Micellization of three-block copolymer poly[styrene-b-(ethene-co-butene)-b-styrene] in mixed solvents of tetrahydrofuran/ethanol

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The behaviour of dilute solutions of a three-block copolymer poly[styrene-b-(ethene-co-butene)-b-styrene] in mixtures of tetrahydrofuran (THF)/ethanol was studied using viscometry, osmometry and light scattering. In solutions with a lower ethanol content the copolymer dissolved, but in solutions with a higher ethanol content it became associated, to form spherical micelles with cores composed of middle (aliphatic) blocks. Between the molecular and micellar solutions a region of the so-called anomalous micellization was described. Micelles in mixtures with a higher ethanol content were stabilized by means of fast electrons, isolated and characterized in THF solutions.

(Keywords: block copolymer micelles; light scattering; osmometry; viscometry; radiation crosslinking)

INTRODUCTION

In dilute solutions of block copolymers in selective solvents (i.e. in solvents that thermodynamically favour one block but, at the same time, are unfavourable for others), spherical micelles are formed, with compact cores composed of insoluble blocks and shells formed by soluble blocks[1]. By analogy to similar structures in aqueous solutions of soaps, these structures are called micelles. Like soaps and surfactants, the block copolymers micellize by 'closed association'; the micelles with a narrow size and mass distribution are in equilibrium with the dissolved copolymer (unimer)[1]. The behaviour of the micelles of block copolymers in solutions has been studied by a number of methods (as cited in refs. 1 and 2), such as light scattering, small-angle X-ray scattering (SAXS), photon-correlation spectroscopy, neutron scattering, osmometry, viscometry, g.p.c. and sedimentation analysis.

The study of the properties of micelles is limited by the fact that the molar mass of micelles is sensitive to temperature. In the case of the multicomponent selective solvents it is sensitive to their composition, and the equilibrium, unimer$\rightleftharpoons$micelles, is also sensitive to the concentration of the copolymer. Attempts have been made to stabilize micelles under specific conditions by forming permanent chemical bonds in their cores. In this way micelles with polybutadiene cores have been stabilized using u.v. radiation in the presence of a photoinitiator[2,3] or fast electrons[2] and micelles with aliphatic cores have also been stabilized using first electrons[2]. Attempts to isolate the stabilized micelles containing polybutadiene cores have not been successful, because the products are insoluble even in solvents which thermodynamically favour the core and the shell[2,3]. Micelles containing aliphatic cores stabilized with fast electrons have been successfully isolated (and later dissolved), but the data for their molar masses were not reproducible and were dependent on the method of isolation[2]. (These experiments with micelles containing aliphatic cores used Kraton G-1650, which is a three-block copolymer poly[styrene-b-(ethene-co-butene)-d-styrene], in dioxane, and also in a mixture of THF/24 vol.% ethanol[2].)

In the work presented here the behaviour of Kraton G-1650 in tetrahydrofuran with different ethanol contents using the methods of viscometry, light scattering and osmometry was investigated. Copolymer micelles in a selected solvent mixture have been stabilized, isolated and characterized.

EXPERIMENTAL

Polymers

Samples of polystyrene PS-A and PS-B were prepared by anionic polymerization of styrene using dihydridobis(2-methoxyethoxy)aluminate as the catalyst. The three-block copolymer poly[styrene-b-(ethene-co-butene)-b-styrene], (Kraton G-1650 a Shell product), whose middle block was actually a hydrogenated polybutadiene, was precipitated from benzene in an excess of methanol and dried at 25°C *in vacuo*. The characteristics of the polymers are presented in *Table 1*.

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Table 1 Characteristics of copolymer sample and homopolymers

Polymer	w_{ST}	M_w (10^3 g mol^{-1})	M_n (10^3 g mol^{-1})
Kraton G-1650*	0.28	74.0	70.0
PS – A	1.00	16.0	13.1
PS – B	1.00	87.6	49.5

* Ratio of ethene to 1-butene units 0.55, w_{ST}-mass fraction of styrene

Solvents

Tetrahydrofuran (analytical grade) was dried by boiling with sodium and distillation. The ethanol and methanol (analytical grade) were rectified before use. The ethanol contained 4 vol% of water.

Preparation of polymer solutions

Polymer solutions were prepared in sealed glass ampoules at 80°C and filtered before measurements using Teflon filters with pore sizes of 0.2 μm (molecular solutions) or 0.45 μm (micellar solutions).

Stabilization and isolation of micelles

Stabilization of the micelles of Kraton G-1650 in oxygen-free solutions ($c = 0.01$ g cm^{-3}) in a mixture of THF/24 vol.% ethanol was performed in a nitrogen atmosphere in thermostatically controlled containers (25°C) by fast electrons as described in a previous paper[2]. After irradiation the micelles were either precipitated in methanol and dried *in vacuo*, or lyophilized.

Viscometry

Intrinsic viscosities were measured with an Ubbelohde viscometer at 25°C using five copolymer concentrations, and calculated from the equation

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \qquad (1)$$

where c is a polymer concentration in g cm^{-3}, η_{sp} the specific viscosity, and k_H the Huggins coefficient.

