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Sphere-to-rod transition of triblock copolymer micelles at room temperature

R GANGULY[a], V K ASWAL[b], P A HASSAN[a], I K GOPALAKRISHNAN[a] and J V YAKHMI[c]
[a]Novel Materials and Structural Chemistry Division; [b]Solid State Physics Division;
[c]TP&PED, Bhabha Atomic Research Centre, Mumbai 400 085, India
E-mail: rajibg@magnum.barc.ernet.in

Abstract. A room temperature sphere-to-rod transition of the polyethylene oxide–polypropylene oxide–polyethylene oxide-based triblock copolymer, $(PEO)_{20}(PPO)_{70}(PEO)_{20}$ micelles have been observed in aqueous medium under the influence of ethanol and sodium chloride. Addition of 5–10% ethanol induces a high temperature sphere-to-rod transition of the micelles, which is brought to room temperature upon addition of NaCl. The inference about the change in the shape of the micelles has been drawn from small-angle neutron scattering (SANS) and viscosity studies.

Keywords. Block copolymer; light scattering; small-angle neutron scattering.

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1. Introduction

Self-assembly behaviors of the (PEO)–(PPO)–(PEO)-based triblock copolymers with rich structural polymorphism and numerous applications in the industries, have been the subject of recent studies [1,2]. The self-assembly behaviors in aqueous solutions of these copolymers can be influenced significantly by varying temperature [3,4] and/or by adding water soluble electrolytes [4–7] and solvents [8,9]. Below critical micellar temperature (CMT) and critical micellar concentration (CMC), the copolymer molecules remain as unimers and above them micellar structure consisting of hydrophobic PPO core and hydrated PEO corona is formed [10]. Above CMT, the micellar size increases progressively with increase in temperature before being phase separated at cloud point (CP). Since the maximum size of the spherical block copolymer micelles are limited by an entropically unfavorable stretching of the PPO block, an increase in the size of the micelles to that limiting size, as a function of temperature, leads to a sphere-to-rod transition of them [3,4].

The influence of cosolutes and cosolvents on the micellar behavior of the (PEO)–(PPO)–(PEO) block copolymer aqueous solutions are diverse in nature. Inorganic salts like KCl, NaCl, KF etc. dehydrate the ethylene oxide chains and reduce CMT, CMC, cloud point, whereas salts like KSCN have exactly opposite effects

[4–7]. Presence of salts like KF even facilitates the process of sphere-to-rod transition in the aqueous solutions of these copolymers [4]. Limited number of studies on the effect of addition of cosolvent shows that solvents like ethanol, methanol etc., which are good solvents for both the PPO and the PEO blocks, leads to increase in CMT, CMC and cloud point [8,9].

In this paper, we report a NaCl and ethanol induced room temperature sphere-to-rod transition of the triblock copolymer $(PEO)_{20}(PPO)_{70}(PEO)_{20}$ micelles, leading to formation of room temperature thermoreversible gels. Although the observations of such sphere-to-rod transitions are reported in the triblock copolymer solutions at higher temperatures [3,4], to our knowledge, this is the first observation of such transitions occurring in them at room temperature.

2. Experimental

The block copolymer, $(PEO)_{20}(PPO)_{70}(PEO)_{20}$, was purchased from Aldrich. The copolymer solutions were prepared by weighing out amounts of solvents, copolymer and NaCl (when needed), in to tightly closed glass stoppered vials and keeping them in refrigerator for one week to attain equilibrium. Dynamic light scattering (DLS) measurements of the solutions were performed using a Malvern 4800 Autosizer employing 7132 digital correlator. The light source was argon ion laser operated at 514.5 nm with a maximum output power of 2 W. The average decay rate was obtained from the electric field autocorrelation function, $g^1(\tau)$, using the method of cumulants [11]. For anisotropic micelles where the solutions showed an abrupt increase in the relative viscosity, the length of the micelles were estimated from the translational diffusion coefficient by employing Perrin's formula [12].

