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Photoluminescent Probes for Water-Soluble Polymers. Pressure and Temperature Effects on a Polyol Surfactant

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Received January 11, 1984

ABSTRACT: Five photoluminescent probes have been employed to investigate the behavior of a poly(ethylene oxide)–poly(propylene oxide) block copolymer in aqueous solution. The measured fluorescence probe parameters, at fixed probe concentration, were found to be dependent on the concentration of copolymers and to demonstrate a "low"-, "medium"-, and "high"-concentration domain. In the high-concentration domain the parameters were found to be extremely sensitive to temperature and pressure. The results are interpreted in terms of intramolecular and intermolecular micelle formation by the copolymer.

Introduction

Water-soluble block copolymers with both hydrophobic and hydrophilic blocks (polyol surfactants) are expected to possess versatile properties characteristic of their amphiphilic structures.[1] Studies of macroscopic properties of polyol surfactants by bulk measurements (cloud point, surface tension, interfacial tension, foam height, etc.) have received extensive attention,[2] and structure and aggregation properties have been measured by light scattering and low-angle X-ray scattering.[3] Luminescence probes have provided a powerful method for the investigation of the structure and dynamics of micelles, polyelectrolytes, and other water-soluble macroaggregates[4] but to date have rarely[5] been employed to investigate polyols. Because of the potential similarity of aggregates formed by conventional micelles formed from detergent monomers and the aggregates formed by polyol surfactants, we have initiated photoluminescence probe investigations of water-soluble block copolymers of hydrophilic blocks of poly(ethylene oxide) and hydrophobic blocks of poly(propylene oxide).[6] The probes employed were pyrenecarboxaldehyde (PyCHO), a reporter of environmental micropolarity via shifts in its fluorescence maximum,[7a] [11-(3-hexyl-1-indolyl)undecyl]trimethylammonium bromide (6-In-11$^+$), a reporter of environmental micropolarity via shifts in its fluorescence maximum[7b] and also a reporter of environmental microviscosity via loss of its fluorescence polarization,[7c] 1,3-di-(α-naphthyl)propane (DNP), a reporter of environmental micropolarity via measurements of the extent of intramolecular excimer formation[7d], pyrene (Py), a reporter of aggregation numbers via its excimer fluorescence decay,[7e] and 1,3-bis(*N*-carbazolyl)propane (BCP), a reporter of environmental changes via excimer emission.[7f] In typical experiments, the fluorescence measurements were made and studied as a function of polymer concentration and then as a function of temperature or pressure at fixed polymer concentration.

Experimental Section

PEO–PPO (0.8:1, catalog no. 16275, MW ≈ 3000, Polysciences, Inc.) was used without further purification.[6] PyCHO (Aldrich Co.) was recrystallized from ethanol. The polymer is assumed to be of the A–B–A type (PEO–PPO–PEO), but its purity has not been established. The syntheses of 6-In-11$^+$ and DNP were described in the literature.[8] Pyrene (Aldrich Co.) was recrystallized from ethanol; BCP was prepared by a literature method.[7f] The emission spectra of PyCHO (excitation wavelength 380 nm), 6-In-11$^+$ (excitation wavelength 300 nm), and DNP (excitation wavelength 290 nm) were taken with a Perkin-Elmer MPF-3L or SLM system 4800 S subnanosecond spectrofluorometer. The decay of pyrene emission was taken with a single-photon-counting apparatus.[9] The pressure cell has been described previously.[10]

