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Short Communication

Study of polystyrene–poly(ethylene oxide) block copolymer micelles in aqueous solution by size-exclusion chromatography

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ABSTRACT

Size-exclusion chromatography experiments are reported for aqueous solutions of polystyrene–poly-(ethylene oxide) (PS–PEO) diblock and triblock copolymers. These samples show two peaks: the first peak elutes due to polymer micelles (characterized independently by light scattering), and the second due to individual polymer molecules. Sharp micelle peaks imply slow dynamic exchange. By collecting fractions and examining them by Fourier transform infrared spectrometry we were able to establish that the single-molecule peak contained more PEO and less PS than the micelle.

INTRODUCTION

Size-exclusion chromatography (SEC) is a powerful method for characterizing polymer molecules in solution. It also has a tremendous potential for the study of colloidal systems [1], but these applications have been much slower to develop, either because of technical problems, or because of the complexity of the behaviour of the systems themselves.

The major limitation for using porous gel columns in the separation of colloidal particles in aqueous media comes from the adsorption of particles onto the packing materials or from plugging of the column by aggregated particles. In both instances, the injected materials will either be lost in the column or take a very long time to elute. In the case of micelles, the micelle–single molecule (unimer) association and dis-

sociation processes during elution represent an additional complication which can become particularly severe if the single molecules adsorb strongly onto the packing material. However, if adsorption can be avoided by choosing a proper SEC column and correct experimental conditions, the complications which arise from the micelle–unimer dynamic equilibrium can be utilized to study the association–dissociation behaviour of such systems. Theoretical models to describe these effects have recently been proposed [2–4].

There have been several reports on the use of SEC for the characterization of block copolymer micelles in non-aqueous systems or in organic solvent–aqueous mixtures [5–9]. Berlinova *et al.* [5] investigated the SEC of polystyrene–poly(ethylene oxide) (PS–PEO) block copolymers in water–methanol (1:1). For diblock copolymers they observed two peaks, one of which was assigned to the micelle, and a second peak at longer retention time which was attributed to a PEO homopolymer impurity. From the sharpness of the micelle peak they inferred that the relaxation of these micelles to free chains was very slow. This point of view was originally proposed by Price and co-workers [7,8], who studied several block copolymer micelles in organic solvents and found that the successful elution of copolymer micelles as a single narrow peak in a time period of a few hours was the result of the even slower dissociation process of the copolymer micelles. On the other hand, Spacek and Kubin [9] found that the elution volume and elution concentration of micelles and unimers depended on the solvent composition and measurement temperature for their systems (kraton in dioxane–heptane), and that the shape of the chromatograms was influenced by the disruption and reestablishment of the association equilibrium during the separation.

In this paper, we wish to report results on the SEC of polystyrene–poly(ethylene oxide) diblock (PS–PEO) and triblock (PEO–PS–PEO) copolymers in water. In both systems we observe that micelles and unimers are eluted as well-separated peaks from a conventional aqueous SEC column. The analysis is rapid and convenient. Perhaps the most interesting conclusion from our experiments is that when the block copolymer has a somewhat broad molecular weight distribution [*e.g.*, weight-average molecular weight (M_w)/number-average molecular weight (M_n) = 1.5], the unimer peak derives from material enriched in the component (here PEO) forming the soluble block.

TABLE I

COPOLYMER SAMPLE PROPERTIES AND THE SEC RETENTION TIMES (t)

Sample	M_n (total) (g/mol)	PEO (%, w/w)	M_w/M_n	R_h (nm)	$t_{micelle}$ (min)	t_{unimer} (min)
Diblock						
Jlm5	8500	80	1.6	10	3.55	6.78
DB40	14100	72	1.2	15	3.55	6.72
Triblock						
Jlm6	18000	79	1.1	11	3.50	6.70
Jlm11	25900	80	1.5	18	3.47	6.55

EXPERIMENTAL

The PEO–PS–PEO triblock and PS–PEO samples were prepared in Mulhouse by standard anionic polymerization methods. The details have been reported elsewhere [10,11], and the characteristics of these polymers are listed in Table I.

Solutions for SEC analysis were prepared by weighing sufficient sample to give a final concentration of 1 mg/ml, adding sufficient doubly distilled deionized (Millipore Milli-Q grade) water, and heating the solution at $\approx$ 65°C for 2 h to complete dissolution of the samples. The solutions were then allowed to cool to room temperature (22°C) prior to the SEC analysis.

The SEC measurements were performed using a Micropak TSK-Gel G5000 PW column (Toyo Soda, purchased from Varian; packing material, polyether type; average pore size, $\approx$ 1000 Å)[a] and a Waters Model 510 pump, with a flow-rate of 1.5 ml/min. Deionized water (Millipore Milli-Q water system) was used as the eluent. Two detectors were used: a Waters R401 differential refractometer (RI) and a Kratos fluorometer (FL). As the fluorescence excitation wavelength 268 nm was chosen. The wavelength range (emission wavelength = 310–410 nm) corresponding to that of polystyrene excimer emission, the main emission from polystyrene, particularly in the bulk state, was chosen as the fluorescence emission band. Solutions were introduced onto the column by a Rheodyne six-way injector. The detected refractive index and fluorescence signals were recorded by a PC-XT-type microprocessor through a homemade interface card. The Fourier transform in infrared (FT-IR) measurements were made on a Nicolet Analytical Instruments 5DX FT-IR spectrometer.

