

Characterization of Polystyrene-*b*-poly(ethylene oxide) Diblock Copolymer and Investigation of Its Micellization Behavior in Water

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ABSTRACT: The recent studies deal with a diblock copolymer, polystyrene-poly(ethylene oxide). Infrared spectroscopy, proton resonance spectroscopy (¹H-NMR), and laser light scattering techniques have been used to characterize the polymer. It has been concluded that the sample investigated is diblock copolymer polystyrene-poly(ethylene oxide) having molecular mass 1.656×10^4 g/mol and blocks ratio 1 : 2. The micellization behavior is explored through ¹H-NMR, laser light scattering, light absorption, surface tension, and conductance and viscosity measurements. The results conclude that the critical micelles con-

centration of copolymer is 0.0951 g/dL at 25°C. It has been observed that the surface tension of solution decreases with the temperature and its impact is maxima in dilute concentration region. In addition, new methodologies have been introduced to get accurate critical micelles concentration and critical micelles temperature. © 2010 Wiley Periodicals, Inc., *J Appl Polym Sci* 118: 1704–1712, 2010

Key words: polystyrene-poly(ethylene oxide); block copolymer; light scattering; FTIR; NMR; micellization; conductance

INTRODUCTION

Amphiphilic block copolymers are family of polymeric surfactants with hydrophobic and hydrophilic moieties present simultaneously in the same molecule and have received wide attention both from academic and industrial points of view.^{1–3} Amphiphilic block copolymers also exhibit typical self-assembly and adsorption behavior analogous to the conventional low molecular weight surfactants and at the same time undergo crystallization at higher concentrations.^{4–10} The most common polymer used as hydrophilic part is poly(ethylene oxide) (PEO),¹¹ and the hydrophobic moieties can come from wide variety of polymers such as poly(propylene oxide), poly(butylene oxide), polydimethylsiloxane, polystyrene (PS), polybutadiene, and poly(isobutylene).^{12–16} Many of these copolymers are commercially available with the variation in the molecular characteristics, viz. total molecular mass, different proportion

of hydrophobic/hydrophilic moieties, chain lengths, block (di or tri-) copolymers. Of all these, PEO-PS-PEO block copolymer is the most popular and studied one.^{17,18} Amphiphilic copolymers in general have been one of the strong candidates for potential applications in pharmaceutical and environmental technologies, cosmetic and detergent formulations, and templates for the production of nanostructured materials.^{11,18} As most of these properties are directly linked to the processes of self association and adsorption at interfaces, so quite a good number of research papers have been published, dealing with the characterization and understanding of the surface active properties of copolymers in aqueous media. However, in most of the studies, the techniques used are based over exploitation of physical properties like viscosity, conductance, surface tension, or light scattering. Very few deal with the application of small angle neutron scattering, but in such cases, the concentration of the copolymer is kept considerably high which is beyond the requirement of usual (surface activity) applications of the polymers. On the other hand, although the physical properties of copolymer solutions, such as electrical conductivity, surface tension, light scattering, and ultrasound velocity, change at the critical micelle concentration (CMC), these changes can be abrupt or regular. In the first case, the CMC can be easily determined by the intersection between two straight lines above and below the CMC. In the second case,

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it is difficult to obtain a precise CMC value, as several straight lines can be obtained by fitting the experimental points.¹⁹ In some cases, the used property does not follow a linear relationship with concentration, and it becomes very difficult to estimate CMC.

To overcome this problem, we have introduced novel ways and means to interpret the data for CMC determination; NMR spectroscopy has also been used for the purpose, and the results obtained are compared and precision of the techniques is estimated. The material used for the purpose was diblock copolymer polystyrene-*b*-poly(ethylene oxide) (PSPEO). It is first characterized as a copolymer and then as surface active agent.

EXPERIMENTAL

Materials

The diblock copolymer PSPEO was purchased from Polymer Laboratories, Germany and used as such. The solvent used were tetrahydrofuran (THF), deuterated chloroform (CDCl₃), deuterium oxide (D₂O), and water. THF, CDCl₃, and D₂O were obtained from E-Merck Germany, being of analytical grade used without further purification. The water used as a solvent was deionized having conductance 6–10 μ S/cm.

Characterization of copolymer

The copolymer investigated was characterized with respect to its structure, mass ratio of styrene to ethylene oxide block, refractive index increment (dn/dc), molecular mass (M), radius to gyration (R_g). For this purpose, Fourier transform infrared (FTIR), NMR spectroscopy, differential refractometry, and laser light scattering (LLS) was used. The solvents used were CDCl₃ and THF.

FTIR spectrum was recorded in solid form, using FTIR spectrophotometer obtained from Bruker TENSOR27, Switzerland.

Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded with Bruker-Biospin-AMX 300-MHz spectrometer in deuterated chloroform.

The refractive index increment (dn/dc) was obtained in THF using digital Optilab Differential Refractometer, supplied by Wyatt, USA.