Pyrenecarboxaldehyde (PyCHO). The fluorescence emission maximum (λ_m^P) of PyCHO has been shown to be very sensitive to its environment in homogeneous solutions.[7a] Under the assumption that the results from homogeneous solution can be applied to microheterogeneous systems, the fluorescence emission of PyCHO has been employed as a probe of micropolarity in micellar and other aggregates. The fluorescence maximum of PyCHO in aqueous solutions containing PEO–PPO[6] was investigated as a function of PEO–PPO concentration. Figure 1 summarizes the results of these studies. The solid curve shows a plot of λ_m^P for a fixed concentration of 5×10^{-5} M PyCHO. The magnitude of λ_m^P can be classified as having values characteristic of three regions: (1) a region at low polymer concentration (less than 0.1 g/dL) for which the value of λ_m^P is relatively constant and comparable to that of PyCHO in aqueous solution, (2) a region at higher concentrations (ca. 0.1–10 g/dL) for which the value of λ_m^P of PyCHO undergoes a significant blue shift as the polymer concentration is increased, and (3) a region at still higher polymer concentration (>10 g/dL) for which a further, sharper blue shift of λ_m^P occurs as the polymer concentration is increased.

[11-(3-Hexyl-1-indolyl)undecyl]trimethylammonium Bromide (6-In-11$^+$). The fluorescence maximum (λ_m^I) of 6-In-11$^+$ has been shown to be a monitor of microscopic polarity,[7b] and the loss of fluorescence polarization of 6-In-11$^+$ has been shown to be a monitor of microscopic viscosity.[7c] The variation of λ_m^I with PEO–PPO concentration was found to parallel the behavior of λ_m^P as shown in Figure 1. The magnitude of the loss of fluorescence polarization of In-6-11$^+$ was measured by conventional methods[7c] as a function of PEO–PPO concentration. The data were translated into microviscosity (η^I, units of cP) and the results are summarized in Figure 1. As was found for λ_m^P and λ_m^I, the values for η^I fall into three regions, with remarkably good correspondence of the λ_m and η^I methods.

1,3-Di(α-naphthyl)propane (DNP). The ratio of intramolecular excimer fluorescence emission to monomer fluorescence emission (I_e/I_m) has been shown to be a monitor of microscopic viscosity[7d] in microheterogeneous media. The parameters I_e/I_m can be translated into microviscosities, η^N. The results of mea-

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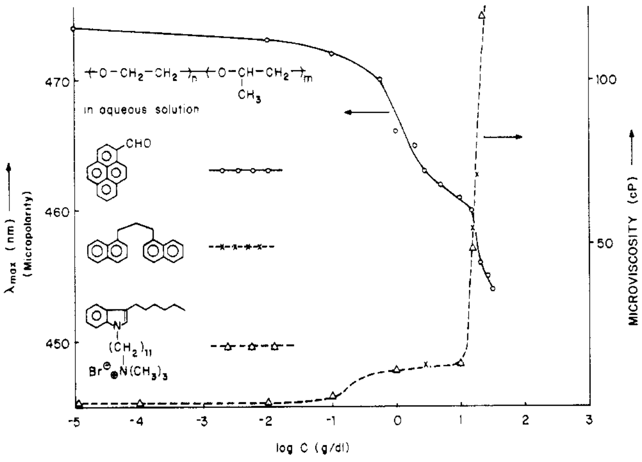

Figure 1. Aqueous PEO–PPO concentration effects on λ_{max} of PyCHO fluorescence (solid curve) and microviscosity (dashed curve; (△) measured by 6-In-11$^+$ fluorescence depolarization method, (×) by DNP excimer formation method).

Table I
Pressure and Temperature Effects on λ_{max} and Intensity of PyCHO Fluorescence in 20 g/dL PEO–PPO Aqueous Solution

press, atm	temp, °C	λ_{max}, nm	$I(P)/I$(atm)	$I(T)/I(20\ °C)$
1	20	458	1.0	
250	20	463	3.6	
500	20	465	5.2	
1000	20	467	6.7	
2000	20	470	7.9	
1	5	462		1.8
1	10	461		1.6
1	20	458		1.0
1	25	452		0.22
1	35	449		0.11
1	45	446		0.091
1	60	442		0.048

surements of η^N as a function of PEO–PPO concentration are shown in Figure 1 and are completely superimposable on the curve defined by the plot of η^I vs. PEO–PPO concentration.