RESULTS AND DISCUSSION

Fig. 1 shows a typical SEC trace from injection of an aqueous solution of our block copolymers onto the TSK-Gel G5000 PW polyether type column. In independent studies using quasi-elastic light scattering (QELS) and static light scattering (SALS), this particular sample was shown to form a narrow distribution of spherical micelles with a hydrodynamic radius R_h = 18 nm and a mean aggregation number N = 43 [12].

We assign the peak at a retention time of 3.5 min, which has both strong RI and FL signals, to eluting micelles. We found, as shown in Table I, that the measured retention time, t_{micelle}, is insensitive to the sample composition and to the overall hydrodynamic radius (R_h) of the micelles. This is a curious result, particularly since the micelles of Jlm5 have an R_h value (9 nm) half that of the micelles of Jlm11 (18 nm), and independent experiments on surfactant-stabilized latex samples [13] have shown that the elution volume of the micelles is well within the separation range of the column. Although details are not presented, Berlinova et al. [5] reported identical elution times for a series of micelles of diblock copolymers of different molecular weights.

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[a] Our SEC column has been exposed repeatedly to dilute aqueous solutions of sodium dodecyl sulphate. The manufacturer's data sheet indicates that this kind of treatment can modify the column characteristics from that of a new column exposed only to water. Nevertheless, we always obtain reproducible results with this column.
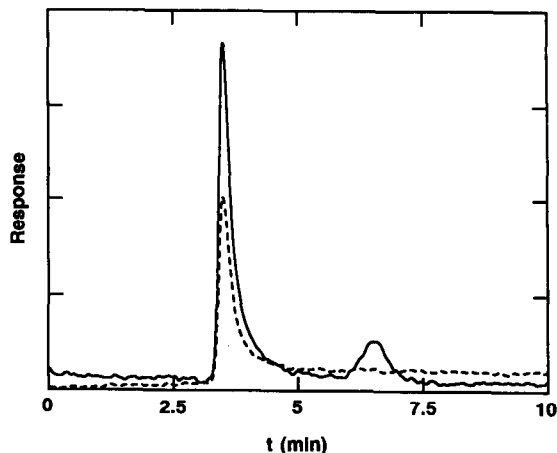
Fig. 1. The SEC trace of Jlm11 in aqueous solution, using a Micropak TSK-Gel G5000 PW size-exclusion column at a flow-rate of 1.5 ml/min. The solid line is the response from the refractive index detector and the dashed line is the fluorescence signal (excitation wavelength 268 nm and emission wavelength 310–410 nm).

Eluent samples containing the substances eluted at 3.5 min and 6.7 min were collected, concentrated and analyzed by FT-IR spectroscopy. Both contain block copolymer. The spectra are shown in Fig. 2. One notes the presence in both samples of a peak at 698 cm^{-1} characteristic of the C–H deformation vibration of PS and a peak at 1115 cm^{-1} characteristic of the C–O stretching vibration of PEO. We assign the SEC peak at 6.7 min to individual block copolymer molecules (unimers). The data in Table I indicate that the retention times for unimers decrease with increasing molecular weight. There is no fluorescence signal observed for the unimers. This important observation indicates that the aqueous medium is able to quench the PS
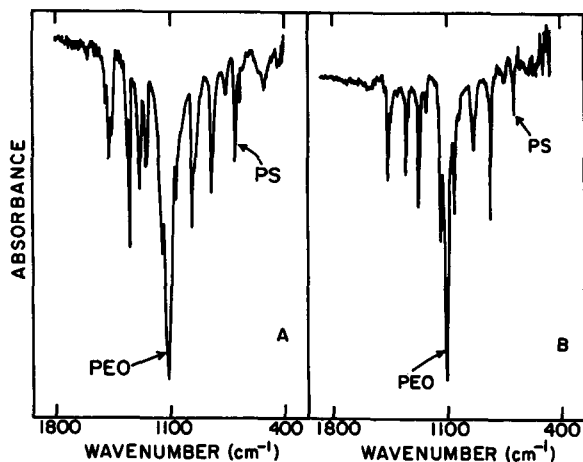

Fig. 2. FT-IR spectra from (A) Jlm11 and (B) substance collected from the monomer peak (the right peak in Fig. 1). The ratio of the two characteristic peaks (PS wavenumber = 698 cm^{-1} and PEO wavenumber = 1115 cm^{-1}) was used as an indicator for the relative PS content in the copolymer molecules.

fluorescence in the unimer, whereas in the larger micelle, the excited groups are protected from quenching.

By using the ratio of the characteristic FT-IR absorbance (A) of PS (wavenumber 698 cm^{-1}) to that of PEO (wavenumber 1115 cm^{-1}) as a measure of composition, we calculated that $(A_{PS}/A_{PEO})_{unimer}/(A_{PS}/A_{PEO})_{original} \approx 0.71$, *i.e.*, there is about 30% less PS in the unimer than in the original sample. The FT-IR analysis indicates that the micelles are formed preferentially from polymer enriched in the insoluble compound due to fractionation during micelle formation. This particular block copolymer sample has a large molecular weight distribution and is also likely to have a significant compositional heterogeneity. We know from independent studies that the critical micelle concentration (CMC) of the block copolymer in water depends critically on the size of the PS block [12,14]. These values are of the order 1–5 mg/l for the samples listed in Table I. Thus, those molecules enriched in styrene units stay in micelle form and those with a lower PS content remain as unimers. Consequently, both the unimer molecules and the molecules in micelles have a different composition distribution when compared with the original block copolymer material. The result suggests that preparative SEC experiments in selective solvents may provide a means of fractionating the block copolymer samples [15].

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