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Study on the micellization of amphiphilic graft copolymer PS-g-PEO in toluene

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ABSTRACT: The micellization of amphiphilic graft copolymer polystyrene-graft-poly(ethylene oxide) (PS-g-PEO) in selective solvent, toluene, was studied by means of ^{1}H-NMR, TEM and viscometry. Micelle formation of PS-g-PEO in toluene was strongly dependent on concentration and temperature. An increase in temperature shifted the micelle formation markedly to lower concentration. The micelle was formatted at certain concentration, and it was spherical structure. The viscosity data were analyzed to estimate the cmc value.
Keywords Amphiphilic copolymer, Polymer solution property, Micellization

INTRODUCTION

The most prominent advantage of amphiphilic polymers is the wide variability of the chemical structure of the polymer. Amphiphilic block and graft polymers can be used for stabilization of dispersion and emulsion [1,2], for stabilization of polymer blends [3], and for surface modification [4]. Especially in the biomedical field the use of amphiphilic block and graft copolymers for modification of the adsorption characteristics of polymer surfaces is of great interest [5,6]. Amphiphilic block and graft copolymers consisting of hydrophilic and hydrophobic parts have become subjects of numerous studies on their solution, solid state, and surface properties[7,8].

The formation of micelles and other structure with segregated component in various polymer systems has attracted great interest [9]. In particular, there is a vast literature on the micellization of block copolymers in liquids that are good solvents for one block but poor solvents for the other block [10-13]. There has been increasing interest in the formation and the properties of well-defined structure graft copolymer micelle in selective solvent [14,15]. There are many methods to understand the factors that influence the block copolymer micellization process, the structural parameters of the micelles and the critical micelle concentration for the block copolymers as the onset of intermolecular chain association [16]. Many such techniques including fluorescence, light scattering, TEM, and viscosity [17] et al. have been used.

Macromonomers bearing a functional polymerizable chains and capable of undergoing copolymerization with acrylic/vinyl monomers provide a facile route of synthesis of various graft copolymers of well-defined structure. In a previous article [14], it has been found that poly(methyl methacrylate)-graft-poly(ethylene oxide) can form micelle in selective solvent. This article deals with solution properties of graft copolymer PS-g-PEO that is prepared by radical copolymerization

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of the macromonomer (PEO-MA) with a vinyl monomer of styrene(S). This study is based essentially on the existence of selective solvents for PS-g-PEO amphiphilic graft copolymer, in this solvent micellization occurs with this graft copolymer. This phenomenon has been examined by ^{1}H-NMR, TEM, and viscometry with varying the concentration of graft copolymer at a given temperature.

EXPERIMENTAL

Synthesis of Graft Copolymer PS-g-PEO

The graft copolymers were synthesized by free radical copolymerization of distilled S with PEO-MA. A detailed description of the synthesis procedure of PEO-MA was given elsewhere [18]. 2,2-azobisisobutyronitrile(AIBN) was used as initiator and toluene as solvent. PEO-MA, S, toluene, and AIBN were added sequentially into a reaction vessel under nitrogen. The feed ratio copolymerization was varied from run to run, but always accurately adjusted to meet different structure requirement for the product. After 24 hours of polymerization at 60°C, the graft copolymers were purified according to the procedure described elsewhere[19].

Structural Characterization of PS-g-PEO

Molecular weight data were obtained by means of GPC using polystyrene standards. ^{1}H-NMR spectra were recorded on a JNM-FX 90Q spectrometer at 24°C with TMS as standard. The composition of the graft copolymers was determined by the ^{1}H-NMR using $CDCl_3$ as a solvent. The content of PEO was calculated from the ratio of the intensities of the signals due to hydrophilic methylene protons of PEO graft chains (at 3.63 ppm) and the signals due to hydrophobic methenyl protons in the benzene ring (at 6.6-7.2 ppm). Characteristic data of synthesized graft copolymers are presented in Table 1.

Table 1 Characterization of PS-g-PEO Graft Copolymers

Sample	M_n (PEO)	M_n (PS-g-PEO)	M_w (PS-g-PEO)	M_w/M_n	Graft Number	Wt% (PEO)
S-20	1021	6636	14775	2.22	2.48	19.04
S-21	2050	6759	14019	2.07	1.29	18.89
S-22	2050	5337	14958	2.80	1.93	26.49
S-23	2050	4611	10101	2.19	1.10	18.22
S-24	2050	4652	11188	2.40	2.13	39.80

Solutions

The samples were not easily dissolved in water, the solutions being prepared by gentle heating for no longer than 2 hours, but they dissolved almost instantly in toluene at ambient temperature at concentration 0.04 g/ml – 0.0025 g/ml. As the amount of samples increased, dissolution required more time.

