolar organic solvents, of polymer colloids, such as polystyrene/polyisoprene AB block copolymers, and block copoly(oxyethylene/oxypropylene/oxyethylene) in organic solvents are presented.

(Keywords: conformation; dynamics; copolymers)

INTRODUCTION

Detergent molecules have hydrophobic and hydrophilic ends, and form micelles in solution. In an aqueous medium, the hydrophilic ends face towards water while the hydrophobic ends aggregate together to form an inner core.

Micelles can further aggregate and change shape to other forms, such as cylinders, which are often referred to as secondary micelles. In a non-aqueous medium, inverted micelles can form, with the hydrophilic ends forming the inner core and hydrophobic ends solubilizing in the non-aqueous medium. The supramolecular formation of micelles is mainly due to the chemical nature of the detergent molecules having hydrophobic and hydrophilic ends and their interactions with the solvent. Stereo packing also plays a role. However, it is important to realize that supramolecular formation can be induced by other forces in addition to hydrophobic/hydrophilic interactions. One example is the supramolecular formation of cobalt monooleate in apolar solvents. There, the aggregation of monooleate can be attributed to the OH bridging between cobalt atoms. The –Co–O(H)–Co– coordination can be quite strong and is unidirectional, resulting in the formation of long cobalt soap chains[1–3].

Another concept of micelle formation is to use a block copolymer, either an AB diblock or an ABA triblock copolymer. If a block copolymer (e.g. an AB block copolymer) is dissolved in a solvent which is a good solvent for one block and a poor solvent for the other block, aggregates resembling micelle formation from small detergent molecules can be observed under certain conditions. Again, the common shape of mono- or polymolecular micelles is spherical, with the insoluble part forming the micelle core and the soluble part forming the outer shell[4]. The structure of these micelles may be varied by changing the molar mass of A and B[5,6]. Furthermore, the nature of A and B may be altered by chemical modification, leading to the formation of a rich variety of supramolecular systems. Unfortunately, at the present time, only a limited number of techniques is available for determining the structure and dynamics of such supramolecules, with the commonly accepted ones being small angle neutron scattering (SANS), small angle X-ray scattering (SAXS) and laser light scattering (LLS).

The analogy between block copolymers and ionic surfactants can be carried a step further. If we take a block copolymer (AB or ABA) and mix it with two solvents (S1 and S2) under the conditions that (i) S1 and S2 are immiscible, (ii) S1 is a good solvent for A and a bad solvent for B, and (iii) S2 is a bad solvent for A and a good solvent for B, a microemulsion may be formed. The microemulsion may be droplets of S1 covered by a monomolecular layer of the copolymer dispersed in the continuous S2 phase in the S2 corner of the ternary S1, S2 and copolymer phase diagram, and S2 droplets dispersed in S1 in the S1 corner of the phase diagram. A microemulsion with a copolymer as a dispersing agent could offer several advantages when compared with microemulsions formed by small detergent molecules.

In this paper, a review of earlier studies related to the cobalt monooleate in apolar solvents and the structure of block copolymers in organic solvents, is presented. For cobalt monooleate in heptane (or benzene), the coordination complex formation is mainly responsible

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for the supramolecular structure. In block copolymers, e.g. a block copolymer of polystyrene (PS) and polyisoprene (PIP), the formation of vesicles, in addition to micelle formation, can be achieved due to the polymer chain length restriction and polymer–solvent interactions. Finally, new results on the formation of micelles and microemulsions by poly(oxyethylene/oxypropylene/oxyethylene) block copolymers are discussed, demonstrating how such supramolecules can be investigated experimentally.

METHODS

The main techniques responsible for determining the structure and dynamics of supramolecular systems are LLS, SAXS and viscometric measurements. In LLS (or SAXS) of copolymers, the Rayleigh ratio at zero scattering angle $R_{C,\theta\to 0}$ can be expressed as:

$$R_{C,\theta\to 0} = H^*\Sigma_i \nu_i^2 C_i M_i = H^*\nu^2 C M_{app} \qquad (1)$$

where ν is the refractive index increment (or electron density increment), H^* is an optical constant, C is the concentration and M_i is the molecular weight of component i. The apparent molecular weight M_{app} has the form:

$$M_{app} = \nu^{-2}\Sigma_i \nu_i^2 C_i M_i / C \qquad (2)$$

For a block copolymer AB, $C_A/C = W_A$, $C_B/C = W_B$ with $W_A + W_B = 1$ and W_i is the weight fraction of block i

$$M_{app} \simeq \nu^{-2}(W_A M_w^A \nu_A^2 + W_B M_w^B \nu_B^2) \qquad (3)$$

which yields $M_{app} = M_w^A/W_A$ if $\nu_B = 0$. Similarly, for the radius of gyration, $\langle R_{app}^2\rangle_z = \langle R_A^2\rangle_z$ with $\nu_B = 0$ and subscript z denoting the z-average.

