Synthesis, Characterization, and Micelle Formation in an Aqueous Solution of Methoxypoly(ethylene glycol) Macromonomer, Homopolymer, and Graft Copolymer

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ABSTRACT: A macromonomer based on methoxypoly(ethylene glycol) (PEG) (molecular weight 350), its homopolymer, and graft copolymer have been synthesized which form micelles in aqueous solution. Methoxy-PEG-350 and macromonomer have been characterized by using ^{1}H NMR, IR, UV–visible, and differential scanning calorimetric (DSC) techniques. The homopolymer and graft copolymer have been characterized by ^{1}H NMR and their respective molecular weights determined by using gel permeation chromatography (GPC). Critical micelle concentrations (cmc) of the macromonomer and polymers in aqueous solution have been determined using a UV–visible spectroscopic technique in both the absence and presence of a probe. Methyl orange has been used as the probe. The cmc values so obtained for the macromonomer, homopolymer, and graft copolymer at 22 °C were found to be 1.2×10^{-4}, 2.0×10^{-6}, and 0.9×10^{-6} M, respectively. The aggregation number, $\bar{N}$, of the macromonomer in an aqueous solution was determined by using a fluorescence spectroscopic technique, and it was found to be 20 at 22 °C. 8-anilino-1-naphthalenesulfonic acid (ANS) and *N*-cetylpyridinium chloride (CPC) were used as the fluorescent probe and quencher, respectively, during fluorescence measurements. The standard free energy change for micelle formation of macromonomer, homopolymer, and graft copolymer was calculated using a biphasic model, and it was found to be −22.1, −32.2, and −34.1 kJ mol^{-1}, respectively, at 22 °C. The macromonomer exhibits liquid crystalline behavior as evidenced by polarizing microscopic and DSC techniques.

Introduction

In recent years polymeric surfactants have attracted the significant attention of several groups of workers[1] and growing interest as emulsion stabilizers, phase-transfer catalysts in enzymatic reactions, and membrane recognition mechanisms as drug carriers. The hydrophilicity or the hydrophobicity of the surface of the polymers can be suitably altered by the use of polymeric surfactants. It is known that such polymeric surfactants provide more anchoring sites for the dispersed particles effecting strong adhesion onto the surface, ultimately restricting the desorption and hence proving more advantageous. Block/graft copolymers are best suited as effective polymeric surfactants because their proper orientation of the hydrophilic and hydrophobic components favors micelle formation. The presence of a polymerizable group allows the preparation of well-defined polymerized species which may show micellar properties even at very low concentration. The term "polymerized micelle" is often used to elucidate these macromolecular species. Due to their ability to trap drugs in the micelles, they are useful not only as carriers but also as a means of targeting cells.[2]

Amphiphilic block copolymers[3,4] derived from poly(methyl methacrylate)-*b*-poly[2-(dimethylamino)ethyl methacrylate] are reported by Chujo *et al.* Studies[4] have already been made on the synthesis of block copolymers of sulfonated glycidyl methacrylate and alkyl methacrylate. As the synthesis of block copolymers requires stringent anhydrous conditions, the graft copolymers are more preferable from the practical point of view of synthesis. Comblike water-soluble graft copolymers have been synthesized by Wesslen *et al.*[5] using a transesterification method. However, synthesis of macromonomers bearing a functional polymerizable chain and capable of undergoing copolymerization with acrylic/vinyl monomers provides a facile route of synthesis of graft copolymeric surfactants. Such macromonomers capable of undergoing polymerization on the surface of the polymeric system are superior, as they confer improved mechanical stability of the polymeric systems.[6] Furthermore, water-soluble macromonomers find application (i) in the synthesis of graft copolymers with adequate water solubility and (ii) as emulsifiers in the emulsion polymerization systems involving monomers like styrene, resulting in polymers with uniform particle size distribution.[7] Water-soluble graft copolymers synthesized from macromonomer derived from methyl methacrylate polymerized in the presence of thioglycolic acid were studied by Tsukahara *et al.*[8]