Pyrene (Py). The aggregation number of micelles and microemulsions can be determined by analyzing the time decay of pyrene monomer emission[7e] in conditions where the [pyrene]/[micelle] ratio is around 1. Applying this method to aqueous solutions of PEO–PPO, the aggregation number of the PEO–PPO "micelle" (at 20 g/dL PEO–PPO) was determined to be ca. 52.

Pressure Effects. The influence of applied pressure on the value of λ_m^P at 20 °C is summarized in Table I for 5×10^{-5} M PyCHO at "high" concentrations of PEO–PPO (20 g/dL). In addition, the intensity (at constant OD) at the maximum of PyCHO fluorescence (I_m^P) was measured as a function of pressure (Table I). Also the influence of applied pressure on the emission spectra of DNP and BCP at 20 g/dL aqueous PEO–PPO solutions was measured and is shown in Figures 2 and 3.

Temperature Effects. The influence of temperature on the values of I_m^P was measured at 1 atm for 5×10^{-5} M PyCHO at 20 g/dL PEO–PPO, and the results are summarized in Table I. The emission spectra of BCP at 20 g/dL aqueous PEO–PPO solution were measured as a function of temperature (Figure 4).

Discussion

The results of five different measurements on four different probes are all consistent with the conclusion that transitions occur in the structure and/or state of aggregation of PEO–PPO and produce "the concentration regions" that occur in Figure 1.

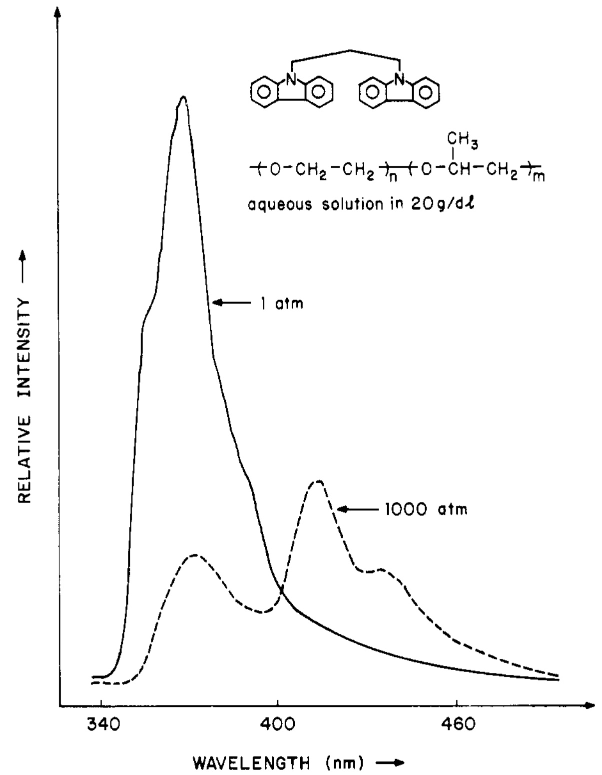

Figure 2. Pressure effect on DNP emission in 20 g/dL PEO–PPO aqueous solution.

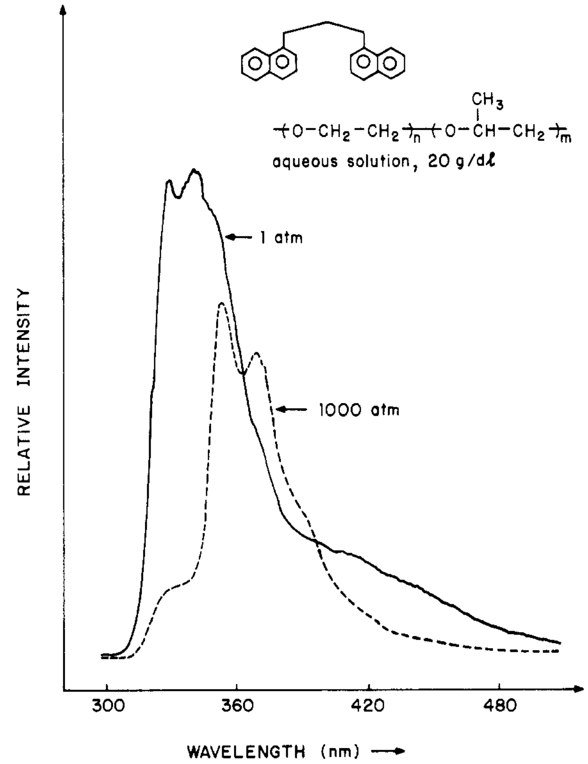

Figure 3. Pressure effect on BCP emission in 20 g/dL PEO–PPO aqueous solution.