The LLS measurement was made for different concentrations while temperature was kept constant. Before LLS measurements, all samples were filtered using a filter of 0.02 μ m and 0.25 μ m pore size for the solvent (THF) and solution, respectively. Instrument used for the purpose was DAWN EOS supplied by Wyatt, USA, with helium-neon laser of 632.8 nm wavelength as light source. A cylindrical cell (SV) of 2 cm diameter was used for the purpose.

To investigate the ratio of two blocks and to know the degree of dispersity, gel permeation chromatography was used which was supplied by Perkin Elmer, USA.

Micellization

The micellization of the block copolymer was investigated in water over the temperature range of 20–60°C by using the following different techniques.

NMR spectrometry

Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded over the instrument used for the characterization of copolymer in deuterated water (D₂O).

Surface tension

Surface tension was measured at different temperatures (20–60°C) by du-Nouy ring detachment technique using digital TE3 tensiometer supplied by Lauda, Germany. Before making the measurements, the platinum ring was washed with pure deionized water and heated to red hot to ensure cleanness. The required temperature was maintained up to $\pm 0.1\%$ using Ecoline Circulation Thermostat Model E-015T, Germany.

Conductivity measurement

Conductivity of diblock copolymer in water was noted by InoLab 720 conductivity meter. Instrument was calibrated by measuring the conductance of 0.01M KCl standard solution at room temperature.

Light scattering measurements

Dynamic and static light scattering (SLS) measurements were performed over the same instrument. The digital correlator was used for dynamic measurements.

Light transmittance measurement

The percent transmittance of the copolymer solutions was measured at R & M-300D UV-Vis spectrophotometer at 480 nm wavelength.

RESULTS AND DISCUSSIONS

Characterization of PSPEO block copolymer

A representative FTIR spectrum of PSPEO is displayed in Figure 1. The spectra show a wide strong absorption characteristic peak for ether linkage at 1102 cm^{-1} . Benzene ring single peak at 3025 cm^{-1} and multiple absorption peaks at 1492, 1452, 756,

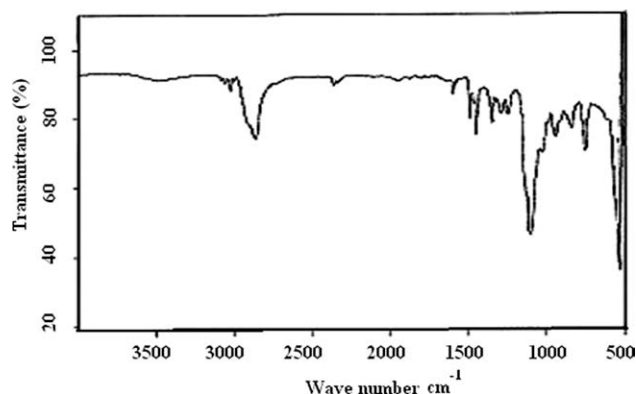


Figure 1 FTIR spectrum of the sample showing PS and PEO blocks.

and 699 cm^{-1} are due to C—H over aliphatic and aromatic compounds and adjacent hydrogen to aromatic rings. A single peak was observed at 2804 cm^{-1} for methylene group. From the spectra, it can be concluded that the sample is copolymer of polystyrene and PEO.

$^1\text{H-NMR}$ spectra of the sample PSPEO in deuterated chloroform (CDCl_3 , $\delta = 7.25$) is presented in Figure 2. The spectra display a peak at $\delta = 3.64$ for methylene protons of PEO block, and peaks at $\delta = 7.1$ and 6.6 for aromatic protons of PS blocks which concludes the same as by FTIR spectrometry.

Change in refractive index (dn) measured in THF is plotted as a function of concentration in Figure 3. The dn/dc was obtained from the slope of the data which is equal to 8.955×10^{-4} .

SLS was used to measure and analyze the time-averaged light scattered intensities. The method is used to determine the z-average radius of gyration (R_g), the weight-average molecular weight (M_w), and the second virial coefficient (A_2) according to eq. (1):

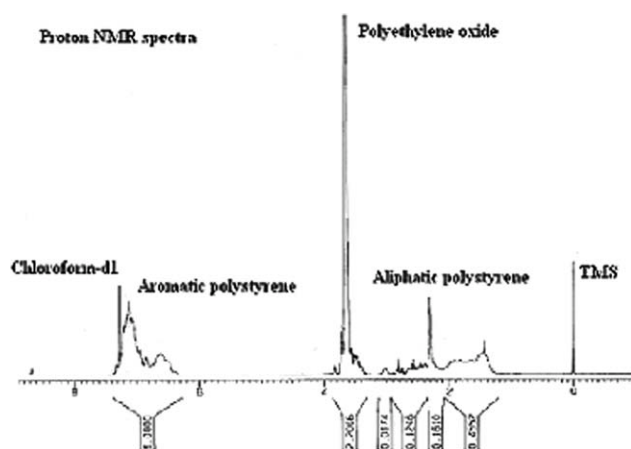


Figure 2 $^1\text{H-NMR}$ spectra of PSPEO block copolymer dissolved in CDCl_3 , showing styrene and ethylene oxide groups. TMS was used as an internal standard.