In our present investigation, we have chosen to synthesize water-soluble macromonomer based on poly(ethylene glycol), as the latter offers unique characteristics such as solubility in water and organic solvents, nontoxicity, commercial availability, and a narrow molecular weight distribution. Also poly(ethylene oxide) blocks in polymers are known to have a high degree of crystallinity and a low glass transition temperature. Application of the polymer of poly(ethylene oxide)/polyacrylates has the advantages of binding properties,[9–12] hydrophilic character,[13] and biocompatibility.[14] Papers published on the synthesis of graft copolymers from poly(ethylene glycol) methacrylate and acrylonitrile[15]/styrene[16] did not reveal the mode of synthesis of macromonomer and its micellar characteristics. Therefore, in this paper, it is worthwhile to report the synthesis of the macromonomer based on methoxypoly(ethylene glycol) (molecular weight 350) with a slight modification of the earlier procedure.[17] The macromonomer was characterized by using ^{1}H NMR, IR, and differential scanning calorimetric (DSC) techniques. The micelle-forming characteristic of the model compound of the macromonomer bearing 25–45 oxyethylene units was established by Ito *et al.*[18] using a light scattering technique. In this paper, we report the evidence of micelle formation and aggregation number of the macromonomer in an aqueous solution, bearing 9 oxyethylene units, using UV–visible and fluorescence spectroscopic techniques,

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respectively. The unusual rapid rate of polymerization of micelle-forming macromonomers has been reported recently.[18-20] Thus, our synthesized micelle-forming macromonomer offers an advantage in the preparation of homopolymer and graft copolymer with styrene in aqueous medium without the use of external emulsifiers. Homopolymer and graft copolymer were characterized by ^1H NMR and their molecular weights determined by using GPC. The micelle-forming properties of the above polymers have been established using a UV-visible spectroscopic technique.

Experimental Section

Materials. Methoxypoly(ethylene glycol) (molecular weight 350), received from Aldrich, was freed of water by azeotropic distillation using toluene and dried over molecular sieves (3 Å). Acryloyl chloride was synthesized by the published procedure,[21] and distilled acryloyl chloride was used. All solvents (methylene chloride, benzene) were of analytical grade. Triethylamine was distilled freshly and stored over molecular sieves. Styrene, received from Aldrich, was washed with NaOH and then distilled water, followed by drying over anhydrous $CaCl_2$ and distillation under vacuum. $K_2S_2O_8$ used was of analytical grade. Methyl orange was BDH analar grade. The Mg salt of 8-anilino-1-naphthalenesulfonic acid (ANS) was from Sigma. *N*-Cetylpyridinium chloride (CPC) was also from Sigma and was recrystallized twice from ethanol. For the grade, purity, characteristics, and dynamics of the CPC surfactant, refer to our recent works.[22] Doubly-distilled conductive water of a specific conductance, 2–3 $\mu S\ cm^{-1}$ at 25 °C, was used as the solvent medium throughout the experiment.

Synthesis and Purification of the Macromonomer. To a stirred solution of 39.8 g of water-free methoxypoly(ethylene glycol) (0.1 mol) in 70 mL of CH_2Cl_2 was added 30.3 g of freshly distilled triethylamine (0.3 mol). The solution was flushed with N_2 and cooled to 10 °C. A total of 27.5 g of distilled acryloyl chloride (0.3 mol) in 30 mL of CH_2Cl_2 was added in the above mixture over a duration of 30 min under continuous stirring. The mixture was kept under stirring in a N_2 atmosphere for a period of 12 h at 10 °C. Triethylammonium chloride was filtered off. A minimum amount of benzene was added to the syrupy liquid to separate the residual triethylammonium chloride. The solvent was removed by distillation under reduced pressure; the liquid again was dissolved in CH_2Cl_2 and washed well with dilute saline water. The combined organic layer is then filtered through a "Fuller's earth" bed, and the solvent was removed from the filtrate under vacuum. The obtained macromonomer was dried over molecular sieves overnight and studied for characterization. The synthesis of macromonomer was carried out using an excess of acryloyl chloride (not specified in ref 17) in CH_2Cl_2 instead of toluene. The former offers advantages of effective solubilization of PEG and more volatility and avoids the risk of polymerization of macromonomer during purification processes.

Yield: 47.5 g (72%), colorless, liquid. ^1H-NMR (300 MHz, $CDCl_3$): δ 3.1 (s, 3H, $-OCH_3$), 3.3-3.41 (m, 35H, $(-OCH_2CH_2)_n$), 3.9 (t, 2H, $-CH_2COO-$), 5.54 (d, 1H, $-COOCH{=}CH$), 5.86 (m, 1H, $-COOC{=}CH$ cis), 6.1 (d, 1H, $-COOC{=}CH$ trans). IR: ν 2980 (CH, str), 1720–1730 (–C(O)–), 1630–1640 (–C=C, str), 1410 ($-CH_2$, CH def.), 1200 ($-OCH_2$), 1110–1120 ($-OCH_2CH_2-$), 990 ($-CH_{(w)}$, trans), 940 ($-CH_{2(w)}$).