For a micellar system with a closed association mechanism:

$$nM \rightleftarrows Mn \qquad (4)$$

the Debye model yields:

$$\frac{H(C-CMC)}{R-R_{CMC}} = \frac{1}{(M_n)_W} + 2A_2(C-CMC) + \cdots \qquad (5)$$

where H is an optical constant and is equal to $H^*\nu^2$, M_n is the micelle molecular weight containing n-mer, CMC is the critical micelle concentration, R_{CMC} is the Rayleigh ratio at CMC. For an open association model, the molecules associate without a threshold CMC. In a closed association mechanism, micelles have narrow size distributions, while in an open association mechanism, the supramolecules (or aggregates) have broad size distributions.

In SAXS, the scattered intensity due to supramolecules can be expressed as:

$$I(q) \propto S(q)P(q) \simeq P(q) \qquad (6)$$

where, for the particles under consideration, $S(q) \simeq 1$ for $q > 0.2\,\text{nm}^{-1}$. The form factors $P(q)$ for a hard sphere (HS) of radius R and for a hollow hard sphere (HHS) with an outer radius of R_0 and an inner radius of R_i and a shell thickness of $d = R_0 - R_i$ are given by:

$$P_{HHS}(q, R_0, R_i) \sim \left\{R_0^3 \frac{3[\sin(qR_0) - qR_0\cos(qR_0)]}{(qR_0)^3} - R_i^3 \frac{3[\sin(qR_i) - qR_i\cos(qR_i)]}{(qR_i)^3}\right\}^2 \qquad (7)$$

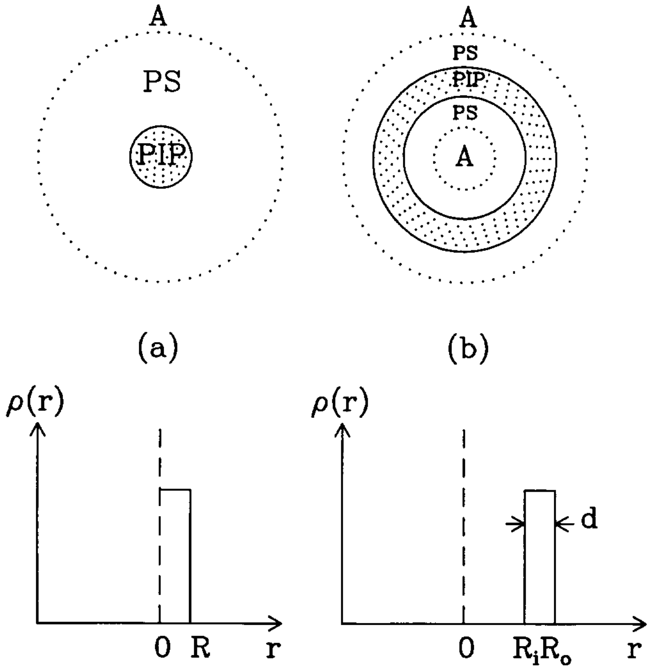


Figure 1 Schematic representation of (a) a micelle and (b) a vesicle. Straight lines denote sharp boundaries and dashed lines denote diffuse boundaries. PS, polystyrene; PIP, polyisoprene; A, aniline. Aniline is a solvent for PS and is isorefractive, and has isoelectron density with PS

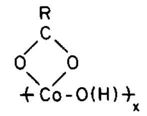
$$P_{HS}(q, R) \sim \left\{R^3 \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3}\right\}^2 \qquad (8)$$

and are shown schematically in *Figure 1*.