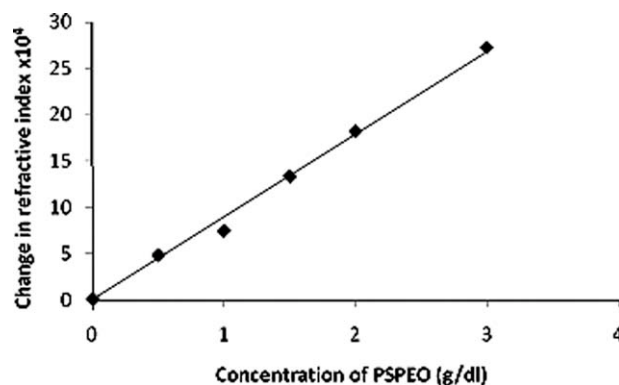


Figure 3 Change in refractive index of the sample as a function of its concentration dissolved in THF at the wave length of 630 nm.

$$\frac{KC}{R_\theta} = \left[1 + \frac{16\pi^2 n^2 \langle R_g^2 \rangle \sin^2(\theta/2)}{3\lambda^2} \right] + 2A_2C \quad (1)$$

R_θ is the Rayleigh ratio, C is the concentration of the polymer solution, n is the refractive index of the solvent, θ is the angle of measurement, and λ is the wavelength of laser light. K is explained in eq. (2).

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \quad (2)$$

N_A is Avogadro's constant and (dn/dc) is the refractive index increment of the polymer solution. A plot of (KC/R_θ) versus $[kC + \sin^2(\theta/2)]$ (k is an arbitrary constant) was used to determine the molecular parameters. By extrapolating the data to zero angles and concentrations, R_g and A_2 can be obtained from the slopes, respectively. A simultaneous extrapolation to zero angle and concentration yields an intercept, which is the inverse of the M_w . A typical such

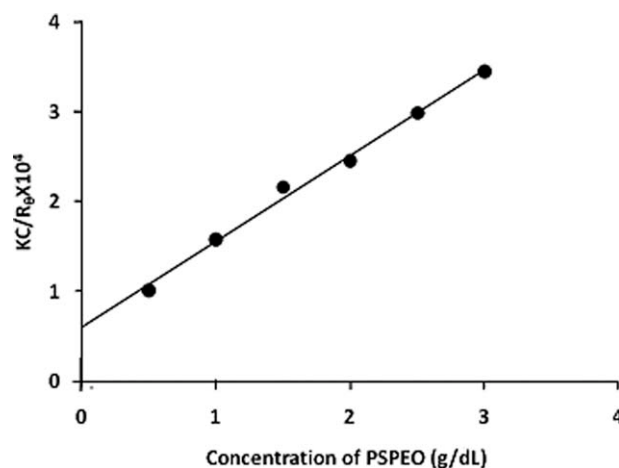


Figure 4 A typical Debye plot of PSPEO block copolymer dissolved in THF and measured at 25°C .

TABLE I
Characteristics of PSPEO in THF and in Water, Obtained Through Laser Light Scattering Technique

Solvents/Parameter	THF	Water
M_w (g/mol)	1.656×10^4	6.89×10^5
A_2 (dL mol/g ²)	5.78×10^{-5}	4.2×10^{-5}
R_g (nm)	1.09	2.01
CMC(g/dL)		9.51×10^{-2}

graph plotted according to Debye is displayed in Figure 4. The results obtained for molecular mass, radius of gyration, and second virial coefficient (A_2) are 1.656×10^4 g/mol, 1.09 nm, and 5.78×10^{-5} dL mol/g², respectively. It is pointed out that the molecular mass is almost equal to the one provided by the supplier which is 1.5×10^4 g/mol. Some of the important characteristics of the copolymer are listed in Table I.

The ratio of two blocks and the degree of dispersity obtained through GPC was 1 : 2 of PS to PEO and 1.21, respectively.

Micellization of PSPEO

¹H-NMR spectroscopy

¹H-NMR spectra of PSPEO having concentration 0.0857 g/dL and 0.2 g/dL are noted in D₂O and presented in Figure 5. As it is shown that a signal at $\delta = 3.85$ is observed for the methylene protons of PEO block and a weak signal at $\delta = 6.41$ for aromatic protons of PS block ($\delta = 4.78$ is for D₂O). However, in case of higher concentration (0.2 g/dL), only a signal at $\delta = 3.67$ for methylene protons of PEO block is observed, and the peaks assigned to the phenyl ring protons of PS block completely disappeared. To explain such phenomenon, we have to consider that polyethyleneoxide is soluble in water up to quite high concentration depending upon molecular mass of the polymer. However, on the other hand, polystyrene is totally insoluble in water. This phenomenon can explain as that if the concentration is low ($c < \text{CMC}$) then both the blocks remain suspended in water due to polyethylene oxide block. As the concentration of copolymer is further increased up to $c > \text{CMC}$ then polystyrene block is precipitated and becomes invisible, and hence, we do not get the signals for styrene group. It is, therefore, possible to conclude that at 0.2 g/dL concentration the copolymer is in micelles form.