Polymerization of Macromonomer. Polymerization of the macromonomer in dimethylformamide (20% solution) was carried out in the presence of a benzoyl peroxide initiator (2%) at 60 °C for a period of 4–6 h, resulting in the formation of a gellike material which is capable of absorbing solvent. However, the polymer obtained by this method exhibits poor solubility characteristics in water and other organic solvents. ^1H NMR spectra of the above polymer in $CDCl_3$ indicated the absence of the vinyl proton signal (the peak between 5.4 and 6.1 ppm). The water–soluble homopolymer was synthesized by published procedures.[17]

Synthesis of Graft Copolymer. To the macromonomer solution in water (0.01 mol in 25 mL of water) was added 0.01 mol of styrene under a N_2 atmosphere, and the mixture was kept under stirring for $^1/_2$ h to get uniform dispersion of styrene.

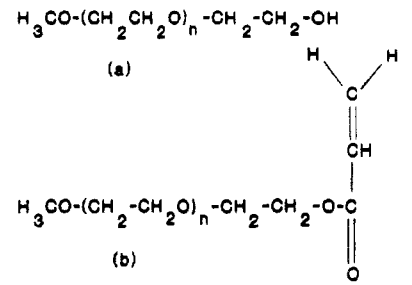

Figure 1. Structures of (a) methoxy-PEG (molecular weight 350) and (b) the investigated macromonomer surfactant.

Polymerization was performed in the presence of 1 mol % $K_2S_2O_8$ under a N_2 atmosphere for a period of 5 h. The reaction was terminated by pouring into excess water the polymer freed from insolubles by filtration, salt removed by dialysis, and the pure polymer recovered by freeze drying.

Yield: 2.8 g (55%), rubbery solid. ^1H NMR (90 MHz, D_2O): δ 3.7 (s, $-OCH_2CH_2)_n$, 7.3 (s, C_6H_5-).

Methods. NMR measurements were performed on Bruker MSL-300P (300-MHz) and CXP-90 (90-MHz) spectrometers. Tetramethylsilane was used as an internal standard. IR spectra were recorded on a Perkin-Elmer spectrometer. GPC measurements were carried out on a GPC 440 water associates chromatograph fitted with ultrastyragel columns (10^3, 10^4, and 10^5 Å). Apparent molecular weights and polydispersity indices were calculated using polystyrene calibration. Differential scanning calorimetric (DSC) measurements were performed on a general V_4IC Du Pont-2000 calorimeter using a heating rate of 5 °C/min. Liquid N_2 was used as a purge gas for measurements below 300 K and dry N_2 for those above. The stability of the base line was checked before each experiment. Less than 10 mg of sample, dried under vacuum at 60 °C for polymer, or 23 °C for monomer, for 48 h, was used each time. The heating–cooling cycle was repeated two or three times until reproducible scans were obtained. The same rate was used for heating and cooling. For details regarding DSC measurements, we refer to an earlier publication.[23] UV-visible and fluorescence spectral measurements were made at 22 °C on a Shimadzu UV-260 spectrometer and a Hitachi Model No. 650-40 fluorimeter, respectively. Prior to the measurements, all the solutions were thermostated for >20 min at 22 °C unless stated otherwise. The temperature reproducibilities were in the range ±0.05 °C.

The UV-visible spectra were recorded in the wavelength range 190–550 nm to investigate the micellar and nonmicellar states of the macromonomer and polymers in aqueous solution. The critical micelle concentrations (cmc) of macromonomer and polymers were estimated by plotting the difference in absorbance at the λ_{max} against the respective concentrations. The cmc of the macromonomer was also determined by plotting the change in λ_{max} against the concentration of the macromonomer. These experiments were performed both in the absence and presence of methyl orange (as an external probe) and at neutral pH (pH = 7.0).

Regarding details for the cmc determination, refer to our earlier works.[24,25]

Results and Discussion

NMR and IR Spectra and Structure of the Macromonomers. The structures of the methoxy ether of poly(ethylene glycol) (part a) and its respective macromonomer (part b) are shown in Figure 1.