Transmission Electron Microscopy

The morphologies of micelles were observed by transmission electron microscopy using a 100-

sx transmission electron microscopy. Samples were prepared by freeze drying a dilute solution of micelles (<0.02 g/ml) on a thin layer of graphite layered over a copper grid and then stained with phosphotungstic acid aqueous solution.

Viscosity Measurements

The viscosity measurements were made in an Ubbelohde viscometer, which was placed in a thermostatically controlled bath with a precision of ±0.1 °C. The measurements were repeated at least three times and the times obtained were arithmetically averaged, then converted to the relative viscosity η_{rel}, and further to the specific viscosity η_{sp}. The experiments were carried out by diluting the copolymer solution step by step.

RESULTS AND DISCUSSION

1. NMR Behavior of PS-g-PEO

The ^{1}H-NMR spectra of amphiphilic graft copolymers having poly(ethylene oxide) side chains and poly(S-co-MA) main chain have been taken in deuterated chloroform ($CDCl_3$), deuterated methylbenzene (C_7D_8), and deuterium oxide (D_2O). The spectrum measured in $CDCl_3$ shows signals due to hydrophobic methyl, methylene and methenyl protons in the main chain, methenyl protons in the benzene ring as well as signals due to hydrophilic methylene protons of PEO graft chains [Fig. 1 (a)]. The spectrum in C_7D_8 shows signals mainly due to hydrophobic protons in the main chain and the benzene ring are significantly broadened and heightened [Fig. 1 (b)]. On the other hand, in the spectrum taken in D_2O, only sharp signals of hydrophilic protons of PEO graft chains are seen [Fig. 1 (c)]. The phenomena may be explained by the consideration that the amphiphilic graft copolymer has a strong surfactant activity. In chloroform, the copolymer is dissolved as a stretched polymer conformation; however, the graft copolymer forms a reversed-micelle in selective solvent toluene and a micelle in water.

It is well established that amphiphilic molecules can interact to form polymolecular aggregates (micelles) in aqueous solution. According to one model a micelle can be described as a compact sphere consisting of a hydrophobic core surrounded by polar or ionic groups. In aqueous solution the hydrophobic backbone can form a dense coil through hydrophobic interactions, with the PEO side chains facing outwards forming a hydrophilic shell, which effectively minimizes the interfacial free energy. On the other hand, in selective solvent toluene, the hydrophilic graft chains PEO can form a dense coil through hydrophilic interactions, with the hydrophobic backbone facing outwards forming a hydrophobic shell.

2. Morphology of Reversed-Micelles

The morphology of amphiphilic copolymer in selective solvent can be observed by means of TEM [20,21]. Figure 2 shows the micrographs of the reversed-micelles that are formed in selective solvent toluene. From Figure 2 we can conclude that the reversed-micelles are of a spherical structure in shape and their diameters increased with increasing the concentration of amphiphilic graft copolymer PS-g-PEO; moreover, when the concentration of the graft copolymer is higher [Fig. 2 (b)], the micrograph shows two types of particles including both micelles and aggregates of micelles.