Laser light scattering measurements

The apparent molecular mass of copolymer was measured in deionized water through SLS using eq. (1). The results are obtained as 6.89×10^5 g/mol, 2.01 nm, and 4.2×10^{-5} dL mol/g² for molecular

mass, R_g , and second virial coefficient, respectively. The aggregation number in this case was 41.6 which was calculated as "apparent molecular mass/actual molecular mass ($6.89 \times 10^5/1.656 \times 10^4 = 41.6$)." Further the A_2 (THF) is noted to be higher than A_2 (H₂O), which shows THF is a better solvent than H₂O for PSPEO.

The R_H values obtained at different temperatures by dynamic light scattering are displayed in Figure 6. The data show that R_H increases slowly and smoothly till the concentration of copolymer approaches to about 0.09 g/dL. When the concentration is increased further, the R_H value increases sharply and it continues even up to highest investigated (1.0 g/dL) concentration. The concentration at which R_H increases sharply is considered as CMC which is found to be 0.095 g/dL at 25°C (Table I). The R_H values obtained at other temperatures also show the same trend; however, the difference in values obtained at different temperatures when the concentration of copolymer is below CMC is very small. If the concentration is more than CMC then the R_H is noted to be highest for 60°C and lowest for 20°C. These observations can be explained in term of solubility of copolymer in water which increases with the temperature and as temperature increases the solubility increases and micelles expand and hence give high R_H values. The R_H values obtained at 60°C are also plotted versus concentration in the same figure, although it is hard to get accurate CMC from such curves, but it tells us that R_H value increases very sharply when the concentration is higher than CMC till 0.5 g/dL; however, if the concentration is increased further then the rate of increase in R_H values with concentration goes down. These observations conclude that shape of the micelles changes with the concentration. The CMC obtained from these plots is displayed in Figure 7 which showed increase with increase in temperature and the reason of such trend is the same as provided for R_H . This phenomenon could be explained by considering that the solubility of copolymer increases with the temperature. It is acknowledged that micelle formation in aqueous media for PSPEO block copolymers is due to the hydrophobic block (PS) of the copolymer.^{20,21} An increase in temperature caused to increase the solubility of hydrophobic block and resulted to take micellization at higher concentration. The R_H /temperature and R_H values are plotted as a function of temperature in Figure 8. The figure shows that it is easy to get accurate critical micelles temperature (CMT) by plotting R_H /temperature rather than R_H values versus temperature. The CMT obtained in this way is depicted in Figure 9. The CMT of the system decreases very sharply till the concentration approaches to CMC; however, further increase in