Light scattering

Light scattering measurements were performed using a Sofica apparatus with vertically polarized light ($\lambda = 546$ nm) within the angle range of 30°–150° at 25°C. The weight-average molar mass M_w (g mol^{-1}), was established using the Zimm extrapolation method (for five polymer concentrations). In these plots Kc/R_θ was plotted against $\sin^2(\theta/2) + k'c$, where K is an optical constant including the refractive index increment, R_θ is the difference between the Rayleigh ratio of the solution and that of the solvent at angle θ, and k' a suitably chosen constant. For micellar solutions M_w represents the weight-average molar mass of all particles in the solution (unimer and micelles) and is denoted as $M_w^{(p)}$.

$$M_w^{(p)} = M_w^{(u)} w^{(u)} + M_w^{(m)} w^{(m)} \qquad (2)$$

$M_w^{(u)}$ and $M_w^{(m)}$ are the molar masses of the unimer and of the micelles, respectively, and $w^{(u)}$ and $w^{(m)}$ ($w^{(m)} = 1 - w^{(u)}$) are the respective mass fractions.

The values for the refractive index increment, dn/dc, were established using a Brice–Phoenix differential refractometer. The dn/dc values for the mixed solvent THF/ethanol were determined under the condition of a dialysis equilibrium between the polymer solution and the solvent, as described in our previous paper[2] (*Table 2*).

Osmometry

The number-average molar mass, M_n, was determined using a Knauer automatic membrane osmometer at 25°C with Sartorius membranes (allerfeinst grade) (Göttingen, FRG). M_n was obtained from the equation

$$\pi/c = (1/M_n + A_2^{MO}c)RT \qquad (3)$$

where π is the osmotic pressure value. For the number-average particle molar mass, $M_n^{(p)}$, in micellar solutions a relation analogous to (2) holds, the mass fractions being replaced by molar fractions. When the measurements were carried out in a THF/ethanol mixture, the osmotic pressure was measured for each polymer concentration against a fresh solvent of known composition.

RESULTS AND DISCUSSION

Solubility of Kraton G-1650 in a THF/ethanol mixture

THF is a thermodynamically favoured solvent for both blocks of Kraton G-1650. Ethanol efficiently precipitates the middle aliphatic block. The solutions of Kraton G-1650 can be prepared in THF/ethanol mixtures (containing not more than 28 vol.% ethanol) either by direct dissolution of the copolymer in a solvent mixture, or by its dissolution in pure THF with the subsequent addition of ethanol. The $[\eta]$, M_n and M_w values are independent of the manner of solution preparation. Solutions in mixtures containing not more than 14 vol.% of ethanol are clear (and, as will be shown below, the copolymer is molecularly dissolved in them), whereas solutions in mixtures containing not more than 16–28 vol.% of ethanol have a bluish tint, characteristic of the presence of compact spherical micelles. Solutions of the copolymer in THF/28–36 vol.% ethanol cannot be prepared by direct dissolution (not even at 100°C in sealed ampoules), but only by dissolution in a mixture with a lower ethanol content with the successive addition of ethanol. These solutions are stable with respect to time but exhibit a white opalescence due to the presence of particles substantially larger than ordinary spherical micelles. The following part of our study will be concerned with solutions of Kraton G-1650 in mixtures containing not more than 28 vol.% ethanol.

Light scattering

The concentration dependences of Kc/R_0 in mixtures of THF/0–24 vol.% ethanol (*Figure 1*) indicate a different behaviour of the copolymer in the three regions of solvent composition: THF/0–12 vol.% ethanol, THF/12–16 vol.% ethanol, and THF/16–24 vol.% ethanol.

Table 2 Refractive index increments (in cm^3 g^{-1}) measured before, $(\mathrm{d}n/\mathrm{d}c)_c$, and after dialysis, $(\mathrm{d}n/\mathrm{d}c)_\mu$ at 25°C

	vol.% ethanol in a mixture			
	0	6	12	24
$(\mathrm{d}n/\mathrm{d}c)_c$	0.116	0.118	0.120	0.124
$(\mathrm{d}n/\mathrm{d}c)_\mu$	–	0.120	0.124	0.128

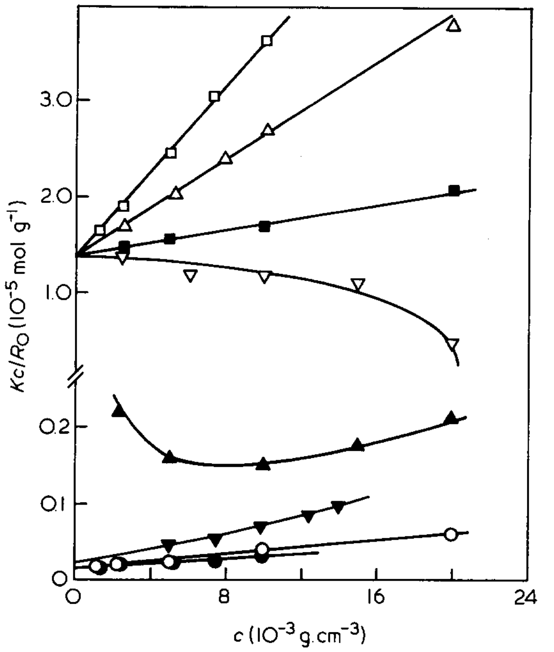

Figure 1 Concentration dependences of Kc/R_0 for Kraton G-1650 in THF and in the mixed solvent THF/ethanol at 25°C: (□) THF; (△) THF/6 vol.% ethanol; (■) THF/12 vol.% ethanol; (◇) THF/14 vol.% ethanol; (▲) THF/16 vol.% ethanol; (◆) THF/18 vol.% ethanol; (○) THF/20 vol.% ethanol; (●) THF/24 vol.% ethanol