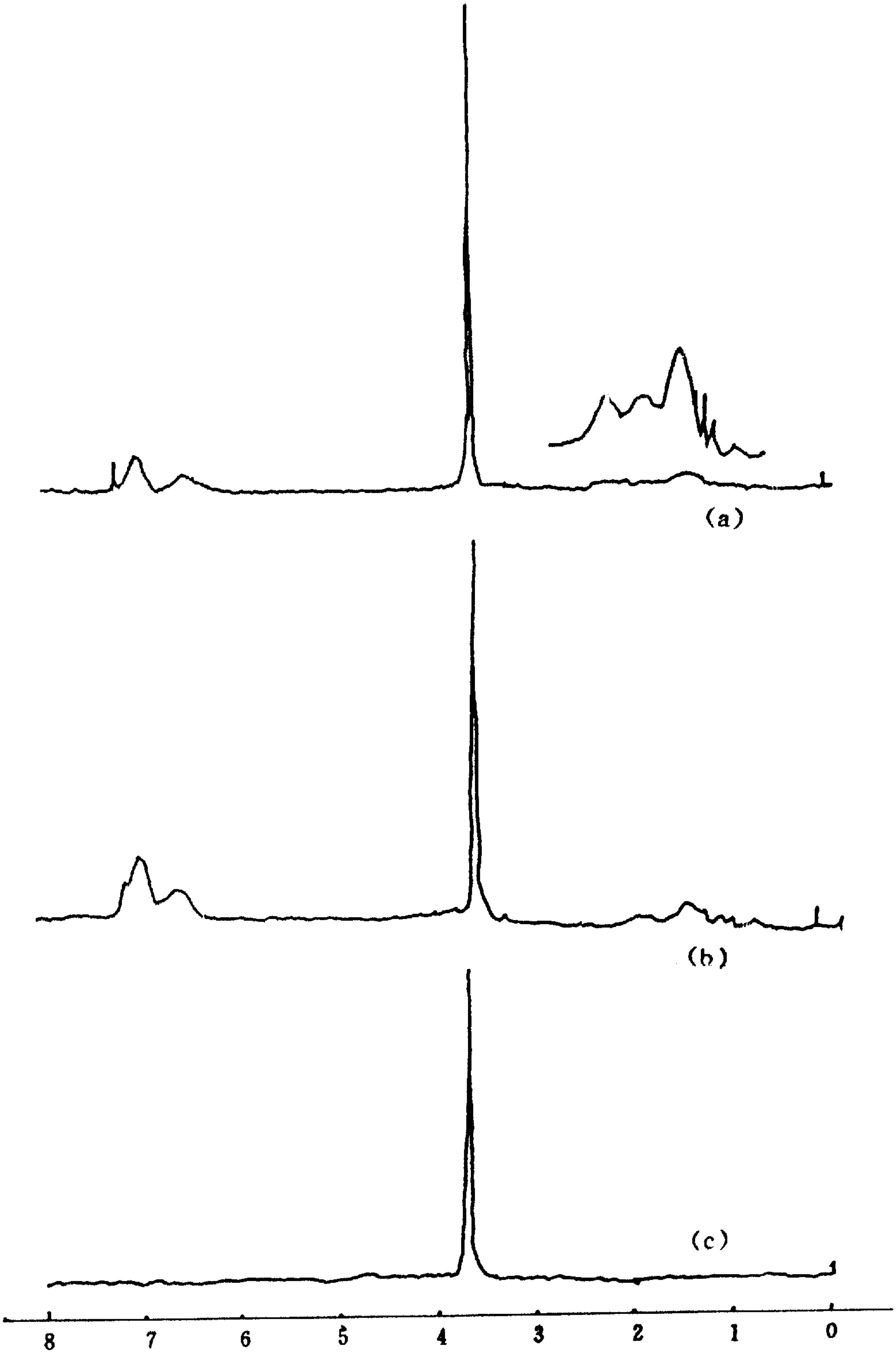

Figure 1 ^{1}H-NMR spectra of copolymer PS-g-PEO in:
(a) $CDCl_3$, (b) C_7D_8, (c) D_2O

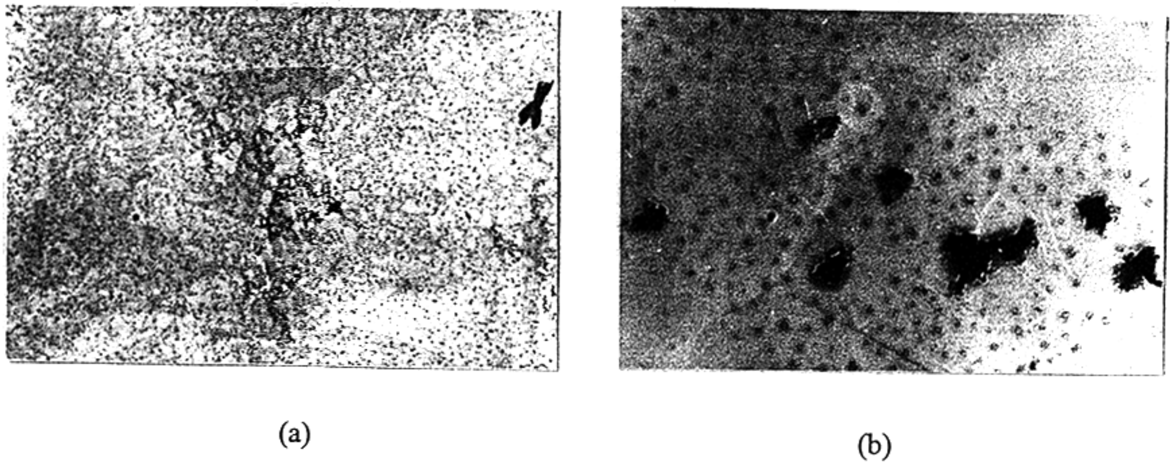

Figure 2 TEM photograph of the reversed-micelles prepared from PS-g-PEO (S-22):
(a): 0.0002 g/ml, (b): 0.002 g/ml
(magnifying object 2 × 10^4 diameters)

