Chromatographic Separation of Micelle-Forming Three-Block Copolymers: Effect of the Finite Rate of Micelle Formation on the Chromatographic Result

INTRODUCTION

In our recent study[1] we investigated micelle-forming three-block copolymers during the separation carried out in the mode of high-efficient size-exclusion chromatography. The copolymer under study was polystyrene-block-poly(ethene-stat-butene)-block-polystyrene (Kraton G 1652, Shell) in a mixed solvent *n*-heptane-1,4-dioxane. The experiments were carried out so that in the system under the conditions of chromatography both the individual molecules of the copolymer (unimer[2]) could coexist with their associates (micelles). In ref.[1] it was stated, using an analogy between this associating system and a theoretical anaylsis[3] valid for the isomerizing solutes, that if the solution derived for isomerizing systems is valid also for micelle-forming molecules, the half-life time of at least one of the reversible reactions (i.e., formation or decomposition of the micelles) is not negligibly small compared with the duration of the chromatographic experiment.

In an effort to reduce somewhat such a wide time range, and also to verify the validity of solution[3] for the system investigated by us, experiments in this study were performed so that the polymer was injected onto the chromatographic column at such composition of the solvent when either predominantly the unimer, or on the contrary practically only micelles can exist in the solution, and the composition of the mobile phase was chosen to guarantee predominantly the existence of micelles or of the unimer, respectively. Under such conditions one may assume that a comparison between the retention times of the polymer which during the chromatographic analysis must be completely transformed from the micellar (unimer) form into the unimer (micelles) and the corresponding retention times determined under conditions when such transformation does not take place will provide direct data on the transformation time micelle unimer and vice versa.

EXPERIMENTAL

Chemicals, apparatus, and experimental arrangement were the same as in ref.,[1] with the only difference that the system was thermostated throughout the measurement to a constant temperature of 28°C in an air thermostat and the apparatus was supplemented with an integrator (Minigrator, Spectra Physics, USA). Four different columns packed with silica gel produced at this Institute were used in the experiments: A (500 × 4 mm ID, mean particle diameter d_p = 8 μm, exclusion limit for polystyrene in tetrahydrofuran $M_e = 1 \times 10^5$), B (250 × 6 mm ID, d_p = 5 μm, $M_e = 10^6$), C (250 × 6 mm ID, $M_e < 10^5$), D (250 × 6 mm ID, $M_e > 10^6$). Stock solutions of the copolymer (26.9 mg/ml) were prepared in a heptane/dioxane mixture in the volume ratio 20/80 (at 28°C predominantly micelles exist in the solution, M solvent), and in the volume ratio 45/55 (copolymer exists predominantly as the unimer, U solvent) and stored in sealed glass ampoules. The same compositions of the mixed solvent were used as the mobile phase; the volume flow rate was 0.2 ml/min. Samples, 20 μL in volume, were injected by using a stop-flow valve directly onto the top of the column used.

RESULTS AND DISCUSSION

The measured retention times (rt), along with the $\bar{A}$ values (numbers proportional to the size of the integrated area) obtained as rounded-off averages from five repeated measurements for the particular types of columns are summarized in Table I.

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TABLE I
Retention Times and Areas of the Peaks for Copolymer Kraton G 1652

	Inject-Micelles				Inject-Unimer			
	M-solvent as a mobile phase		U-solvent as a mobile phase		M-solvent as a mobile phase		U-solvent as a mobile phase	
Column	$\overline{A}$	rt (s)	$\overline{A}$	rt (s)	$\overline{A}$	rt (s)	$\overline{A}$	rt (s)
A	160	900	155	1170	110	950	153	1180
B	145	930	155	1150	100	960	155	1180
C	155	720	145	820	110	720	140	850
D	165	1260	155	1430	112	1300	153	1430

It can be seen from results in Table I that the retention times of the analyzed copolymer depend only on the composition of the mobile phase (i.e., if we have an M solvent or a U solvent) and virtually do not depend on the form in which the polymer has been injected (i.e., associated or dissociated). The minimal differences found here can be compared with the error (reproducibility) of the experiments and are probably caused by the instability of flow in the "stop-flow" injection used. We may assume, therefore, that both the formation and decomposition of the micelles proceed immediately at the start of the chromatographic run within a time shorter than 20–30 sec, and that the time for which the polymer remains in the column is virtually unaffected by the kinetics of the micelle $\rightleftarrows$ unimer transition.