In mixtures containing $\leqslant 12$ vol.% ethanol the concentration dependences of Kc/R_0 indicate only the decreasing thermodynamic quality of the solvent (A_2) with the increasing ethanol content. The common intersection of these dependences with the Kc/R_0 axis for $c=0$ gives the molar mass of the molecularly dissolved copolymer, i.e. the unimer ($M_w^{(u)}$). The dependences Kc/R_θ *versus* $\sin^2(\theta/2)$ (called the radiation envelopes) are linear with a virtually zero slope. The values for the dissymmetry of scattered light, z, (ratio of intensities of scattered light at angles 45° and 135°) approaching unity, indicate that the scattering particles are 'small' relative to the wavelength of the scattered light. In mixtures containing 16–24 vol.% of ethanol the asymetry is only slightly higher (≈ 1.1–1.2), but the concentration dependences of Kc/R_0, extrapolated to $c=0$, provide the values two orders higher compared to those for $M_w^{(u)}$. Like many similar systems the strongly scattering particles can be regarded as compact polymolecular micelles. Owing to the fact that the concentration dependences of Kc/R_0 are linear even for very low concentrations, the equilibrium (unimer$\rightleftharpoons$micelles) can be assumed to shift in favour of the micelles in these solvent mixtures, i.e. the values $M_w^{(p)}$ approach those of $M_w^{(m)}$.

In a THF/14 vol.% ethanol mixture the slope of the concentration dependence of Kc/R_0 is negative. However, it is impossible to decide whether the negative value of A_2 or association is responsible. In a mixture containing 16 vol.% ethanol the concentration dependence of Kc/R_0 can serve as a classical example of an associating system[1,4]. Whereas in a solvent containing 16 vol.% ethanol the asymetry of scattered light approaches unity for all the concentrations measured in a solvent containing 14 vol.% ethanol it attains higher values depending on the copolymer concentration and temperature (*Figure 2*). Since the radiation envelopes in this mixture exhibit strong curvatures at small angles, thus making an extrapolation to Kc/R_0 from the whole angle range impossible, the values given in *Figure 1* were obtained by extrapolation from large angles, as shown in *Figure 3*. The increase in the dissymmetry of scattered light under the conditions of the onset of micellization has been described many times, e.g. in refs. 1, 5, 6 and 7, without being unambiguously explained. A strong curvature of the radiation envelopes seen in other systems as well[8] indicates the presence of a small number of unusually large particles. Certain kinds of formations which can be regarded as large particles have been observed by electron microscopy after evaporating the solvent from the solution of a three-block copolymer poly(styrene-b-butadiene-b-styrene) in ethyl acetate[9]. One of the causes

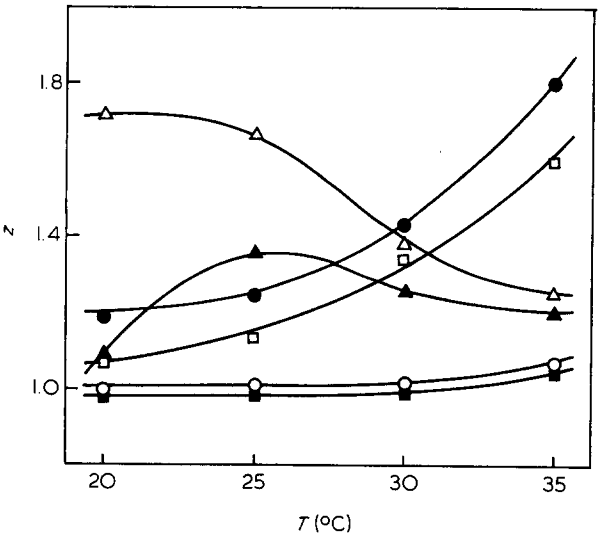

Figure 2 Dependences of dissymmetry of scattered light, $I_{45°}/I_{135°}$, for solutions of Kraton G-1650 in the mixed solvent THF/14 vol.% ethanol on the temperature, T, for the following polymer concentrations: (●) 0.05 g cm^{-3}; (□) 0.03 g cm^{-3}; (○) 0.02 g cm^{-3}; (■) 0.01 g cm^{-3}; (△) 0.005 g cm^{-3}; (▲) 0.0025 g cm^{-3}

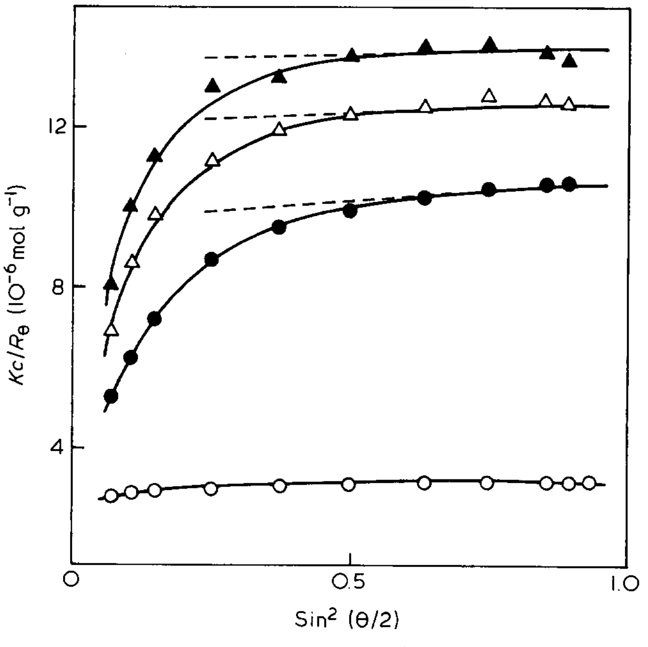

Figure 3 Dependences of Kc/R_θ on $\sin^2(\theta/2)$ (radiation envelopes) for Kraton G-1650 in mixed solvent THF/14 vol.% ethanol at the polymer concentration of 0.005 g cm^{-3} at the following temperatures: (○) 20°C; (●) 25°C; (△) 30°C; (▲) 35°C

of the formation of extremely large paticles at the onset of micellization may be the contamination of the block copolymer by a homopolymer corresponding to the insoluble blocks[10].