3. The Viscosity Behavior and Critical Micelle Concentration of PS-g-PEO

Toluene is a good solvent for the PS backbone but a poor solvent for the PEO chains. The formation of reversed-micelles by the amphiphilic PS-g-PEO in toluene can be demonstrated using viscometry (solutions of each differently labeled sample are prepared). To get complementary information about the reversed-micelle dimension, viscosity measurements were carried out. The concentration dependencies of η_{sp}/c for PS-g-PEO in toluene is plotted in Figure 3. As can be seen, the experimental dependence of η_{sp}/c on the concentration is increase – decrease – increase within the concentration range used. This behavior is similar to conventional low molecular mass surfactant [22]. The same copolymer presents a " normal " behavior of polymer solution in the first variation of η_{sp}/c as a function of c in the region of very low concentrations. It thus appears more reasonable to explain this initial decrease in the η_{sp}/c as being due to the progressive aggregation of PS-g-PEO molecule and the formation of reversed-micelles. The insoluble graft chains in an unfavorable solvent are in a collapsed conformation and, as the polymer concentration increases, the insoluble graft chains are attracted to each other and begin to associate. It is known that η_{sp}/c is proportional to the ratio V/M, where V is the hydrodynamic volume of the polymer and M is molecular mass. The decrease of η_{sp}/c with increasing concentration indicates that the increase of the molecular mass is faster than the increase of the hydrodynamic volume during the formation of reversed-micelle[23]. During this process, the solvent is progressively driven out of the reversed-micelle core, which would explain the swelling of the micelle near the cmc that has been observed on dilution in some systems [24]. After the decrease, the plot shows a increase. It is likely that a higher concentration of PS-g-PEO increases the reversed-micelle concentration and reduces its distance. As a result, the interactions of reversed-micelles arise.

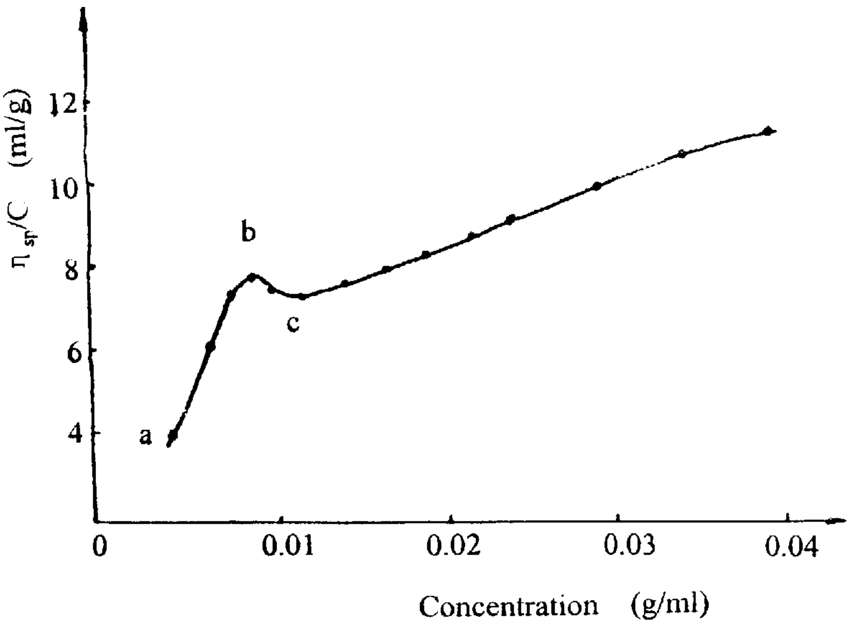

Figure 3 The η_{sp}/c for PS-g-PEO copolymers vs. concentration in toluene

4. Effect of Temperature on η_{sp}/c of PS-g-PEO Solutions

The η_{sp}/c of PS-g-PEO solutions in toluene were measured at different temperature (20-70 °C). Plots of η_{sp}/c vs temperature shown in Figure 4 are characterized by a initial decrease in η_{sp}/c with increase in temperature. This initial decrease in the η_{sp}/c may be considered as being