SANS measurements were carried out on samples prepared in D_2O at the SANS facility at Dhruva reactor, Trombay. The incident wavelength was 5.2 Å with $\Delta\lambda/\lambda = 15\%$. The magnitude of the scattering vector was varied from 0.02 to 0.2 $Å^{-1}$.

3. Results and discussion

3.1 *Effect of copolymer concentration*

The structure of the block copolymer micelles and the nature of the interaction between them were inferred from SANS measurements carried out at three different polymer concentrations (table 1, figure 1), which are well above CMC of the copolymer [13]. For 1% w/w polymer concentration, no correlation peak is observed which indicates the absence of any intermicellar interaction. The spectra of 10 and 25% w/w polymer concentrations were analysed by taking into consideration the inter-micellar interaction. The observed correlation peaks in these solutions are consistent with the expectations that an increase in number density of micelles leads to a decrease in intermicellar distance, as the position of the correlation peak ($q_{\max}$) can be approximated to the interparticle distance d by the relation $d \approx 2\pi/q_{\max}$.

3.2 *Effect of ethanol*

Unlike water, which is a PEO-block selective solvent, ethanol is known to be a good solvent for both the PEO and PPO blocks, and thus leads to an increase in the CMT and CMC of triblock copolymer aqueous solutions, besides leading to a decrease in aggregation number of the micelles [8,9]. Figure 1 (inset) shows the evolution of the SANS spectra of 1% copolymer solutions at different ethanol concentrations. Analysis of the data clearly shows that the core size and subsequently the aggregation number of the micelles decrease steadily with increase in ethanol concentration.

Table 1. Core radius (R_C), hard sphere radius (R_{HS}) and aggregation numbers calculated from SANS study for different copolymer solutions.

Composition	R_C (nm)	Aggregation number	R_{HS} (nm)
1% Copolymer			
(a) 0% Ethanol	6.2	149	
(b) 20% Ethanol	5.0	78	
(c) 30% Ethanol	4.1	43	
10% Copolymer	6.4	164	8.1
25% Copolymer	5.7	116	8.1

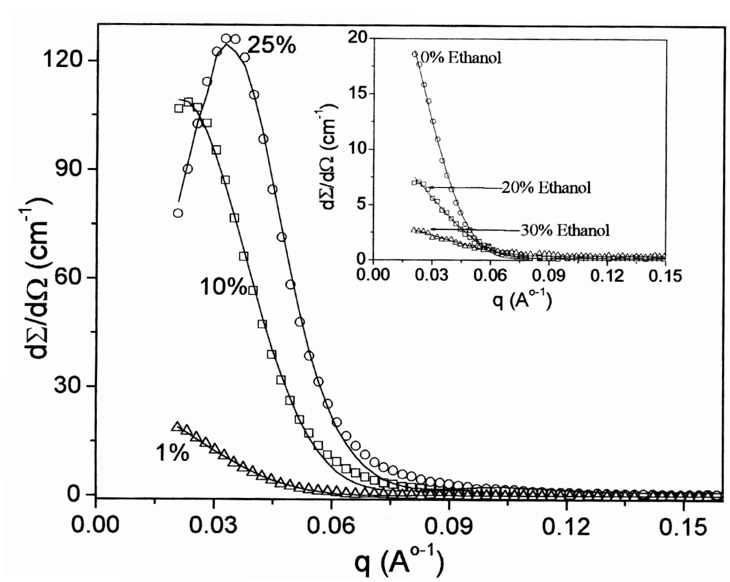

Figure 1. SANS patterns of 1, 10 and 25% aqueous copolymer solutions. The solid lines are fit to the data using a model for interacting hard sphere colloids. Inset shows SANS patterns of 1% aqueous copolymer solutions with different ethanol concentrations.

Table 2. Micellar rod length as a function of NaCl concentration for the 10% aqueous solution with 20% ethyl alcohol content.