Osmometry

Measurements of polymer solutions by membrane osmometry in multicomponent solvents may be influenced by the selective sorption of one solvent component onto the polymer. In establishing the osmotic equilibrium a difference in the composition of the mixed solvent on either side of membrane will occur as a result of selective sorption. In a Kraton G-1650–THF/ethanol system, however, the selective sorption of THF onto the copolymer is not large enough[2] for the measurements to be affected by the change in the solvent composition.

The dependences of the reduced osmotic pressure on the copolymer concentration in the THF/ethanol mixtures (*Figure 4*) are similar to the concentration dependences of Kc/R_0 in *Figure 1*. In pure THF and in the THF/12 vol.% ethanol mixture the molar mass of the unimer, $M_n^{(u)}$, can be obtained by extrapolation to $c = 0$. In mixtures containing 14 and 16 vol.% of ethanol the concentration dependences of π/c are similar to the theoretical concentration dependences of $1/M_n^{(p)}$ for the associating systems[4]. Recently it has been shown[8] that the similar experimental dependences of π/c for poly(styrene-b-2-vinyl pyridine) in toluene agree well with the model of closed association. The decreasing values of π/c with increasing concentration for a solvent of a given composition thus indicate a shift of the unimer$\rightleftharpoons$micelles equilibrium in favour of micelles. The linear concentration dependence of π/c in *Figure 4* (like that of Kc/R_0 in *Figure 1*) suggests that starting from a certain polymer concentration the amount of the unimer is more or less constant. Whereas for the light scattering data (*Figure 1*), (e.g. in the THF/16 vol.% ethanol mixture), this 'apparent' limiting concentration can be estimated as ≈ 0.01 g cm^{-3}, but for the osmotic measurements it is higher, ≈ 0.016 g cm^{-3}. For the THF/20 vol.% ethanol mixture this concentration for the light scattering data has to be lower than the lowest concentration measured, (i.e. 0.001 g cm^{-3}), while in the osmotic measurements it can be estimated as ≈ 0.008 g cm^{-3}. The fact that the decrease in the π/c values in the region of lower concentrations takes place in a wider concentration range than the decrease in the Kc/R_0 values has also been observed in a two-block copolymer poly(styrene-b-2-vinyl pyridine) in toluene[11]. It can be explained by the higher sensitivity of the osmometric method to the lower molar mass portions in the solution measured (i.e. the unimer) as well as to the polydispersity of the sample.

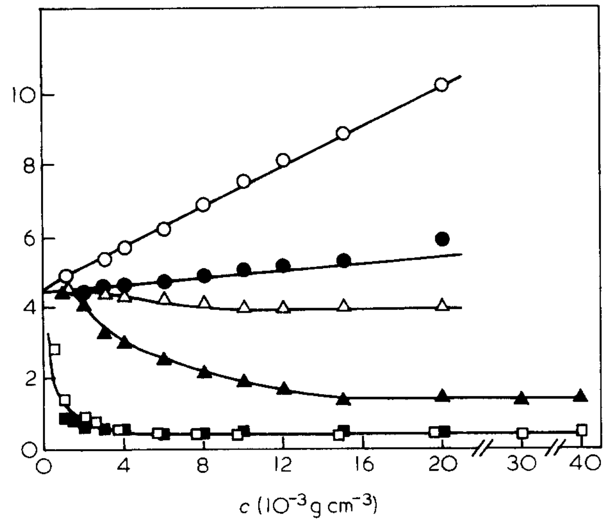

Figure 4 Concentration dependences of reduced osmotic pressure, π/c, for Kraton G-1650 in a mixed solvent THF/0–24 vol.% ethanol at 25°C: (○) THF; (●) THF/12 vol.% ethanol; (△) THF/14 vol.% ethanol; (▲) THF/16 vol.% ethanol; (□) THF/20 vol.% ethanol; (■) THF/24 vol.% ethanol

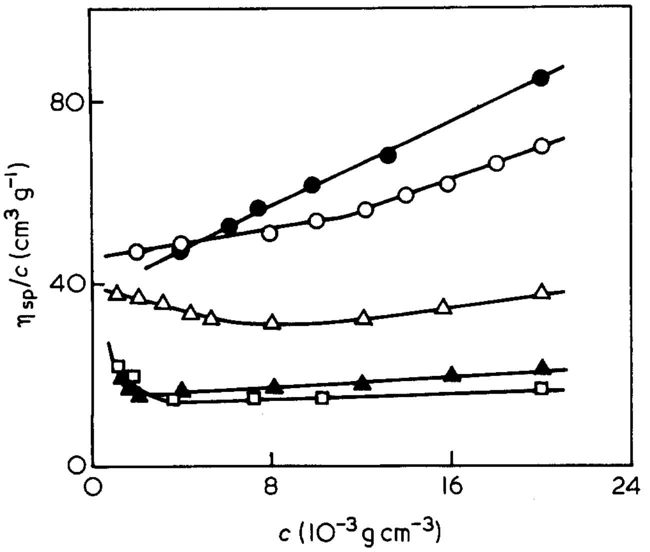

Figure 5 Concentration dependences of reduced specific viscosity, η_{sp}/c, for Kraton G-1650 in a mixed solvent THF/ethanol at 25°C: (●) THF vol.% ethanol; (○) THF/14 vol.% ethanol; (△) THF/16 vol.% ethanol; (▲) THF/20 vol.% ethanol; (□) THF/24 vol.% ethanol

The $M_n^{(p)}$ values in mixtures with a higher ethanol content obtained by extrapolation from the linear concentration dependences of π/c from higher c values will be discussed below.