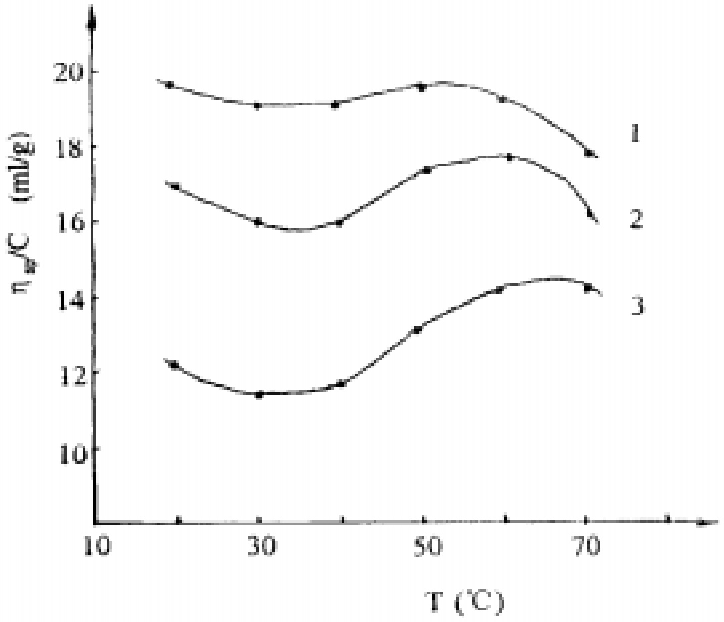

Figure 4 The η_{sp}/c for PS-g-PEO graft copolymer vs temperature at different concentration

1: 0.02 g/ml, 2: 0.01 g/ml, 3: 0.0067 g/ml due to the change in the shape of the reversed-micelles, the possibility of transitions from rod-like to spherical. Then the η_{sp}/c begins to increase with increase in temperature; this may be due to the interactions of reversed-micelles[25]. Finally the η_{sp}/c decreases again at a higher temperature; this can be considered as being due to transitions from reversed-micelle to unimer.

5. Effect of PS-g-PEO Structure on Its cmc Value

In analogy to the low molecular mass surfactants, the critical micelle concentration (cmc) can be defined for the amphiphilic graft copolymers as the onset of intermolecular chains association [26]. The cmc value for PS-g-PEO in toluene can be determined by measuring η_{sp}/c as a function of concentration; thus, in Figure 3, the cmc value was identified as the concentration at which the decrease of η_{sp}/c with increasing concentration occurs (Tables 2 and 3). It can been seen that the cmc value decreases with increasing temperature; this may be due to the interaction of PEO graft chains being increased with raising temperature[10]. The cmc value varies with the PEO content and PEO side chains length in graft copolymer.

Firstly, if we consider a set of graft copolymers with the same PEO side chains length, the cmc value varies with the PEO content, as shown in Table 2. It can be seen that cmc value decreases with increasing the PEO content of the graft copolymers.

Table 2 The effect of the PEO content on the cmc value in toluene

Sample	M_n (PEO)	PEO Content (Wt%)	cmc × 10^3 (g/ml)			
			20℃	30℃	40℃	50℃
S-23	2050	18.22	12.5	11.0	10.0	9.5
S-22	2050	26.49	11.8	10.5	9.5	8.0
S-24	2050	39.80	10.8	10.0	8.0	7.8

Turing to the second case in which we consider a set of copolymers with comparable compositions but different PEO side chains lengths, the cmc value varies with the PEO side chains lengths, as shown in Table 3. It can be seen that cmc value increases with increasing the PEO side chains lengths.

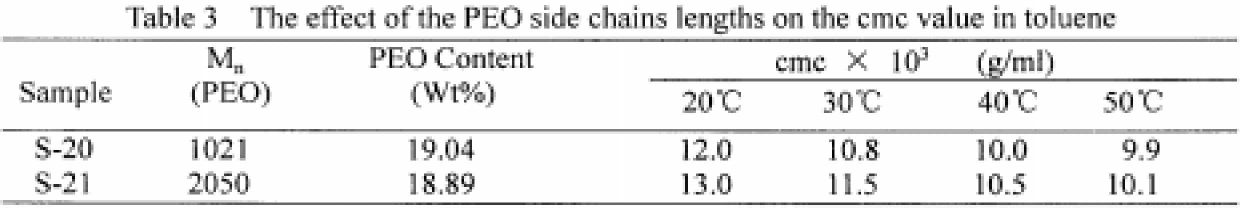

Table 3 The effect of the PEO side chains lengths on the cmc value in toluene

Sample	M_n (PEO)	PEO Content (Wt%)	cmc × 10^3 (g/ml)			
			20℃	30℃	40℃	50℃
S-20	1021	19.04	12.0	10.8	10.0	9.9
S-21	2050	18.89	13.0	11.5	10.5	10.1

In summary, the present results demonstrate that the cmc value depends on the PEO content and PEO side chains lengths in PS-g-PEO amphiphilic graft copolymers.

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