NaCl conc. (mol/l)	Rod length (nm)
1	40.8
2	80.4
2.5	115.5
3	156.8
3.4	262.6

Since cloud points of the aqueous copolymer solutions are related to the dehydration of the PEO blocks with increase in temperature, higher solvation of the PEO blocks in the presence of ethanol is reflected in an increase in cloud point (CP) of aqueous copolymer solutions with increase in ethanol concentration [6]. In the present study, the CP of solutions in the copolymer concentration range 1–25% w/w, which show a nearly constant value (≈50°C) in the absence of ethanol, becomes more than 100°C in the copolymer solutions with 20% ethanol. Moreover, presence of 5–10% ethanol induces a sphere-to-rod transitions of the copolymer micelles below the cloud point of the solutions, leading to the formation of thermoreversible gels by the solutions with 15–25% copolymer concentrations. The temperatures at which such gels are formed are henceforth referred in this paper as gelation points. The effects of addition of ethanol and NaCl on the gelation point and the cloud point of the 25% block copolymer aqueous solution is depicted in figure 2. All the solutions shown in the figures show sharp cloud points and gelation points, which were measured in a temperature controlled water bath with ±0.5°C accuracy. The gelation point increases from 60 to 68°C with increase in the alcohol concentration from 5 to 10% and is no longer observed with increase in alcohol concentration further to 15% (figure 2a). This clearly shows that increase in the ethanol concentration destabilizes the process of gelation.

3.3 *Effect of NaCl*

Inorganic salts like NaCl, KCl, KF are in general known to have opposite effects to that of ethanol on the aggregation behavior of the copolymer micelles in water [4–7]. In view of these, we have studied the influence of NaCl on gelation characteristics of the 25% copolymer solutions with or without ethanol. In the absence of ethanol, addition of NaCl only reduces the cloud point of the aqueous solution and fails to induce any gelation. Addition of NaCl in the 25% copolymer solution containing 10% ethanol, however, results in a steady decrease in the gelation point and cloud point of the solution with increase in the NaCl concentration (figure 2b). This facilitated the formation of a room temperature thermoreversible gel at 2.5 M NaCl.

Since a sphere-to-rod transition of the micelles in the copolymer solutions brings about large change in viscosity of the solutions, we attempted to make a system-

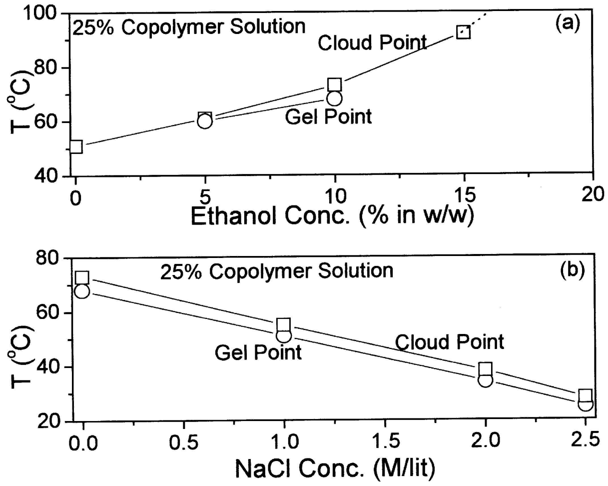

Figure 2. Cloud point and gel point vs. ethanol and NaCl concentration plots for 25% aqueous copolymer solutions.

atic study on the effect of NaCl on the hydrodynamic (DLS) size of the copolymer micelles and on relative viscosity at room temperature. Figure 3 shows the effect of addition of NaCl on the micellar size and viscosity of 10% block copolymer solution containing 20% ethanol. As shown in it, the micellar size increases steadily with increase in the NaCl concentration, and this increase in the micellar size is accompanied by a large increase in viscosity. Since for the present block copolymers it is unrealistic to have spherical micelles with a radius as high as 40 nm (shown in table 2 for 3.4 M NaCl), due to the fact that the maximum extended length of PPO and PEO chains in it is much less than this value, the micelles of that apparent size have to undergo anisotropic growth to have a prolate or oblate ellipsoids. Since changes in viscosity for oblate ellipsoid is much less than that for prolate ellipsoid, the observed large increase in viscosity (shown in figure 3) as a result of an increase in the micellar size suggests that shape of the micelles changes from sphere to prolate ellipsoid. Progressive increase in viscosity with NaCl concentration shown in this figure clearly suggests that the length of the micellar rod increases progressively with increase in the NaCl concentration. This is supported by DLS measurements, which also shows that the micellar rod length (shown in table 2) calculated using Perrin's formula (for prolate ellipsoid), increases with increase in the NaCl concentrations.