From dynamic light scattering, one can determine the hydrodynamic radius (R_h) from measurements of the translational diffusion coefficient by means of the Stokes–Einstein relation at dilute supramolecular concentrations. This can be achieved since if $\nu_B(=\nu_{PS}) = 0$, and if block PIP is insoluble in the solvent (aniline), then according to *Figure 1a*, measurements of R_h yield the hydrodynamic radius of the supramolecular micelle, including the PS chains, even though the PS chains are invisible. On the other hand, measurements of the apparent molecular weight and the apparent radius of gyration yield the molecular weight of the aggregated A blocks, M_w^A and the radius of gyration of the inner core. If we know the weight fractions of A/B blocks, we can determine the aggregation number of the copolymer micelle from the molecular weight of the copolymer. From the amount of A (PIP) blocks and its size (R_g of inner core), we can then model how the inner (PIP) core is assembled. From the inner core size and the overall size (from R_h), we can determine the (PS) shell thickness. Together with the amount of PS from the original PS/PIP ratio, the copolymer molecular weight and the aggregation number, the chain conformation of the outer (PS) shell can be estimated.

COLLOIDAL BEHAVIOUR OF COBALT MONOOLEATE

Cobalt monooleate ($Co(OH)(C_{17}H_{33}COO)$) has the ability to form OH bridges between cobalt atoms in non-polar solvents, such as heptane and benzene, with Co–O(H)–Co coordination which provides the main backbone of the aggregated complex. The hydrocarbon chains, with $R \equiv C_{17}H_{33}$ in the present case, interact with the apolar solvent making the aggregated complex stable and yielding a chain:



The complex formation of cobalt monooleate can be observed by its non-Newtonian flow behaviour. In a 0.7% soap solution in benzene, three distinct flow regions exist. At low shear rates (e.g. 10^{-2}–$10^{-3}\,s^{-1}$) a Newtonian flow behaviour of very high viscosity is observed. In the medium shear rate region ($\gamma = 1$–$10^3\,s^{-1}$), a finite increment of the shear stress results in an increase of the shear rate by several orders of magnitude, known as the shear thinning effect. When $\gamma > 10^3\,s^{-1}$, the flow properties are similar to that of the pure solvent. The low shear rate/high viscosity behaviour denotes that the solution is likely at semidilute concentrations. Aggregation of cobalt monooleate to form fairly long (up to micrometre lengths) and stiff chains, drastically lowers the overlap concentration. Thus, only a small amount of cobalt monooleate can produce a large increase in the solution viscosity at low shear rates because entanglement of aggregated chains produces the high solution viscosity. At higher shear rates the supramolecular chains are being aligned, the aggregation can be broken up, and the amount of entanglement is reduced, resulting in a shear thinning effect. At high shear rates the aggregated molecules have mostly been broken up and the soap solution acts like a binary liquid mixture. Addition of chemical compounds that contain groups having a strong coordination tendency with cobalt atoms, could break down the supramolecular structure. Thus, pyridine and acetylacetone could break up the supramolecular formation, while water and i-propyl alcohol could not.

From light scattering and transient electric birefringence studies[1], the cobalt monooleate in heptane yields $M_w = 3.41 \times 10^6\,g\,mol^{-1}$, $\langle R_g^2 \rangle_z^{1/2} = 320\,nm$, $D_r = 32\,s^{-1}$, $L_c/2l = 11$, and $l = 108\,nm$, where D_r, L_c and l are the rotational diffusion coefficient, the contour length and the persistence length of a worm-like chain, respectively.

The worm-like chain behaviour can be tested at semidilute concentrations with the overlap concentration C^* given by the relation[7]:

$$C^* = 2^{3/2} M/(N_A L_e) \qquad (9)$$

where $L_e = (lL_c)^{1/2}$ and N_A is Avogadro's number. For cobalt monooleate soap in benzene at 20°C, $C^* \sim 0.19\,mg\,ml^{-1}$, in reasonable agreement with $C^* \sim 0.22\,mg\,ml^{-1}$ from the viscosity experiments[2].

SOLUTION BEHAVIOUR OF BLOCK COPOLYMERS (PS–PIP) IN A SELECTIVE SOLVENT

In a block copolymer consisting of PS and PIP in a solvent aniline (A), which: (i) is a selective solvent for PS; (ii) is isorefractive; and (iii) has isoelectron density with PS, condition (i) promotes aggregation, while conditions (ii) and (iii) render the interpretation of LLS and SAXS straightforward. The experimental results, by means of equations (4) and (5) for static light scattering and the use of the Stokes–Einstein relation with dynamic light scattering studies, are summarized in *Table 1* and *Figure 2* (b, c with PIP forming the inner core). Values of R_g (core) for samples b and c were determined by SAXS.