Viscometry

The concentration dependences of the reduced specific viscosity of Kraton G-1650 in THF/ethanol mixtures (*Figure 5*) supplement the information from light scattering (*Figure 1*) and osmometry (*Figure 4*). The dependences in *Figure 5* for the molecularly dissolved copolymer (i.e. in THF/0–12 vol.% ethanol mixtures) are linear over the whole concentration range, and the decreasing values of the intrinsic viscosity $[\eta]$ indicate the impairing quality of the solvent.

The osmotic and light scattering data have shown that in mixtures containing 14 and 16 vol.% ethanol the number of micelles in the solution increases with increasing copolymer concentrations. The concentration dependences of Kc/R_0 (16 vol.% ethanol) and π/c (14–24 vol.% ethanol) have a lower concentration limit above which the amount of unimer in the associating system does not change. Also the dependences of η_{sp}/c *versus* c show a change of the slope at certain concentrations, (14 vol.% ethanol, ≈ 0.01 g cm^{-3}), (16 vol.% ethanol, ≈ 0.008 g cm^{-3}) and (18–24 vol.% ethanol, 2–3 $\times 10^{-3}$ g cm^{-3}). These concentrations represent the lower limits above which the viscosity is insensitive to the changes in the unimer$\rightleftharpoons$micelles equilibrium. According to Elias[12], who studied association phenomena in detail, the shape of the dependences η_{sp}/c *versus* c is given by the

k_H and $[\eta]$ values of the unimer and micelles the molar mass of the $[\eta]$ unimer and the micelles, and the equilibrium association constant. If the change in the polymer concentration in the solution results in a change in the ratio of the micelles and unimer, the plot η_{sp}/c *versus* c is non-linear. Thus the change of the slope and the curvature of the dependences in the region of low copolymer concentrations in *Figure 5* can be roughly accounted for by the variation of the ratio of the unimer and the micelles (both having different hydrodynamic volumes) and by their mutual interaction. In view of the findings in the work cited (ref. 12) it should be noted that the values $[\eta]$ and k_H (equation (1)) obtained from the linear concentration dependences of η_{sp}/c in the region of higher c values can depend to some extent on the association equilibrium.

Properties of the unimer and micelles of Kraton G-1650 in THF/0–24 vol.% ethanol mixtures

A comprehensive review of the values $M_w^{(p)}$, $M_n^{(p)}$, second virial coefficient, A_2^{LS}, obtained from light scattering measurements and, A_2^{OM}, obtained from osmotic measurements, $[\eta]$ and k_H for Kraton G-1650 solutions in THF/0–24 vol.% ethanol mixtures, is presented in *Figures 6* and *7*.

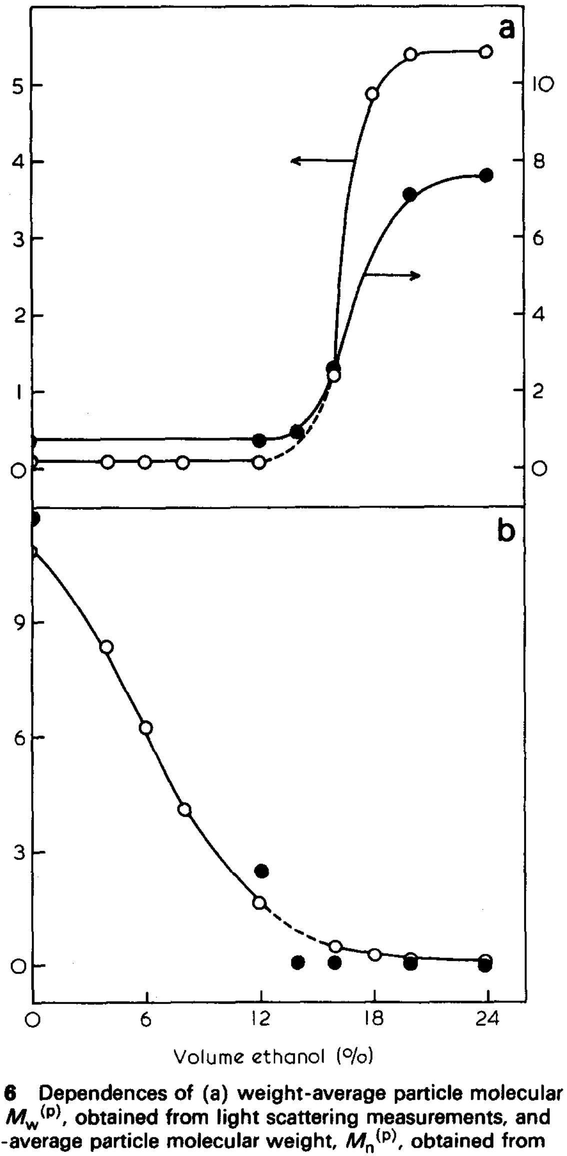

Figure 6 Dependences of (a) weight-average particle molecular weight, $M_w^{(p)}$, obtained from light scattering measurements, and number-average particle molecular weight, $M_n^{(p)}$, obtained from osmotic measurements of Kraton G-1650 and (b) second virial coefficients, A_2^{LS} and A_2^{OM}, on the composition of a mixed solvent THF/ethanol at 25°C: (○) light scattering; (●) membrane osmometry