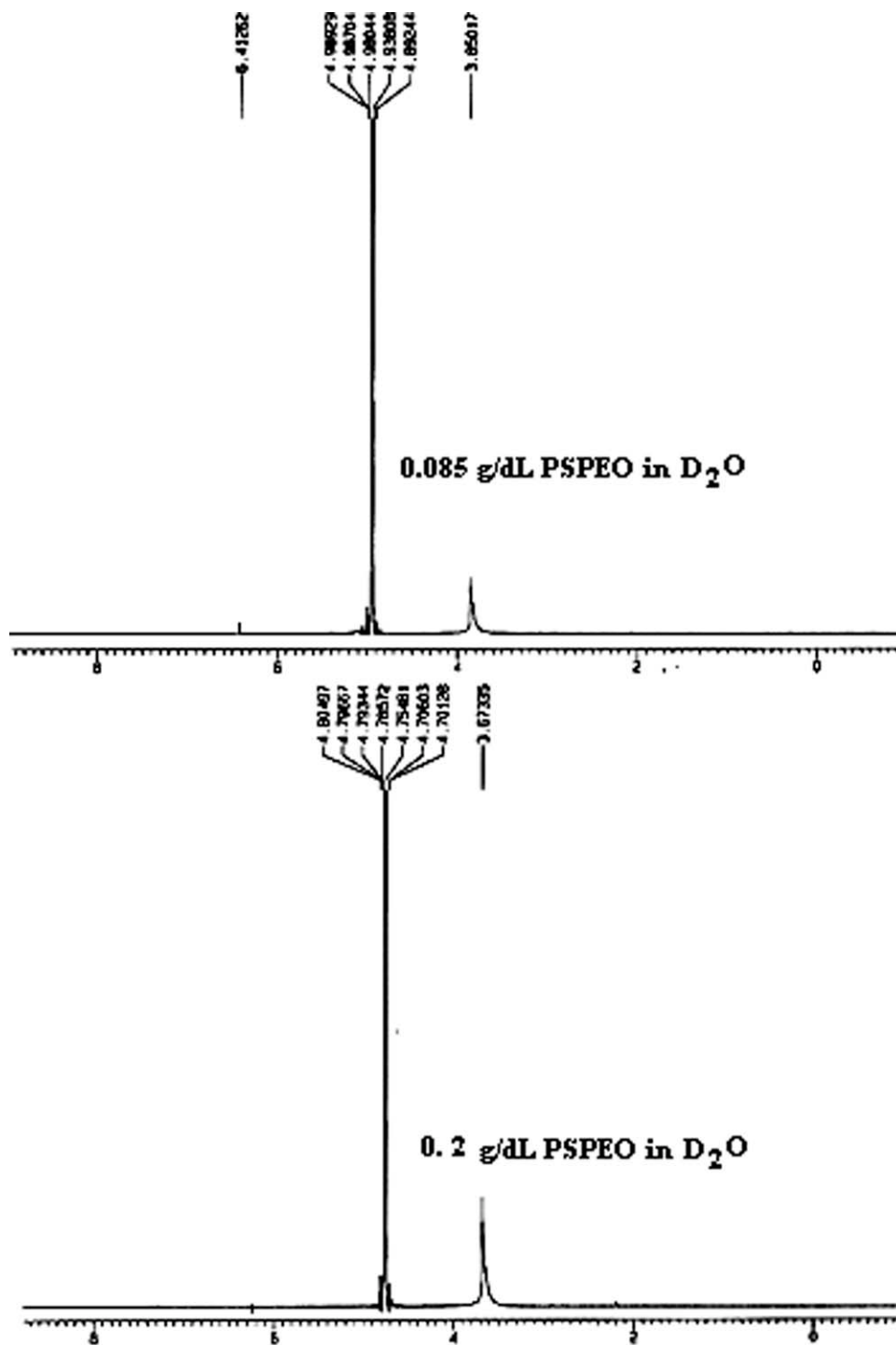


Figure 5 $^1\text{H-NMR}$ spectra of PSPEO block copolymer dissolved in D_2O , having concentration 0.0875 g/dL and 0.2 g/dL.

concentration, the effect over CMT becomes negligible but does not approach to zero as observed in other cases.²²

Light transmittance measurements

Representative transmittances versus concentration of PSPEO are shown in Figure 10. The figure shows a decrease in transmittance with concentration; how-

ever, the decreasing rate is small and the temperature effect is negligible until the concentration approaches to CMC. The effect of temperature becomes visible when the concentration approaches to CMC and increases with further increase in concentration as observed in case of R_H . Further the values of transmittance remain lowest for lowest temperature and vice versa. This trend is attributed to the fact that as the temperature increases, micelles

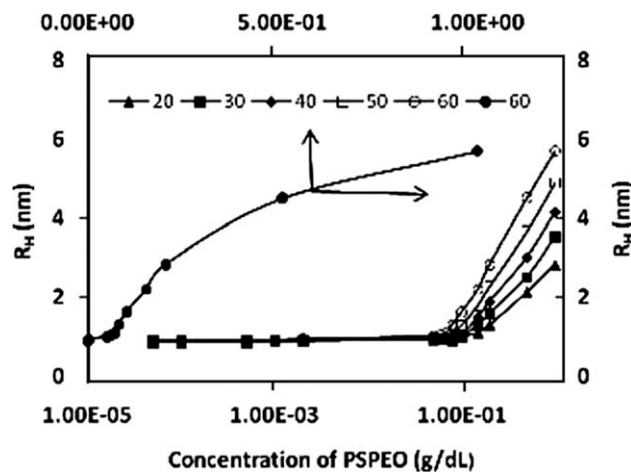


Figure 6 The hydrodynamic radius of PSPEO block copolymer dissolved in water as a function of its concentration and temperature.

first expand after that aggregation number decreases and ultimately may lead to disintegration of micelles which can result formation of unimers. The same figure also displays a plot of transmittance versus log concentration. This plot also shows a decrease in transmittance with the concentration and the variations are bit sharp at CMC, providing a better chance to get accurate CMC. The data show that the CMC depends upon temperature as observed in case of light scattering measurements. The same results are also plotted as $[(\text{Transmittance}) \times (\text{concentration}) / \text{Temperature}]$ versus Log (concentration) in Figure 11; it can be noted that presentation of data in this way are more helpful in determining CMC as compare to the previous presentation (Fig. 10).

To extract the value of CMT, same results are also plotted in Figure 12 as a function of temperature. It is to be noted that in this way one can get more

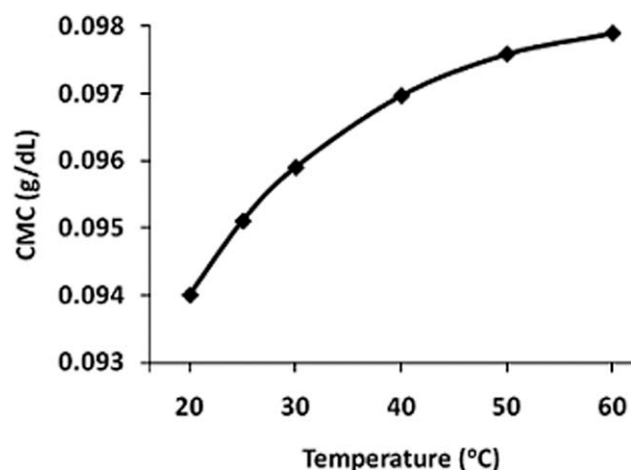


Figure 7 CMC of PSPEO dissolved in water as a function of temperature.