For samples b and c, the polymers form dense aggregates which can be represented by a hard sphere model as revealed by a combination of light scattering and viscosity studies and shown in *Figure 1a*. The polymer micelles consist of a PIP core, which is insoluble in aniline and has a density close to that of the liquid PIP, and a PS shell with a loose structure. However, for sample a, the PIP core size disagrees with the liquid core computation and the shell thickness is unreasonable if we base the supramolecular structure on the schematic representation of *Figure 1a*. By using synchrotron SAXS and by taking account of the shell structure of *Figure 1b* with $R_g = 60\,nm$, we can confirm the vesicle formation of sample a with an inner and outer vesicle radius of 48 and 69 nm, respectively. The 21 nm shell thickness corresponds to a shell volume of $(4\pi/3)[(69)^3 - (48)^3] \sim 9 \times 10^{-6}\,cm^3$ for a PS/PIP vesicle which contains 650 blocks of PIP, each with $M_w \sim 19\,000\,g\,mol^{-1}$. Thus, based on the above very approximate estimate, we may suggest that the PIP shell is not packed as tightly as a liquid PIP core.

Table 1 Experimental results from static and dynamic light scattering[5] and SAXS[6]

	Sample a	Sample b	Sample c
M_w(PS) (kg mol^{-1})	28	41	61
M_w(PIP) (kg mol^{-1})	19	19	19
$(M_n)_w$ (10^6 g mol^{-1})	30	6.2	6.1
n	650	103	75
R_g(core) (nm)	60	9	10
R_1(core) (nm)	17	10	9
R_h(total) (nm)	67	41	47
$R_h - R_g$ (nm)	7	32	37

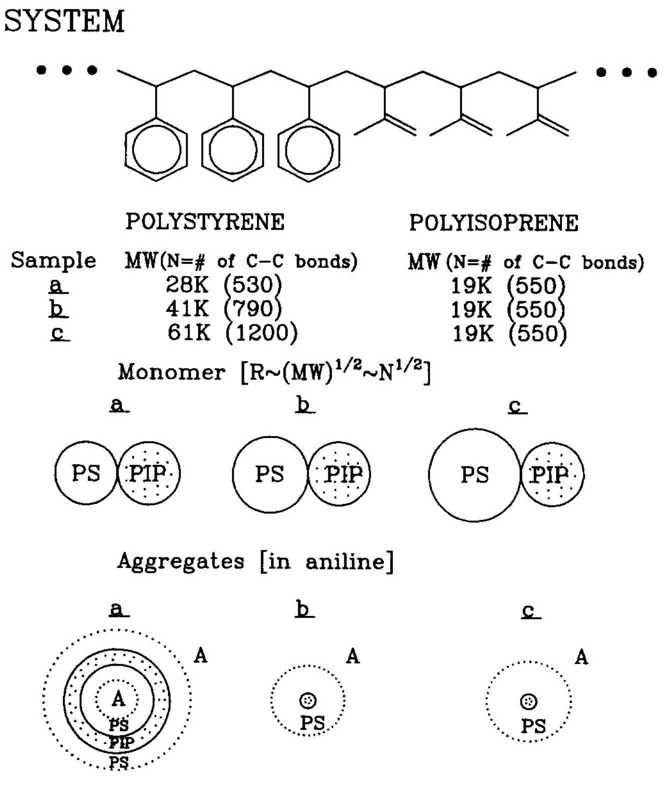


Figure 2 Block copolymers PS–PIP

MICELLE FORMATION OF BLOCK COPOLY(OXYETHYLENE/OXYPROPYLENE/ OXYETHYLENE)

Pluronic L64 (block copoly(oxyethylene/oxypropylene/ oxyethylene), PEO/PPO/PEO), with an EO/PO ratio of 0.8/1.0 by weight and a molar mass of the copolymer of 3×10^3 g mol^{-1}, form micelles with a PPO core in water[8]. The solution behaviour of PEO/PPO/PEO ABA block copolymers in water has been studied extensively[8–20]. Water can interact with the end PEO blocks, therefore the micelle consists of a PEO shell and a PPO core. The micelle size (and possibly shape) could be related to the temperature, the pressure, the copolymer concentration and its composition.