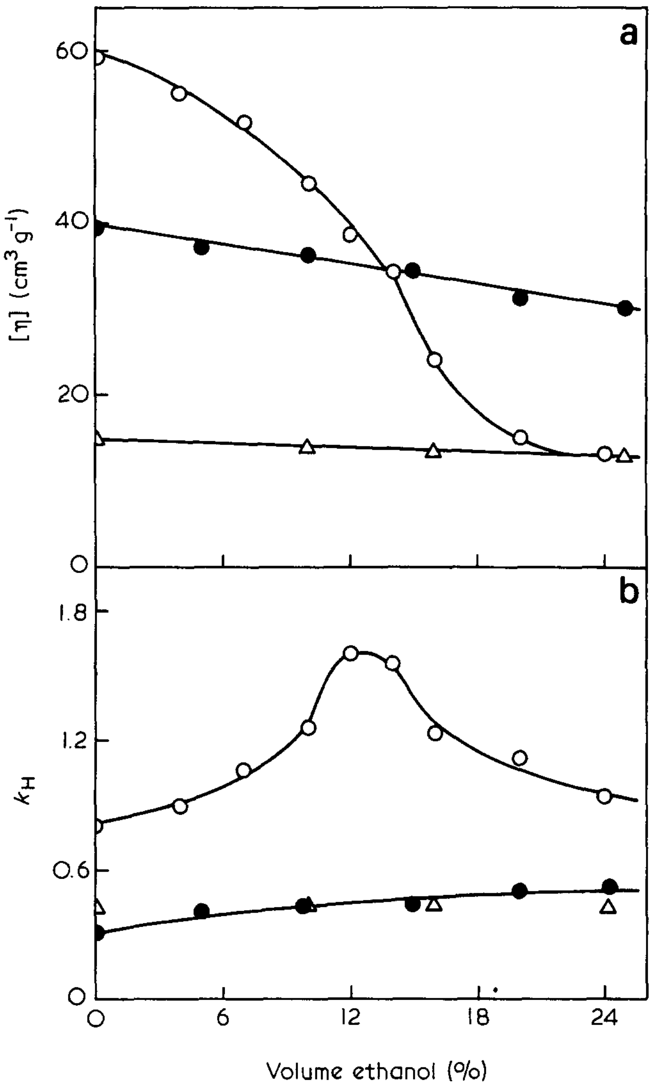

Figure 7 Dependences of (a) intrinsic viscosity, $[\eta]$, (b) Huggins coefficient, k_H, on the composition of a mixed solvent THF/ethanol at 25°C for: (○) Kraton G-1650; (△) PS-A; (●) PS-B

In the solvent mixtures THF/0–12 vol.% ethanol the $M_w^{(p)}$ and $M_n^{(p)}$ values do not change and correspond to the weight-average and number-average molar mass of the unimer. The decrease in the A_2^{LS} and A_2^{OM} values with increasing ethanol content is a result of the decreasing quality of the mixed solvent. A similar decrease in the $[\eta]$ values can then be accounted for by a change in the hydrodynamic volume of the copolymer molecules, which is apparently decisively affected by the conformational changes in the middle aliphatic block. Polystyrene is soluble over the whole THF/ethanol mixture composition range studied, and the decrease in the $[\eta]$ values of the two samples with $M_w = 16\,000$ g mol^{-1} and $M_w = 88\,000$ g mol^{-1} (*Figure 7*), is not pronounced. Although no information is available concerning the behaviour of the homopolymer corresponding to the middle block of Kraton G-1650, it can be assumed that the solvent mixtures containing even less than 12 vol.% ethanol are thermodynamically unfavourable solvents (precipitants) for these blocks. The conformational changes of this block in the interval of the solvent composition THF/0–12 vol.% ethanol will probably manifest themselves (on the basis of theoretical reasoning[13,14]) by a collapse; this means that a microphase separation of this block within one copolymer molecule will take place.

By comparing the results obtained for various micellizing systems (mentioned in ref. 1), the increase in the $M_w^{(p)}$ and $M_n^{(p)}$ values and the decrease in the $[\eta]$ values for Kraton G-1650 in the composition range of the solvent THF/12–18 vol.% ethanol (*Figures 6* and *7*), can be explained by the formation of polymolecular micelles, i.e. by the shift of the unimer$\rightleftharpoons$micelles equilibrium in favour of micelles; by the growing number of the unimers in the micelle, and by the growing compactness of the micelles. In interpreting the values in this composition range of the solvent in *Figures 6* and *7* (particularly of the A_2 and k_H values) one must be cautious owing to the presence of anomalously large particles in the THF/14 vol.% ethanol mixture (discussed below), as well as the manner of extrapolation of the Kc/R_0, π/c and η_{sp}/c values from the higher concentration range in the THF/14–16 vol.% ethanol mixtures.