Methoxypoly(ethylene glycol) (PEG) was used to synthesize macromonomer so as to obtain a monofunctional acrylate monomer. Difunctional monomers act as cross-linking agents, and as a matter of fact they form insoluble polymers. The amount of free PEG was found to be 2% by using a ^1H NMR method. The molecular weight of the methoxy ether of PEG was calculated using the integrals for the backbone with that of the hydroxyprotons[26] (cf. Figure 2A). The molecular weight of the synthesized macromonomer was also calculated using the same pro-

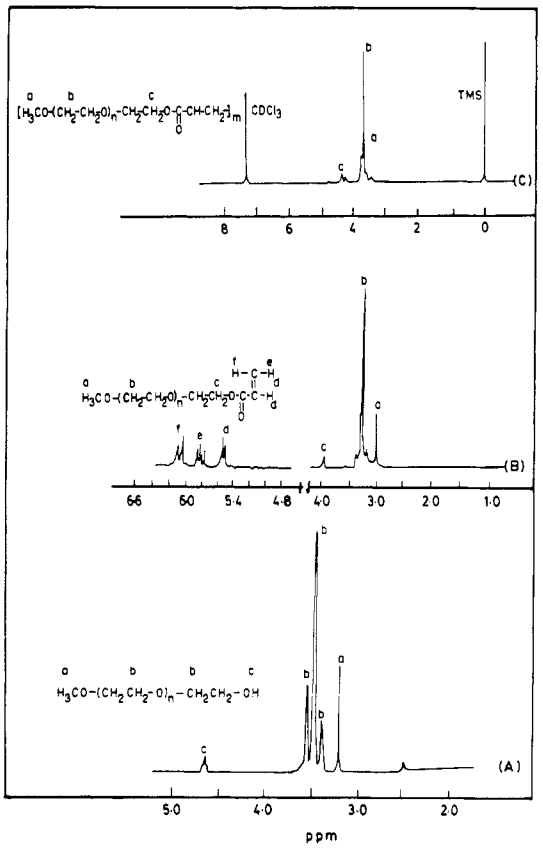

Figure 2. (A) ^{1}H NMR spectrum of methoxy-PEG in DMSO at 22 °C and at 300 MHz. Number of scans = 24. (B) ^{1}H NMR spectrum of a macromonomer surfactant investigated in $CDCl_3$ at 22 °C and at 300 MHz. Number of scans = 128. (C) ^{1}H NMR spectrum of the homopolymer derived from the investigated macromonomer in $CDCl_3$ at 22 °C and at 300 MHz.

Table I. Some Physicochemical Parameters of Methoxy-PEG 350 and the Investigated Macromonomer Calculated from ^{1}H NMR Results

monomer	supplier	OH/OCH_3	vinyl proton/CH_2	mol wt
methoxy-PEG	Aldrich	1.05		398
macromonomer	synthesized		1.52	460

cedure[26] based on the integrals for the vinyl protons and the backbone unit (cf. Figure 2B). The calculated molecular weights of both the methoxy ether of PEG and the investigated macromonomer obtained from a ^{1}H NMR method are given in Table I. A slightly higher ratio of vinyl proton is probably due to the presence of a diacrylate derivative which had been derived from 2% free PEG, and the removal of these free PEGs is not possible which leads a slight increased value of the molecular weight in the calculation (see Table I). An attempt to synthesize homopolymer resulted in the formation of a gel capable of absorbing solvent, however, exhibiting poor solubility characteristics. The ^{1}H NMR spectrum (Figure 2C) of the polymer shows the absence of the peaks between 5.5 and 6.1 ppm (of vinyl protons), confirming the formation of the graft copolymer through a vinyl group by the free-radical mechanism. The higher intermolecular interaction due to the presence of the oxyethylene linkage and the probable chain-transfer reactions to PEG chains accounted for the gel formation. This can be overcome by performing the polymerization with a minimum quantity of initiator, in an aqueous medium, so that the macromonomer organizes into micellar aggregates. Therefore, the soluble homopolymer synthesized according to a published procedure[17] showed the absence of peaks between 5.5 and 6.1 ppm in the ^{1}H NMR spectrum, confirming polymerization through a vinyl group.