By adding a second solvent (*o*-xylene), which is insoluble in water and in PEO but is a selective solvent for PPO, *o*-xylene could be solubilized in the PPO core of the micelle[9]. The addition of *o*-xylene increases the molar mass and the hyrodynamic radius of the micelles. Conversely, Pluronic L64 could be dissolved in *o*-xylene.

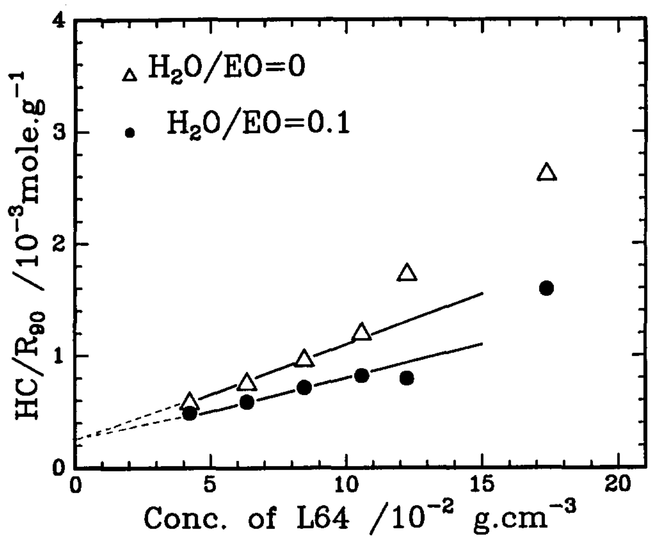


Figure 3 Concentration dependence of HC/R_{90} with and without the presence of water at 26.2°C. R_{90} denotes the excess Rayleigh ratio at 90° scattering angle. Measurements performed by G.-W. Wu

Due to the relative chain length of EO to PO, Pluronic L64 does not form polymolecular micelles in the absence of water nor in the presence of a small amount of water (molar ratio water/EO$<$0.15). Micelles consisting of a PPO shell and a PEO+H_2O core are formed when the molar ratio (R_m) of water to EO in the micelle is greater than 0.2. According to equation (5), a plot of $H(C\text{-}CMC)/(R\text{-}R_{CMC}) \simeq HC/R_{90}$ *versus* $C\text{-}CMC \simeq C$, as shown in *Figure 3*, yields the weight averaged micelle molecular weight containing *n*-mer. The approximation is acceptable because the refractive indices of PPO and PEO are quite similar. $M_n \simeq 4 \times 10^3$ g mol$^{-1} \simeq 3 \times 10^3$ g mol^{-1} $\simeq M_1$, i.e. the molecular weight of the (L64) monomer. Therefore, Pluronic L64 in *o*-xylene forms essentially monomolecular micelles in the absence of water or in the presence of a small amount of water (e.g. $R_m(\equiv H_2O/EO) = 0.1$), provided that the *CMC* and R_{CMC} are negligibly small.

A GE QE-300 n.m.r. spectrometer was used to obtain the n.m.r. results shown in *Figure 4* with tetramethyl silicone as an internal reference. At $R_m = 0.0$ and 0.1, the water molecules were preferably bound with EO. At $R_m = 1.31$, both bound and free water could be present. By solubilizing water into the PEO core, the R_h value of the micelle increased with increasing R_m. *Figure 5* shows a size distribution of the microemulsion from dynamic light scattering base on the CONTIN analysis with $R_h \sim 12$ nm. The increase in R_h from the monomolecular micelle to the micelle (or microemulsion) with free H_2O at $R_m = 2.0$ is 7–12 nm, corresponding to a volume increase by a factor of $(12/7)^3 \sim 5$, which would be difficult to accomplish if the micelles remained as monomolecular micelles. Thus, the addition of water to Pluronic L64 in *o*-xylene promotes polymolecular micelle formation and with a central core of PEO and water that contains both bound and free water, as evidenced by n.m.r., a microemulsion is formed. Further study is in progress.