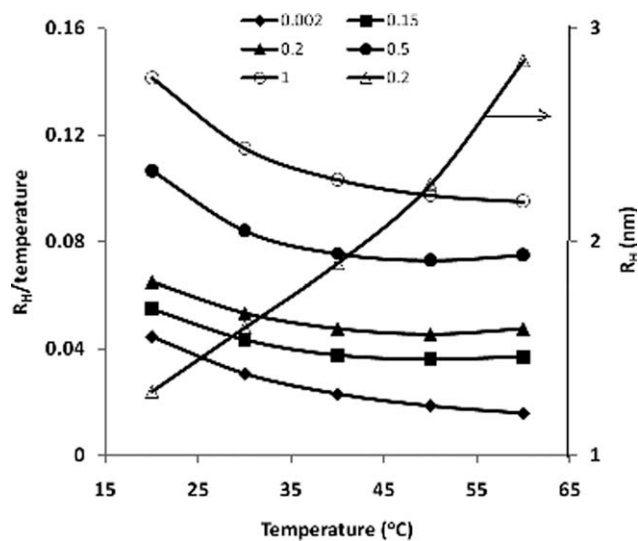


Figure 8 The hydrodynamic radius of PSPEO as a function of temperature, dissolved in water and measured through dynamic light scattering.

accurate results of CMT as compared to plotting transmittance versus temperature (Fig. 12). The CMT of the system obtained in this way showed same trend, and values were also comparable to one obtained through light scattering.

Surface tension measurements

The surface tension of aqueous PSPEO solution measured at various temperatures is presented in Figure 13 as a function of copolymer concentration. The results obtained show that surface tension decreases with the increase in concentration for every temperature. It is to be noted that in dilute concentration range the surface tension decreases slowly till it reaches a concentration called critical aggregation concentration (CAC) after which the surface

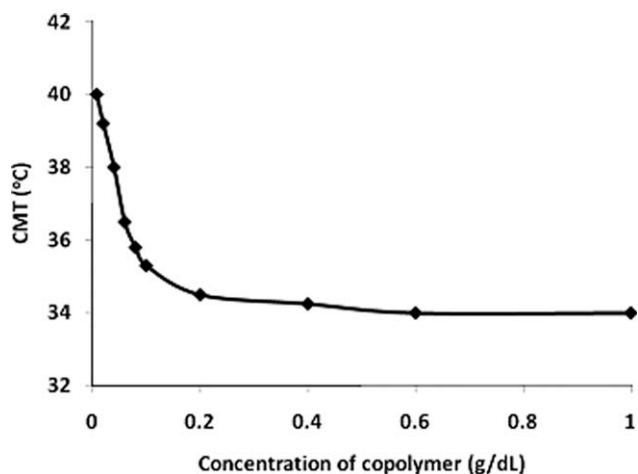


Figure 9 The CMT of PSPEO as a function of its concentration.

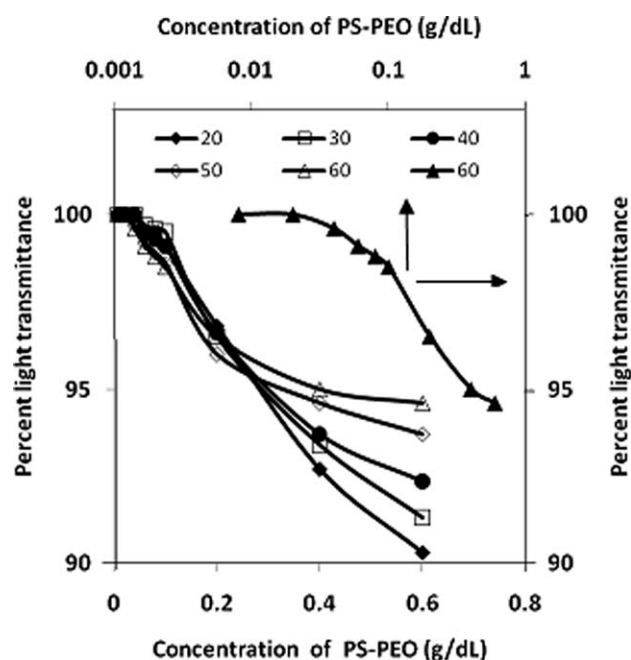


Figure 10 Percent light transmittance of PSPEO as a function of its concentration and temperatures.