With increasing ethanol content in THF/18–24 vol.% ethanol mixtures the $M_w^{(p)}$, $M_n^{(p)}$ and $[\eta]$ values are only slightly altered (*Figure 6*). These data, along with the fact that the concentration dependences of Kc/R_0, π/c and η_{sp}/c (*Figures 1*, *4* and *5*) are linear practically over the whole range of the measured copolymer concentrations, can be interpreted as a shift in the unimer$\rightleftharpoons$micelles equilibrium entirely in favour of the micelles. To calculate the molar mass of the micelles, $M^{(m)}$, and the mass fraction of the unimer in the system, $w^{(u)}$, we can employ equation (2) and the basic relation for $M_n^{(p)}$

$$M_n^{(p)}=\frac{M_n^{(u)}M_n^{(m)}}{M_n^{(u)}(1-w^{(u)})+M_n^{(m)}w^{(u)}} \tag{4}$$

$M_n^{(p)}$, $M_n^{(u)}$ and $M_n^{(m)}$ being number-average molecular weights of all the particles, (unimers and micelles), in the solution. We know that $M_n^{(u)}$ and $M_w^{(u)}$ differ only slightly ($M_n^{(u)}\doteq M_w^{(u)}\doteq M^{(u)}$), and the narrow distribution of the micelles ($M_n^{(m)}\doteq M_w^{(m}\doteq M^{(m)}$) can be assumed on the basis of sedimentation[1], diffusion[2] or electron microscopic[3] data obtained for other micellar systems. Equations (2) and (4) yield the relations for $M^{(m)}$ and $w^{(u)}$:

$$M^{(m)}=\frac{(M^{(u)}-M_w^{(p)})M_n^{(p)}}{M^{(u)}-M_n^{(p)}} \tag{5}$$

$$w^{(u)}=\frac{M_w^{(p)}-M^{(m)}}{M^{(u)}-M^{(m)}} \tag{6}$$

The resulting values (along with the molar fraction of the unimer, $x^{(m)}$, and the number of the unimers in the micelle, N) for the THF/16, 20 and 24 vol.% ethanol mixtures are given in *Table 3*. We can see that the amount of the unimer, as well as the values of $M^{(m)}$ and N, do not practically change in the latter two mixtures.

Table 3 Characteristics of micellar solutions of Kraton G-1650 in mixed solvent THF/ethanol at 25°C

Volume % ethanol	$M_w^{(p)}$ (10^6 g mol^{-1})	$M_n^{(p)}$ (10^6 g mol^{-1})	$M^{(m)}$ (10^6 g mol^{-1})	$w^{(u)}$	$x^{(u)}$	N
16	1.2	0.251	1.57	0.25	0.89	21
20	5.4	0.704	5.92	0.09	0.89	80
24	5.4	0.763	5.85	0.08	0.88	79

$M_w^{(p)}$ – weight-average particle molar mass, $M_n^{(p)}$ – number-average particle molar mass, $M^{(m)}$ – micellar molecular weight, $w^{(u)}$ or $x^{(u)}$ – mass or molar fraction of the unimer, N – number of unimer molecules in a micelle

Owing to a low value of the mass fraction of the unimer ($w^{(u)}=0.08$) in the THF/24 vol.% ethanol mixture, the experimental values of $[\eta]$ and z-average radius of gyration $\bar{S}_z$ (calculated from the angular dependence of Kc/R_0 for $c=0$) can be regarded as the values applying virtually only to the micelles. In general, the $\bar{S}_z$ value for the micelles with different refractive indices of the core and the shell can be regarded as the apparent value[15]. By comparing the data for light scattering and low-angle X-ray scattering on a very similar micellar system (Kraton-G-1650 in dioxane), however, it has been found[16] that the apparent value $\bar{S}_z$ differs from the real one by less than 15%. Therefore also in our system we consider the value $\bar{S}_z$ (17 nm) to be close to the real one.

The roughest approximation of a compact spherical micelle is a model of a solid sphere. For its diameter, D,

$$D=(20\,\overline{S_z^2}/3)^{0.5} \tag{7}$$

the value 43.6 nm is obtained. For the diameter of a hydrodynamic sphere D_H

$$D_H=\left(\frac{3\,M^{(m)}[\eta]}{10\,N_A}\right)^{1/3} \tag{8}$$

for $[\eta]=13.25\ \mathrm{cm^3\,g^{-1}}$ and $M_w^{(p)}=5.4\times10^6\ \mathrm{g\,mol^{-1}}$ the value 44.8 nm is obtained. Such a fairly good fit of D and D_H values can be considered as a corroboration of the assumption of micelle compactness and justification for approximating the micelles as solid spheres.

In studying the hydrodynamic properties of star-branched polymers[18] it has been found that the intrinsic viscosity of such a polymer is approximately twice as large as the intrinsic viscosity of the same linear polymer with M_w corresponding to one branch in the same solvent. Selb and Gallot[19] have found the same relationship for unimolecular micelles of graft copolymers, whose cores were formed by the collapsed backbones and the shells by solvated grafts. In our present study we have found the intrinsic viscosity of the micelles in the THF/24 vol.% ethanol mixture to be approximately equal to the value of intrinsic viscosity of polystyrene having $M_w=16\,000\ \mathrm{g\,mol^{-1}}$ (*Figure 7*), which is $\approx$50% higher than that of M_w of the polystyrene block in Kraton G-1650 ($M_w=10\,500\ \mathrm{g\,mol^{-1}}$). In spite of the qualitative agreement with the results presented[18,19], no general conclusions about the relation between the hydrodynamic behaviour of micelles and the individual blocks forming the micellar shell should be made, mainly due to a limited amount of experimental data.