CONCLUDING REMARKS

We have used static and dynamic light scattering, SAXS, viscosity and n.m.r. measurements to investigate the

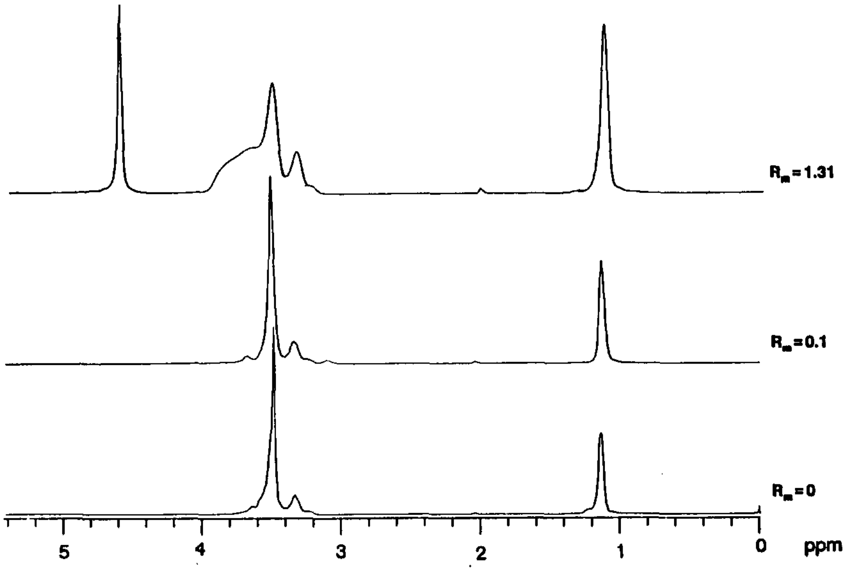


Figure 4 N.m.r. spectra of L64 in *o*-xylene-d10 at different values of the molar ratio, R_m, and room temperature. The concentration of L64 is 0.31 g cm^{-3}. Measurements performed by Z.-D. Zhang

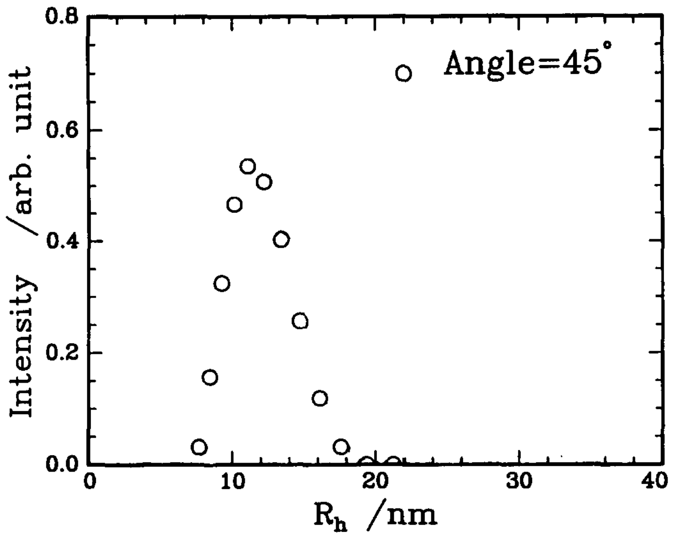


Figure 5 A size distribution curve of micelles by using the CONTIN analysis at $R_m = 2.0$. The concentration of L64 is 0.186 g cm^{-3}. Measurements performed by G.-W. Wu

supramolecular formation by small and polymer molecules. We note that supramolecular formation can be achieved by means other than hydrophobic–hydrophilic or solvent–non-solvent interactions. The example used was cobalt monooleate, which utilized the cobalt co-ordination complex. Copolymer structures which involve supramolecular formation are difficult to study. However, on occasion, one may be able to take advantage of refractive index or electron density matching and thereby simplify the mathematical forms, as exemplified by equations (2) and (3). By this approach, the presence of vesicle formation instead of the more common micellar form for the PS–PIP block copolymer in aniline can be demonstrated by changing the length ratio of PS to PIP. Finally, we show how ABA block copolymers (PEO/PPO/PEO) can be made to form micelles by inducing aggregation of the inner (PEO) core with a selective solvent (H_2O) for the inner core. Upon further increase in concentration of the selective solvent for the inner core, a larger centre, including free H_2O, can be formed for the PEO/PPO/PEO micelles in *o*-xylene. Thus, microemulsions can be formulated based on the discussions in the Introduction. The main purpose of the previous section is to show that block copolymers can be utilized to form rich colloidal systems and their structures can be investigated by using modern scattering, viscometric and n.m.r. techniques.

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