The micropolarity data, λ_m^P and λ_m^I (see Figure 1), suggest that the probes PyCHO and 6-In-11$^+$ reside mainly in the aqueous phase in region 1. In this region, the values of λ_m^P and λ_m^I are those expected if the probe resides mainly in the aqueous phase or in a highly polar environment. Thus, the polymer structure is evidently unable to bind to or accommodate a hydrophobic probe in this region. In region 2, however, the steady blue shift of λ_m^P indicates that the probe is being drawn into a hydrophobic environment. We suggest that this new environment is due to a change in the conformation of the solvated strands of single molecules of the block copolymer to form monomolecular polymer micelles. The second transition

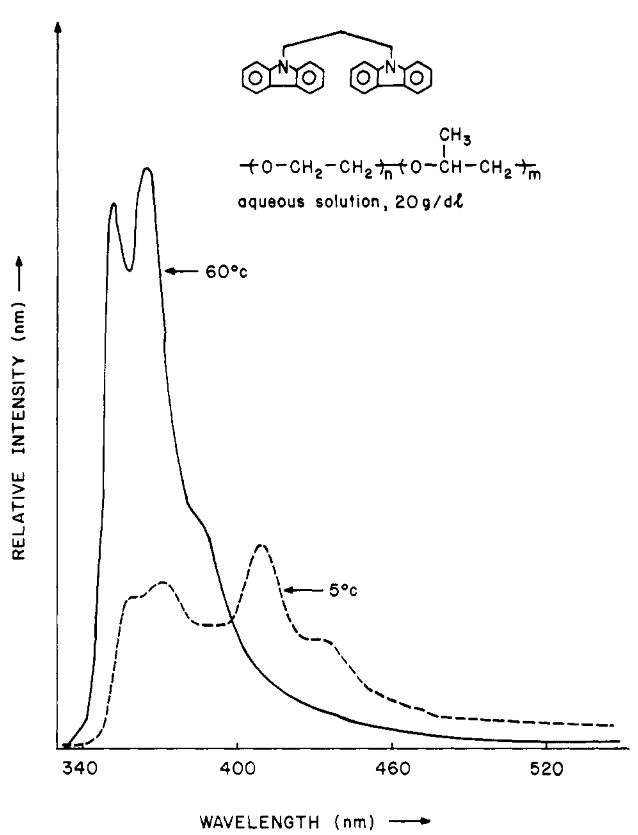

Figure 4. Temperature effect on BCP emission in 20 g/dL PEO–PPO aqueous solution.

(region 2 to region 3) is due to polymer aggregation to form polymolecular polymer micelle with aggregation number ca. 52 at 20 g/dL PEO–PPO aqueous solution.

Behavior similar to that shown in Figure 1 was observed when a fluorescence probe and light scattering were employed to investigate the behavior of a water-soluble ABA block copolymer of hydrophobic poly(2-hydroxyethyl methacrylate) and hydrophilic poly(ethylene oxide).[5] The first transition (in our terminology region 1 to region 2) was assigned to formation of a hydrophobic domain of contracted polymer chains undergoing a conformational change and forming a monomolecular polymer micelle. The second transition (in our terminology region 2 to region 3) was assigned to intermolecular aggregation of the polymer micelles.

