Photoluminescent Probes for Water-Soluble Polymers. Pressure and Temperature Effects on a Polyo1 Surfactant

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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. Studies of macroscopic properties of polyol surfactants by bulk measurements (cloud point, surface tension, interfacial tension, foam height, etc.) have received extensive attention, and structure and aggregation properties have been measured by light scattering and low-angle X-ray scattering. Luminescence probes have provided a powerful method for the investigation of the structure and dynamics of micelles, polyelectrolytes, and other water-soluble macroaggregates but to date have rarely 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). The probes employed were pyrenecarboxaldehyde (PyCHO), a reporter of environmental micropolarity via shifts in its fluorescence maximum; [11-(3-hexyl-1-indolyl)undecyl]trimethylammonium bromide (6-In11+), a reporter of environmental micropolarity via shifts in its fluorescence maximum and also a reporter of environmental microviscosity via loss of its fluorescence polarization; 1,3-di-(a-naphthyl)propane (DNP), a reporter of environmental micropolarity via measurements of the extent of intramolecular excimer formation, pyrene (Py), a reporter of aggregation numbers via its excimer fluorescence decay, and 1,3-bis(N-carbazolyl)propane (BCP), a reporter of environmental changes via excimer emission. 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. 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-In11+ and DNP were described in the literature. Pyrene (Aldrich Co.) was recrystallized from ethanol; BCP was prepared by a literature method. The emission spectra of PyCHO (excitation wavelength 380 nm), 6-In11+ (excitation wavelength 300 nm), and DNP (excitation wavelength 290 nm) were taken with a Perkin-Elmer MPF-5L or SLM system 4800 S subnanosecond spectrofluorometer. The decay of pyrene emission was taken with a single-photon-counting apparatus. The pressure cell has been described previously.

Pyrenecarboxaldehyde (PyCHO). The fluorescence emission maximum (λmax) of PyCHO has been shown to be very sensitive to its environment in homogeneous solutions. The magnitude of λmax is expressed 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 λmax 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 λmax 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 λmax occurs as the polymer concentration is increased.

1,3-Di-(a-naphthyl)propane (DNP). The ratio of intramolecular excimer fluorescence emission to monomer fluorescence emission (Ie/Im) has been shown to be a monitor of microscopic viscosity in microheterogeneous media. The parameters Ie/Im can be translated into microviscosities, η′. The results of mea-
Pressure and Temperature Effects on $\lambda_{\text{max}}$ and Intensity of PyCHO Fluorescence in 20 g/dL PEO-PPO Aqueous Solution

<table>
<thead>
<tr>
<th>Press, atm</th>
<th>1</th>
<th>250</th>
<th>500</th>
<th>1000</th>
<th>Py</th>
<th>1</th>
<th>5</th>
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<th>10</th>
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<th>1</th>
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<th>1</th>
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<tr>
<td>Temp, °C</td>
<td>20</td>
<td>20</td>
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<td>45</td>
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<td>60</td>
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<tr>
<td>$\lambda_{\text{max}},$ nm</td>
<td>458</td>
<td>483</td>
<td>485</td>
<td>487</td>
<td>480</td>
<td>462</td>
<td>461</td>
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<td>449</td>
<td>446</td>
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<tr>
<td>$I(P)/I(atm)$</td>
<td>1.0</td>
<td>3.6</td>
<td>5.2</td>
<td>6.7</td>
<td>7.9</td>
<td>1.8</td>
<td>1.6</td>
<td>1.0</td>
<td>0.22</td>
<td>0.11</td>
<td>0.091</td>
<td>0.048</td>
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<td></td>
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<tr>
<td>$I(20^\circ\text{C})$</td>
<td>5.2</td>
<td>6.7</td>
<td>7.9</td>
<td>7.9</td>
<td>7.9</td>
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Pressure Effects. The influence of applied pressure on the value of $\lambda_{\text{max}}$ at 20°C is summarized in Table I for 5 $\times$ 10^{-6} M PyCHO at "high" concentrations of PEO-PPO (20 g/dL). In addition, the intensity (at constant OD) at the maximum of PyCHO fluorescence ($I_{\text{max P}}$) 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 $I_{\text{max P}}$ was measured at 1 atm for 5 $\times$ 10^{-6} 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.