Further evidence of growth of micelles with the addition of NaCl is produced by a comparative analysis of the SANS patterns of 10% copolymer solution containing 20% ethanol, before and after addition of 3 M NaCl (inset of figure 3). A large increase in the scattered intensity and disappearance of the correlation peak upon addition of 3 M NaCl again points to a possible growth of the copolymer micelles with the addition of NaCl. The data for the solution containing 3 M NaCl could be best described in terms of prolate ellipsoidal shape of the micelles. From such an analysis, the length of the micelles present is found to be 14.3 nm with a radius of 4.8 nm. The length obtained from SANS spectra is much smaller than that

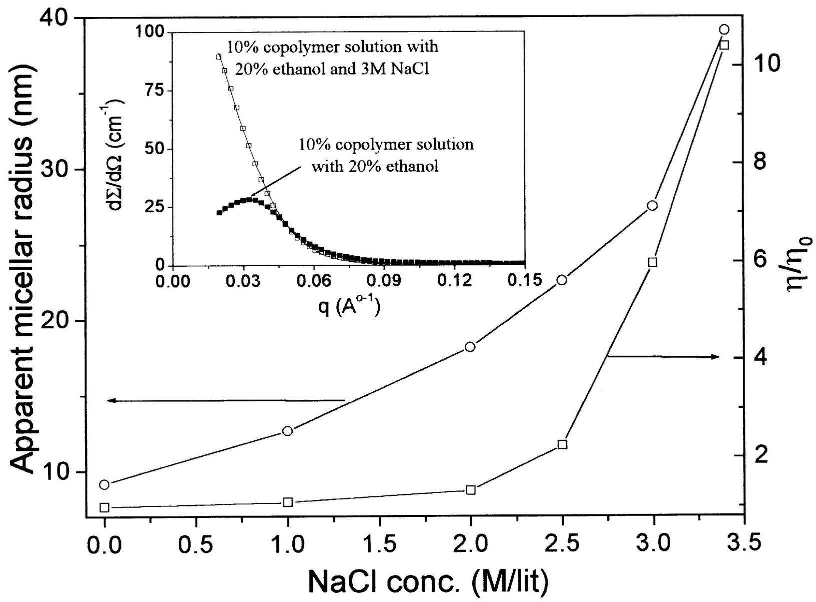

Figure 3. Micellar size (DLS) and the relative flow viscosity vs. NaCl concentration plots measured from data for the solutions with 10% copolymer concentrations and 20% ethanol. Inset shows SANS patterns of 10% copolymer solutions with 20% ethanol in the presence and absence of 3 M NaCl.

calculated from DLS data. The observed difference in the length of the micelles measured here from that calculated from DLS measurements arise from our limit of SANS measurement up to the lowest q value of 0.015 $Å^{-1}$. The micellar rods of bigger size could only be detected from measurements at lower q values only. Thus the length obtained from SANS data reflects the minimum length of the micelles present in the solution.

4. Conclusions

A room temperature sphere-to-rod transition influenced by the addition of sodium chloride (NaCl) and ethanol in the aqueous solutions of the triblock copolymer, $(PEO)_{20}(PPO)_{70}(PEO)_{20}$, have been studied. As observed from the room temperature dynamic light scattering (DLS) studies, a manifold increase in the hydrodynamic radius of micelles is observed upon addition of NaCl in the 10% copolymer solutions containing 20% ethanol. SANS studies suggest that this increase in the micellar size arises from a change of shape of the micelles from sphere-to-rod.

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