A significant temperature dependence was observed in the measured properties and was interpreted as resulting from contraction of monomolecular micelles which leads to densification of the hydrophobic core at low temperature. However, in the region of polymolecular micelles, the more hydrophobic probe anilinonaphthalene (AN) experienced a more hydrophilic environment (λ_m red shift) with increasing temperature, while the more hydrophilic probe 8-anilinonaphthalene-1-sulfonate (ANS), experienced a less hydrophilic environment (λ_m blue shift) with increasing temperature. Data from low-angle X-ray scattering were consistent with a significant intermixing of the hydrophobic and hydrophilic phases as the temperature was increased.

Our results concerning the temperature dependence of PyCHO emission in the aqueous solutions of PEO–PPO parallel those of the ANS probe discussed above; i.e., in region 3, PhCHO experiences a more hydrophobic environment at higher temperatures (λ_m^P undergoes a blue shift in addition to an intensity decrease, Table I). The opposite temperature effects demonstrated by the more hydrophobic and more hydrophilic probes can be rationalized in terms of their different site locations in a polymolecular micelle. Both PyCHO and ANS probes are expected to dissolve in the interfacial region of the polymolecular micelle (in analogy to their locations in conventional micelles formed from surfactant monomers), while AN is expected to reside, on average, more in the hydrophobic core of the polymolecular micelle.

As the temperature is increased, a greater mixing of the PEO chains into the hydrophobic core due to increased thermal agitation is expected, a conclusion consistent with low-angle X-ray scattering. Thus, the AS molecule, located in the hydrophobic micellar core, experiences a more hydrophilic environment at higher temperatures, while PyCHO or ANS, located in the hydrophilic micellar interface, experiences a more hydrophobic (less polar) environment at higher temperatures.

Since the results of a *decrease* in *temperature* parallels that of an *increase* in *pressure* for the PyCHO system in PEO–PPO polymolecular micelles, we propose that an increase in pressure causes a reduction in the mixing of the hydrophobic and hydrophilic portions in the interfacial region of the micelle.

The new emissions observed for BCP at high pressures or low temperatures appear to be due to intramolecular excimer formation. If so, the denser hydrophobic core created by the lowering of temperature or the increasing of pressure appears to cause more efficient overlap of the carbazole aromatic rings.

It must be pointed out that until the purity of the copolymer has been established, some of the effects might be related to the presence of impurities, e.g., A–B-type copolymers. Investigations of purified samples by fluorescent probe methods are in progress.

Conclusion

The use of fluorescent probes has been found to reveal concentration-dependent structural changes in a block copolymer of ethylene oxide and propylene oxide. Evidence was found that at high concentration (ca. 10 g/100 g of water) this copolymer undergoes exceptional pressure-dependent structural changes. The fluorescent probe method promises to be useful to investigate the structure of aggregates formed by water-soluble polymers.

Acknowledgment. We thank the National Science Foundation and the Army Office of Research for their generous support of this research.

Registry No. (PEO)·(PPO) (copolymer), 9003-11-6; PyCHO, 3029-19-4; 6-In-11$^+$, 51097-79-1; DNP, 14564-86-4; BCP, 25837-66-5; Py, 129-00-0.

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Electrical Conductivity of Urethane-Substituted Poly(diacetylenes): Effect of Substituent Side Groups and Molecular Weights

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ABSTRACT: Direct-current conductivity σ_{dc} of $CHCl_3$-cast films of three urethane-substituted poly(diacetylenes) [poly(*x*ACMU)] was studied as a function of dopant (iodine) concentration *Y*, temperature *T*, and molecular weight. The polymers were poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], poly[4,6-decadiyne-1,10-diol bis([(ethoxycarbonyl)methyl]urethane)], and poly[3,5-octadiyne-1,8-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(3BCMU), poly(3ECMU), and poly(2BCMU), respectively. In all cases, the doping increased the σ_{dc} of $CHCl_3$-cast films, which were poorly crystalline. The substituent side groups affected the conductivity very little. The log σ_{dc} vs. log *Y* curves showed a break at characteristic dopant concentrations Y_c, which were roughly the same for the three poly(*x*ACMUs). The log σ_{dc} vs. log $1/T$ curves also showed a break at characteristic temperatures T_c. There appeared to be two different conduction regimes above and below T_c. Possible conduction mechanisms were discussed. The dependence of σ_{dc} on molecular weight was investigated for $CHCl_3$-cast films of seven poly(3BCMU) samples. The σ_{dc} at given *Y* was proportional to the number-average molecular weight M_n. The thermal activation energy E_a of conduction in the region $T > T_c$ was independent of *Y* but proportional to M_n^{-1}, and the value at $M_n \rightarrow \infty$ was approximately 0.44 eV.