Micelle stabilization by radiation crosslinking

The results presented here show that the micelles most suitable for stabilization are those of Kraton G-1650 in THF/20 and 24 vol.% ethanol solvents, where the unimer$\rightleftharpoons$micelles equilibrium is markedly shifted in favour of micelles. In our recent paper[2] we demonstrated the possibility of stabilizing the Kraton G-1650 micelles in THF/24 vol.% ethanol mixture and in dioxane by means of fast electrons; unfortunately, the values for the molar masses of micelles, isolated by lyophilization from the irradiated solutions, were not reproducible.

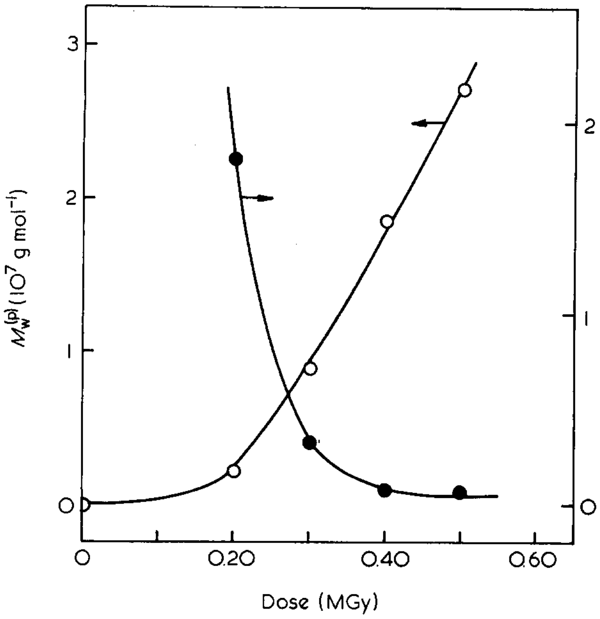

Figure 8 Light scattering data on Kraton G-1650 isolated after irradiation (in MGy) in THF/24 bol.% ethanol. $M_w^{(p)}$ and A_2^{LS} were measured in THF at 25°C

In repeated attempts to isolate stabilized micelles we have found that during irradiation of micelles in THF/24 vol.% ethanol mixture a certain amount of poly(oxybutylene) was formed, apparently as a result of radiation-initiated polymerization of THF. This polymer has been identified (by ^{1}H n.m.r.) only in products obtained by lyophilization of irradiated solutions and its molar mass, estimated from light scattering data in methanol, was lower tha 5000 g mol^{-1}.

Owing to the good solubility of poly(oxybutylene) in methanol this polymer has not been found in the products of irradiated solutions of Kraton G-1650 in THF/24 vol.% ethanol after multiple precipitation in methanol. The reproducibility of the $M_w^{(p)}$ and A_2^{LS} values for the samples containing radiation-stabilized micelles obtained by precipitation was subject to a ±5% error (*Figure 8*). No explanation, however, has been found for the high values of $M_w^{(p)}$ (compared to the same value for the non-irradiated sample in the THF/24 vol.% ethanol mixture) for higher radiation doses. Studies on radiation-stabilized and isolated micelles using different methods are in progress.

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REFERENCES

1 Tuzar, Z. and Kratochvíl, P. *Adv. Colloid Interface Sci.* 1976, **6**, 201

2 Tuzar, Z., Bednář, B., Koňák, Č., Kubín, M., Svobodová, Š. and Procházka, K. *Makromol. Chem.* 1982, **183**, 399

3 Procházka, K., Baloch, M. K. and Tuzar, Z. *Makromol. Chem.* 1979, **180**, 2521

4 Elias, H.-G. in 'Light Scattering from Polymer Solutions', (Ed. M. Huglin), Academic Press, London, 1972

5 Utiyama, H., Takenaka, K., Mizumori, M., Fukuda, M., Tsunashima, Y. and Kurata, M. *Macromolecules* 1974, **7**, 515

6 Lally, T. P. and Price, C. *Polymer* 1974, **15**, 325

7 Mandema, W., Zeldenrust, H. and Emeis, C. A. *Makromol. Chem.* 1979, **180**, 1521 and 2163

8 Sikora, A. and Tuzar, Z. *Makromol. Chem.* 1983, **184**, 2049

9 Canham, P. A., Lally, T. P., Price, C. and Stubbersfield, R. B. *J. Chem. Soc., Faraday Trans. I* 1980, **76**, 1857

10 Tuzar, Z., Bahadur, P. and Kratochvíl, P. *Makromol. Chem.* 1981, **182**, 1751

11 Hutchinson, E., Shinoda, K. 'Solvent Properties of Surfactant Solutions' (Ed. K. Shinoda), Marcel Dekker, New York, 1967, Ch. 1

12 Elias, H.-G. in 'Order in Polymer Solutions', (Ed. K. Šolc), Gordon and Breach Science Publishers, New York, 1976

13 Bendler, J., Šolc, K. and Gobush, W. *Macromolecules* 1977, **10**, 635

14 Bendler, J. and Šolc, K. *Polym. Eng. Sci.* 1977, **17**, 622

15 Benoit, H. and Froelich, D. in 'Light Scattering from Polymer Solutions', (Ed. M. Huglin), Academic Press, London, 1972

16 Tuzar, Z., Pleštil, J., Koňák, Č., Hlavatá, D. and Sikora, A. *Makromol. Chem.* 1983, **184**, 2111

17 Debye, P. and Bueche, A. M. *J. Chem. Phys.* 1948, **16**, 537

18 Zilliox, J.-G., Rempp, P. and Parrod, J. *J. Polym. Sci.* 1968, **C22**, 145

19 Selb, J. and Gallot, Y. *Makromol. Chem.* 1981, **182**, 1775