tension decreases very rapidly. Further increase in concentration leads to a sharp decrease in the surface tension until the concentration of copolymer approaches to its critical micelles concentration (CMC). If concentration is further increased, the surface tension remains almost constant. This trend clearly indicates that the copolymer behaves as a good surfactant with a reasonable high surface activity.²³ The CMC obtained in this way also shows the same trend and values as obtained through R_H values. To obtain CMT, the surface tension data are plotted as a function of temperature (Fig. 14); it can

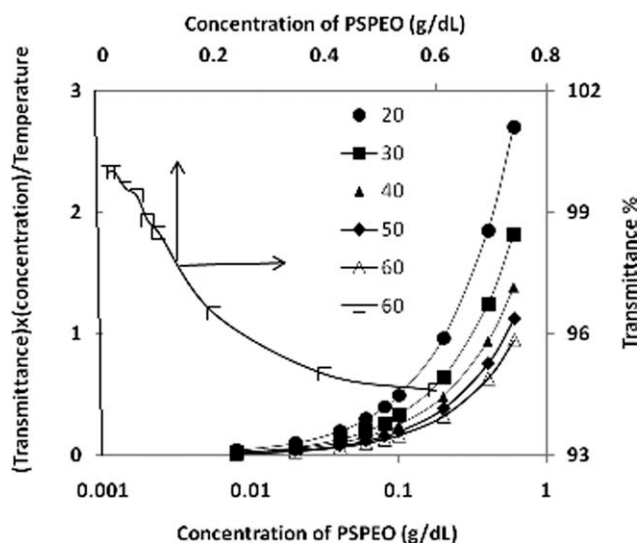


Figure 11 Light transmittance of PSPEO as a function of concentration and temperature.

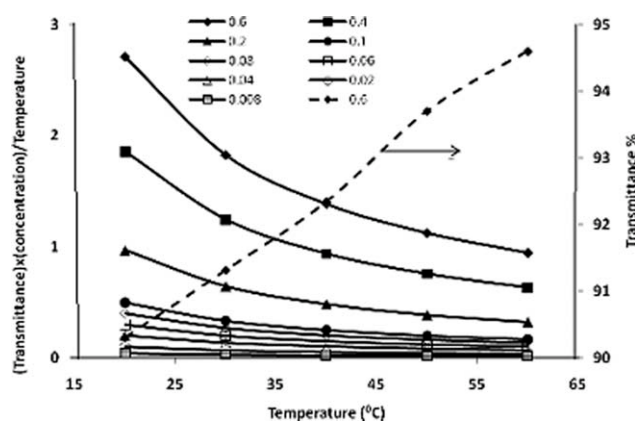


Figure 12 Light transmittance as a function of temperature and concentration.

be noted that it is possible to get accurate values of CMT in this way rather than plotting only surface tension versus temperature. The CMT obtained in this way give the same values as obtained through light scattering. It can be noted that transmittance show less effect of temperature in low concentration, whereas surface tension other way round. The reason behind it is the dependence of the parameters over the size of micelles and concentration variation at the surface, respectively.

Electrical conductivity

The conductance of copolymer is presented in Figure 15 as a function of its concentration. The data highlight the increase in conductance with concentration; however, this increase is slow until the concentration approaches to CMC and further increase in its concentration leads to a sharp increase in conductance as observed for other such systems.²⁴ It is hard to get precise CMC as data do not show a sharp

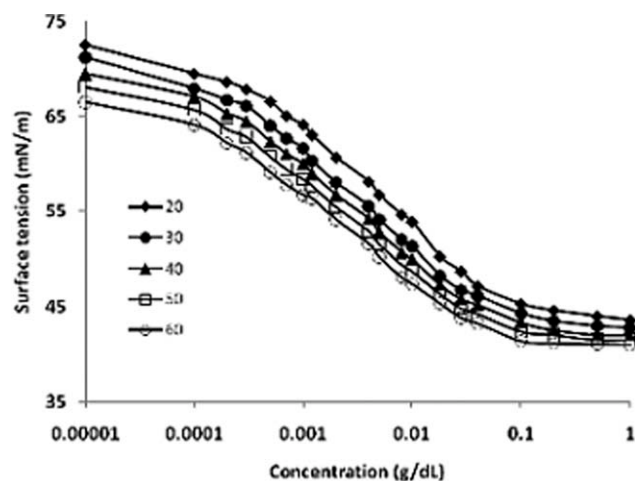


Figure 13 Variation in surface tension of PSPEO copolymer as a function of its concentration measured at different temperatures.