Data in Table I indicate yet another interesting phenomenon. If a copolymer dissolved in a U-type solvent is injected into the mobile phase of the M solvent type (and only in this case, cf. column 6 of the Table I), there is a remarkable decrease in the area $\overline{A}$ proportional to the amount of the polymer leaving the chromatographic column. This material deficit is evidently larger than the error to which the reproducibility of injection is subjected. It should be stated that the peaks thus obtained remain symmetrical, without any sign of tailing. The phenomenon just described can be explained by assuming that one part of micellar formations due to association inside silica gel pores cannot leave particles of the sorbent for steric reasons. Under described conditions, the polymer in the injected volume is present as unimer and in this form, along with the injected U-solvent, it diffuses into pores of silica gel at the very beginning of the column. During the subsequent chromatographic separation the polymer remains in the region of the mobile phase of the M solvent type, and micelles formed inside the sorbent cannot leave narrow pores accessible to the unimer; this causes the deficit of the polymer at the column outlet. With another combination of the injection and mobile phase composition such phenomenon cannot obviously take place.

If one accepts such an explanation, it is possible, on the basis of a strongly simplified diffusion model in the spherical particle of a porous packing, to estimate quantitatively the time needed for the formation of micelles under the conditions used in the investigation. By assuming that the void volume of the column amounts to 34% of its total volume and that pores occupy 70% of the volume of each particle, then, for example, for column A we obtain the elution volume for micelles $V_{e,m}$ = 3.00 mL, the elution volume for the unimer $V_{e,u}$ = 3.93 mL, the inner volume of the gel V_i = 2.90 mL, and the void volume of the column V_o = 2.14 mL. If the whole polymer which in the injection region has diffused into the gel were retained in the form of micelles, the integrated area $\overline{A}$ = 153 would decrease by (3.93 − 2.14)153/3.93 = 70, and the value obtained in the M solvent would be 153 − 70 = 83 integrated units; the real measured value is 110. Under the above assumption, (110 − 83)100/70 = 38.5% of the copolymer would be able to diffuse from gel particles before micelles could be formed.

The total amount of the compound diffusing into or out of the sphere is given by[4]

$$M_t/M_\infty = 1 - 6/\pi^2 \sum_{n=1}^{\infty} (1/n^2)\exp(-Dn^2\pi^2 t/r^2)$$

where M_t, M_∞ respectively is the amount of the compound transported by diffusion within a time t, $t \to \infty$, D is the diffusion coefficient, and r is the radius of the sphere. This dependence as a function of dimensionless quantities M_t/M_∞ and Dt/r^2 has been treated graphically (cf., e.g., ref. 4, p. 90), so that for the determined value $M_t/M_\infty = 0.385$, $D = 6 \times 10^{-7}$cm^2/s (the assumed average value for polystyrene with $M_w = 6 \times 10^4$ in low-molecular weight solvents), and for the particle radius $r = 4 \times 10^{-4}$ cm we can obtain $t = 4.5 \times 10^{-3}$ seconds. Since t is inversely proportional to D, let it be noted that, if the diffusion coefficient in the gel pores were smaller than in the solvent itself, the calculated t would increase by the same factor.

CONCLUSION

The calculated value of c.4.5 ms as an average time needed for the formation of micelles must of course be regarded as a preliminary one obtained by calculating a very simplified model. In fact, it is very difficult to imagine in detail the concrete behavior of macromolecules at the start of the chromatographic column, and especially to describe and calculate it quantitatively. Let us therefore regard the suggested procedure as a mere attempt to explain the phenomenon observed in this study, or as a suggestion for the further trend of our research. It seems probable, nevertheless, that a theoretical analysis[3] which applies to isomerizing systems is not adequate for a description of the chromatographic behavior of micelle-forming macromolecules.

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