The micropolarity data, $\lambda_{\text{pp}}$ and $\lambda_{\text{mm}}$ (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 $\lambda_{\text{pp}}$ and $\lambda_{\text{mm}}$ 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 $\lambda_{\text{pp}}$ 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
parallel those of the ANS probe discussed above; i.e., in temperature was increased. PyCHO emission in the aqueous solutions of PEO-PPO hydrophobic and more hydrophilic probes can be ration-
ized in terms of their different site locations in a poly-
molecular micelle. Both PyCHO and ANS probes are expected to dissolve in the interfacial region of the poly-
molecular micelle (in analogy to their locations in con-
ventional micelles formed from surfactant monomers), while AN is expected to reside, on average, more in the hydrophobic core of the polymeric 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 Py-
CHO 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 co-
polymer 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 fluores-
cent 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-ll+, 51097-79-1; DNP, 14564-86-4; BCP, 25837-66-5; Py, 129-00-0.

References and Notes

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(2) Chapter 1 of ref 1.
(11) Poly(ethylene oxide)–poly(propylene oxide) (0.8:1) block co-
polymer, MW = 2917, was purchased from Polysciences, Inc.
Poly(diacetylenes): Effect of Substituent Side Groups and Molecular Weights

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ABSTRACT: Direct-current conductivity $\sigma_{dc}$ of CHCl$_3$-cast films of three urethane-substituted poly(diacetylenes) [poly(xACMU)] 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-1,5-diol bis([n-butoxycarbonyl]methyl)urethane)], abbreviated as poly(3BCMU), poly(3ECMU), and poly(2BCMU), respectively. In all cases, the doping increased the $\sigma_{dc}$ of CHCl$_3$-cast films, which were poorly crystalline. The substituent side groups affected the conductivity very little. The log $\sigma_{dc}$ vs. log $Y$ curves showed a break at characteristic dopant concentrations $Y_c$, which were roughly the same for the three poly(xACMU). The log $\sigma_{dc}$ vs. $1/T$ 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 $\sigma_{dc}$ on molecular weight was investigated for CHCl$_3$-cast films of seven poly(3BCMU) samples. The $\sigma_{dc}$ 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 $M_n \to \infty$ 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. One of such polymers is poly(diacetylenes) having a highly conjugated poly(ene) backbone with an admixture of the butatriene structure. The solid-state polymerization of diacetylenes (RC=CR=C=CR) with various substituent groups R has been studied and reviewed by many authors. 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. Usually, poly(diacetylenes) have very low dark conductivities and photoconductivities. However, recent findings on the enhancement of electrical conductivity of polyacetylene by doping has stimulated studies of the conductivity of doped poly(diacetylenes). These findings also motivated us to carry out a series of studies on some poly(diacetylenes) soluble in organic solvents such as CHCl$_3$. 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$_2$)$_x$OCONHCH$_2$COO(CH$_2$)$_y$CH$_3$ with $x = 1$–4 and $y$ = 1 or 3. They are referred to as poly(xACMU), standing for the number of methylene groups, and [alkoxy-carbonyl]methyl)urethane 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), poly(3ECMU), and poly(2BCMU), respectively. In all cases, the doping increased the $\sigma_{dc}$ of CHCl$_3$-cast films, which were poorly crystalline. The substituent side groups affected the conductivity very little. The log $\sigma_{dc}$ vs. log $Y$ curves showed a break at characteristic dopant concentrations $Y_c$, which were roughly the same for the three poly(xACMU). The log $\sigma_{dc}$ vs. $1/T$ 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 $\sigma_{dc}$ on molecular weight was investigated for CHCl$_3$-cast films of seven poly(3BCMU) samples. The $\sigma_{dc}$ 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 $M_n \to \infty$ was approximately 0.44 eV.

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