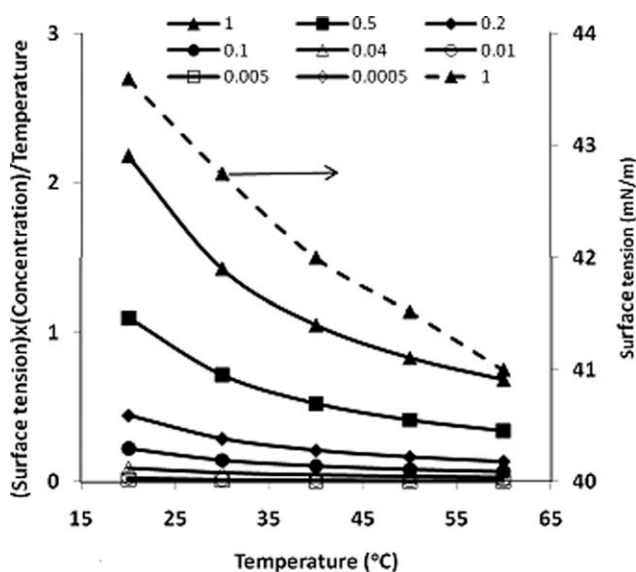


Figure 14 Surface tension of PSPEO copolymer measured at different temperatures, having different concentration.

variation before and after CMC. To overcome this problem, we have plotted conductance/concentration versus concentration in Figure 16. In this way, we got CMC and CAC more precise and equal to the one we got from surface tension. This data conclude that the molar conductance of the PSPEO copolymer is decreased with the increase in temperature, which presumably due to increase in intermolecular interaction of copolymer resulted a reduction in the number of free ions/species present in the solution.²⁵

Viscosity data were also plotted to get CMC and CMT, the results were comparable to other techniques.

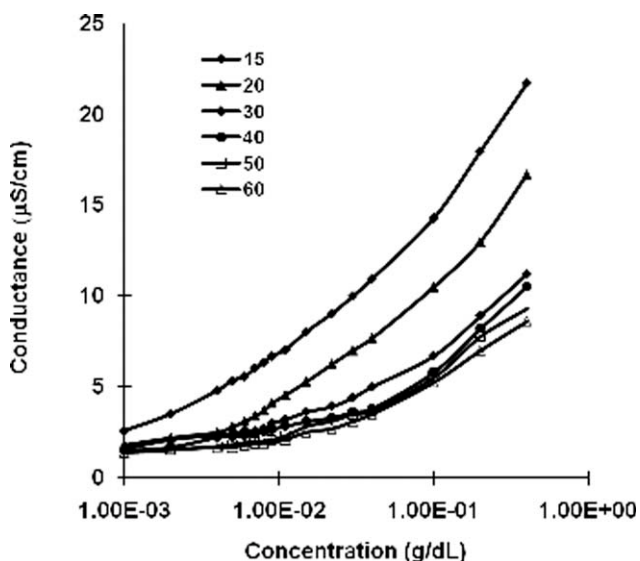


Figure 15 Variation in conductance of PSPEO as a function of its concentration obtained at different temperatures.

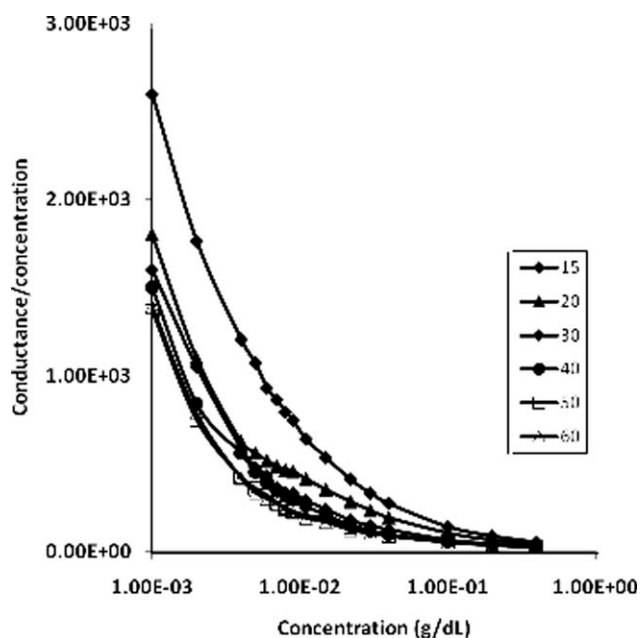


Figure 16 Reduced conductance as a function of copolymer concentration measured at different temperatures.

CONCLUSIONS

The block copolymer PSPEO is investigated through FTIR, ¹H-NMR, laser light scattering; it is concluded that the diblock copolymer having molecular mass 1.62×10^4 g/mol, 1.09 nm R_g , and second virial coefficient 5.78×10^{-5} dL mol/g² in THF form micelles when aggregation number approaches to 41.6. The PS to PEO block ratio was found to as 1 : 2.2. The micellization behavior of the copolymer was investigated in water using different techniques like ¹H-NMR, dynamic light scattering, light absorption, surface tension, conductometry, and viscosity; it is concluded that copolymer form micellizes at concentration 0.095 g/dL. The surface tension decreases with the temperature, whereas CMC increases. The CMT values were found to decrease with concentration. The aggregation number as obtained through dynamic light scattering was 41.6. Keeping in view its micellization behavior and reduction in surface tension, it is concluded that it can work as a good surfactant and will have several important applications. Further, the results obtained through different techniques gave the same results for CMC and CMT, and the methodology introduced for their determination were reliable and provide more accurate results.

The reported work is completed at Gomal University.

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