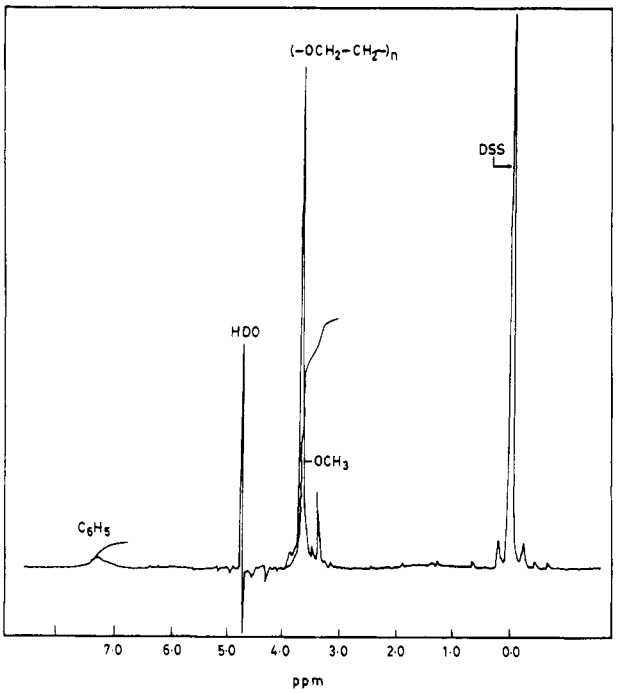

Figure 3. ^{1}H NMR spectrum of the graft copolymer in D_2O at 22 °C and at 90 MHz. Number of scans = 48.

The ^{1}H NMR spectrum of the graft copolymer in D_2O showed peaks at 3.7 (s, $(-OCH_2CH_2)_n$) and 7.3 ($-C_6H_5$) (Figure 3). The graft copolymer was composed of 0.47 parts of styrene and 0.53 parts of poly(oxyethylene acrylate) calculated using the ratio of the integrals between the aromatic and aliphatic protons.

The apparent molecular weights of the homopolymer and graft copolymer were determined by GPC and found to be 1.87×10^4 and 2.7×10^4, respectively. The respective polydispersities are 1.13 and 1.15. It has been shown by Wesslen *et al.*[27] that amphiphilic PEG/polyacrylate graft copolymers prepared either by polymerization of macromonomers or by transesterification were not eluted according to their molecular weights on GPC in THF. The extremely low polydispersity found in the present case points to a similar phenomenon.

Critical Micelle Concentration of Macromonomer and Polymers in Aqueous Solution. The investigated macromonomer is expected to be surface active due to the presence of acryloyl, methoxy groups as hydrophobic tails, and oxyethylene blocks as hydrophilic head groups. Therefore, the knowledge of cmc of the macromonomer is of great importance in stimulating further studies on application in the synthesis of graft copolymeric surfactants, emulsifier-free emulsion polymerization systems, and its interaction with the commercially available surfactants. The macromonomer and graft copolymer are UV active and show absorption maxima at 196–198 nm (vinyl group[28]) and 245 nm (styryl group), respectively. The UV–visible spectra of the macromonomer at various concentrations in the absence and presence of methyl orange in aqueous solutions have been recorded at 22 °C and are shown in parts a and b of Figure 4, respectively. The plots of the difference in absorbance at λ_{max} vs concentrations of the macromonomer and polymers in the absence and presence of probe are shown in parts a and b of Figure 5, respectively. The cmc's of the macromonomer, homopolymer, and graft copolymer obtained from these plots (Figure 5a,b) are found to be 1.2×10^{-4}, 2.0×10^{-6}, and 0.9×10^{-6} M, respectively. Methyl orange shows