Introduction

In recent years the electrical conduction of fully conjugated linear polymers has been attracting attention as a model of low-dimensional conductors.[2-4] One of such polymers is poly(diacetylenes) having a highly conjugated poly(enyne) backbone with an admixture of the butatriene structure.[5,6]

The solid-state polymerization of diacetylenes ($RC\equiv C-C\equiv CR$) with various substituent groups R has been studied and reviewed by many authors.[7-9] Since some poly(diacetylenes) were obtained as almost perfect single crystals without macroscopic defects, impurities, and dislocations, they have been used as model substances for investigation of the properties of conjugated polymers.[6,10] Usually, poly(diacetylenes) have very low dark conductivities and photoconductivities.[11-13] However, recent findings on the enhancement of electrical conductivity of polyacetylene by doping has stimulated studies of the conductivity of doped poly(diacetylenes).[4,14,15] These findings also motivated us to carry out a series of studies on some poly(diacetylenes) soluble in organic solvents such as $CHCl_3$.[16] The soluble poly(diacetylenes) are appropriate for the studies of the relationship between molecular characteristics and electrical conductivity because they can be easily characterized by dilute solution techniques. The poly(diacetylenes) studied here have the substituent R = $-(CH_2)_xOCONHCH_2COO(CH_2)_yCH_3$ with x = 1–4 and y = 1 or 3. They are referred to as poly(*x*ACMU), standing for the number of methylene groups, and [(*a*lkoxycarbonyl)*m*ethyl]*u*rethane side chain.

We have reported the synthesis, characterization, and mechanical and electrical properties of poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(3BCMU), for which x = 3 and B = butoxy (y = 3).[17,18] The results of our study of poly(3BCMU)[18] were as follows. (i) The glass transition temperature T_g of $CHCl_3$-cast film is increased by doping with iodine. (ii) The electrical conductivity of the film is largely increased from 10^{-12} to 10^{-5} Ω^{-1} cm^{-1} by doping with iodine. (iii) The conductivity may depend on the molecular weight and its distribution and/or the degree of crystallinity, although the films are poorly crystalline. (iv) The conduction appears to occur mainly through an electronic mechanism; the iodine dopant interacts with and provides charge carriers along the conjugated main chains.

Recently, we also examined $CHCl_3$-cast films and single crystals of poly[5,7-dodecadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)], abbreviated as poly(4BCMU), for which x = 4 and y = 3.[19] From a preliminary X-ray diffraction analysis on poly(4BCMU) single crystals, the following conclusions were deduced.[19] The fiber period (c axis) and the subcell dimensions perpendicular to the c axis are c = 0.488 nm, a' = 0.533 nm, and b' = 5.436 nm, respectively. The b' axis is almost parallel to the urethane group, and the a' axis is perpendicular to both of the main chain and urethane group directions and hence corresponds to the chain stacking direction. The electrical conductivity of $CHCl_3$-cast films of this polymer was increased from 10^{-13} to 10^{-5} Ω^{-1} cm^{-1} by doping with 2 mol of I_3^- per 4BCMU unit in a manner similar to that of poly(3BCMU). However, a single-crystal specimen could be doped only to a level of 2×10^{-2} mol, and the maximum attainable conductivities along the c axis, $\sigma_{\parallel}$, and along the a' axis, $\sigma_{\perp}$, were 4.1×10^{-7} and 6.5×10^{-8} Ω^{-1} cm^{-1}, re-

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