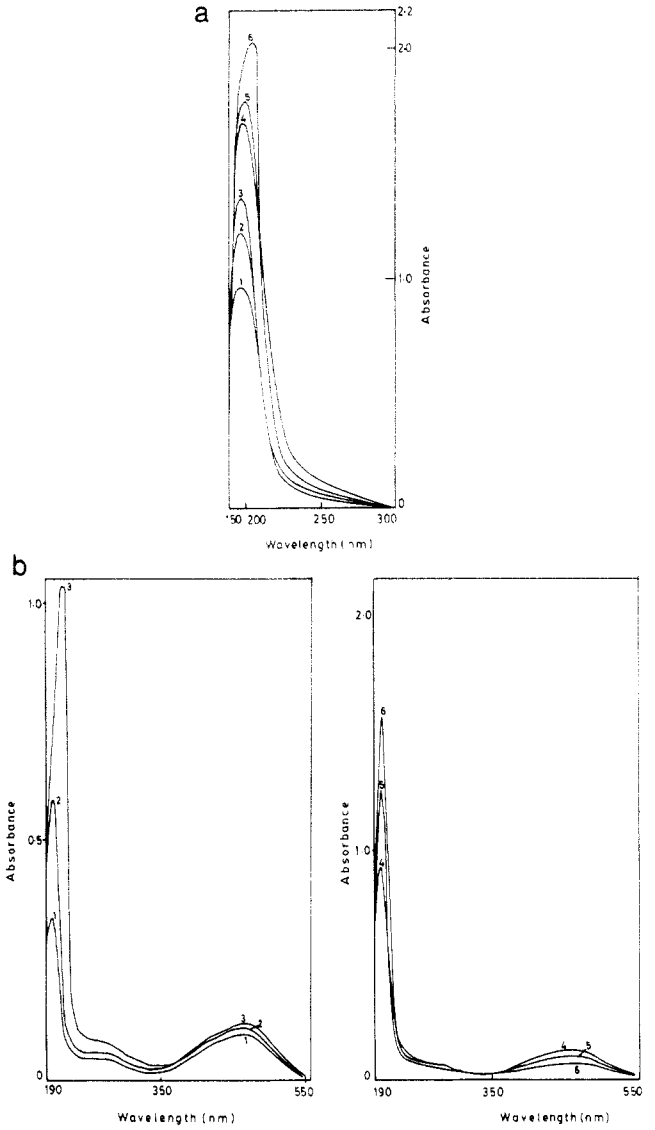

Figure 4. (a) UV–visible spectra of the macromonomer in aqueous solutions at 22 °C in the absence of probe. Curves 1–6; 6×10^{-5}, 8×10^{-5}, 10×10^{-5}, 16×10^{-5}, 20×10^{-5}, and 60×10^{-5} M macromonomer. (b) UV–visible spectra of the macromonomer in aqueous solutions at 22 °C in the presence of a methyl orange probe (1×10^{-6} M, fixed). Curves 1–6: 4×10^{-5}, 6×10^{-5}, 8×10^{-5}, 12×10^{-5}, 16×10^{-5}, and 20×10^{-5} M macromonomer.

λ_{max} at 268.2 and 468 nm. The weak absorbance at 268.2 nm does not show any significant change in the presence of the surface-active macromonomer and homopolymer, and hence absorbance at 468 nm was used to investigate the micelle formation of the macromonomer. However, absorbance at 198–200 nm (due to the presence of a vinyl group of the macromonomer) was also measured in the presence of the probe in order to check the cmc of the macromonomer. Furthermore, the cmc was also determined by plotting the change in λ_{max} against the concentration of the macromonomer (Figure 5c). The cmc obtained in this method is found to be 1.2×10^{-4} M. The cmc's obtained in the absence and presence of the probe are in good agreement with each other. In the determination of the cmc, the concentration of the probe was kept as low as possible (1×10^{-6} M, fixed) in order to avoid the exciplex (or excimer) formation. The lower cmc values of the polymers compared to the macromonomer indicate the advantage of polymeric surface-active agents.

Aggregation of the Macromonomer in Aqueous Solution. Following Turro and Yekta,[29] the aggregation number was determined by measuring the quenching of

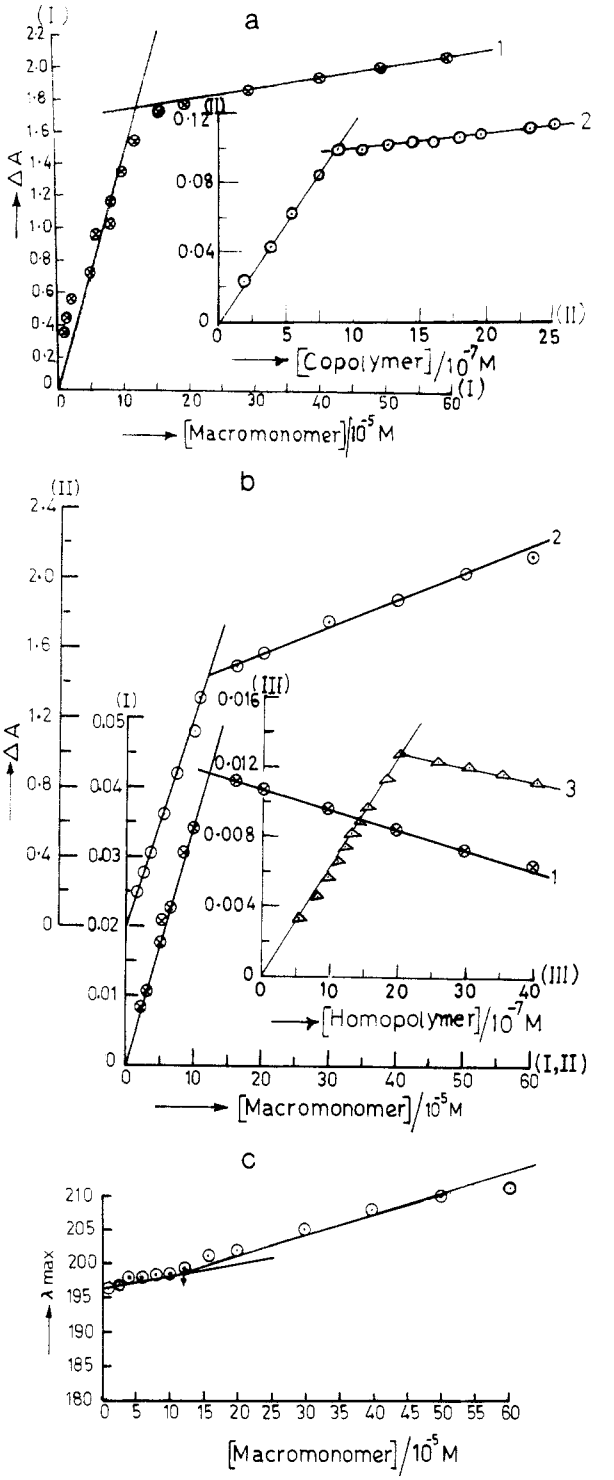

Figure 5. Difference in absorbance: (a) Macromonomer, curve no. 1 scale I, 198–200 nm; 240-nm graft copolymer, curve no. 2 scale II (in the absence of probe) and (b) macromonomer at 198 nm (curve 2, scale II, dotted circles) and 468 nm (curve 1, scale I, crossed circles); homopolymer at 468 nm (curve 3, scale III, dotted triangles) (in the presence of probe) at 22 °C plotted against macromonomer and polymer concentrations in aqueous solution. (c) Plot of λ_{max} against macromonomer concentration in aqueous solution.

a micelle-bound fluorescent probe by the binding of a quencher. This technique assumes that the numbers of both probe and quencher molecules per micelle have Poisson distributions, which leads to the expression[29]

$$\ln(I_0/I) = \bar{N}[Q]/(C_s\text{-cmc}) \quad (1)$$

where I_0 and I are the emitted light intensities with quencher concentrations zero and [Q], respectively, $\bar{N}$ is

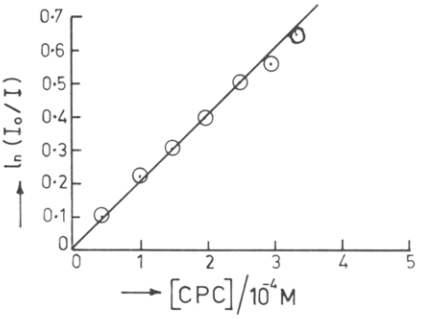

Figure 6. Results of ANS quenching experiments. $\ln(I_0/I)$ plotted against concentrations of *N*-cetylpyridinium chloride for micellar solutions of the macromonomer at 22 °C. [macromonomer] = 8.75×10^{-3} M (fixed) and [ANS] = 1×10^{-5} M (fixed) in aqueous solutions.

the mean macromonomer surfactant aggregation number, and C_s is the total concentration of the macromonomer surfactant; the mean aggregation number, $\bar{N}$, is calculated from the slope of the plot of $\ln(I_0/I)$ against [Q] for a fixed C_s (8.75×10^{-3} M). The probe used was the Mg salt of ANS[30] at a concentration small enough (in the present case 1×10^{-5} M, fixed) to prevent excimer formation so that the ratio $R < 1$, and the quencher used was *N*-cetylpyridinium chloride (CPC).[31] The excitation wavelength was 346 nm, and fluorescence was measured at 435 nm. Figure 6 shows a typical $\ln(I_0/I)$ vs [Q] plot. The aggregation number obtained for the macromonomer in aqueous solution is 20.

Neglecting activity effects and using a biphasic model, the standard free energy change for micelle formation, $\Delta G°_m$, can be written as

$$\Delta G°_m = RT \ln \text{cmc} \qquad (2)$$

where the symbols have their usual significance. Standard state was chosen as the hypothetical solution of the unit molar concentration.

$\Delta G°_m$ values for the macromonomer, homopolymer, and graft copolymer in aqueous solution were estimated and found to be −22.1, −32.2, and −34.1 kJ mol^{-1}, respectively, at 22 °C.

Differential Scanning Calorimetric Behavior of Methoxy-PEG 350, Macromonomer, and Polymer. By incorporation of oligo(ethylene oxide) groups, the methoxy-PEG 350, macromonomer, and polymer exhibit a complicated melting behavior and are shown in Figure 7. Methoxy-PEG 350 shows a glass transition temperature at −50 °C and a melting endotherm in the range of 0–20 °C (Figure 7A), whereas macromonomer surfactant shows a glass transition at −54 °C and a melting endotherm at 0–20 °C (Figure 7B). The results are in accordance with the previously published data.[23,32] The macromonomer shows the existence of liquid crystal modification in the DSC trace at <70 °C. Furthermore, the macromonomer shows birefringence and mobility in the polarizing microscope at a temperature <70 °C and is shown in Figure 8. However, one of the reviewers suggested that Figure 8 has a very strong resemblance of crystalline fibers, for instance, cellulose. A DSC trace of the polymer is shown in Figure 7c. The complicated melting behavior at temperatures >125 °C for methoxy-PEG, macromonomer, and polymer might be due to different endothermal processes, e.g., thermal degradation. However, the melting endotherm of the macromonomer at temperatures >70 °C may be due to thermal polymerization.

Conclusions

The macromonomer and polymers based on methoxypoly(ethylene glycol) are surface active in nature, and the

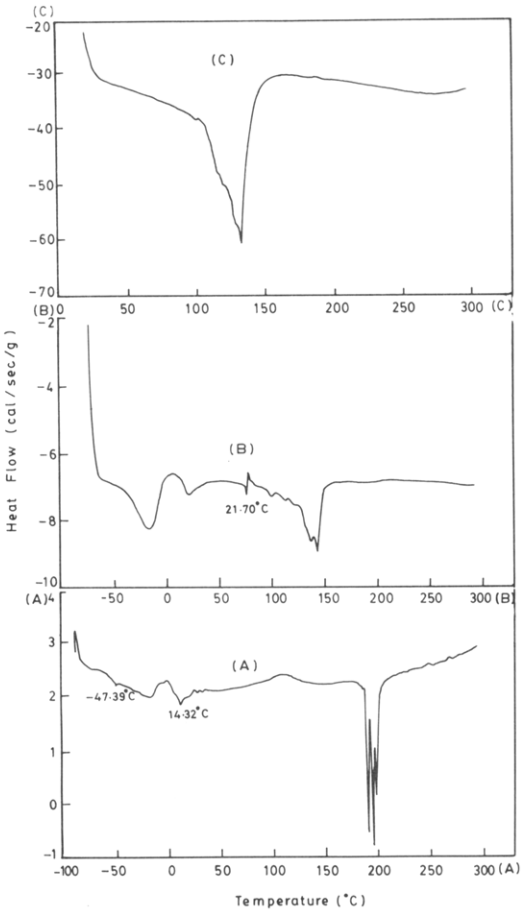

Figure 7. DSC traces of (A) methoxy-PEG, (B) investigated macromonomer, and (C) the derived homopolymer. Scale numbers correspond to curve numbers.

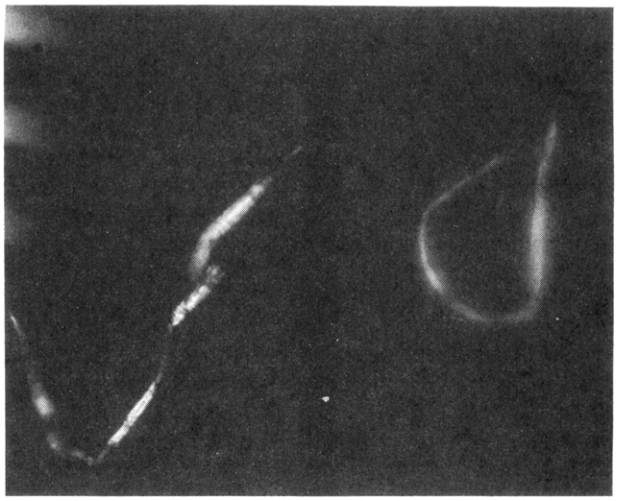

Figure 8. Liquid crystalline behavior of the macromonomer with a cross polarizer at <70 °C.

presence of oligo(ethylene oxide) groups has a marked influence on the aggregation behavior in an aqueous system. The low cmc value of the macromonomer finds useful components in the design of surfactants and an emulsion polymerization reaction free of emulsifier. The graft copolymer with a polystyrene hydrophobic domain has a lower cmc compared to the homopolymer and, therefore, finds application in the design of a variety of industrial formulations. The macromonomer is found to exhibit liquid crystalline behavior as evidenced by DSC and a polarizing microscope. We have found that the

polymers are soluble in aqueous surfactant micelles to a greater extent so that polymer–surfactant micelle interaction[24,33] and thermodynamic studies will be worthwhile in our next program. It will also be worthwhile to study the shape, size, hydration, dynamics, phase transition behaviors, partition coefficient, and self-diffusion studies of the macromonomer micelles by using several spectroscopic, transport, and electrochemical techniques[22,24-25,33-41] in our next program.

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