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Nonradiative energy transfer studies of block copolymers in selective solvents

B. Bednář
Merck Sharp Research Laboratories, WP 26-431, Pennsylvania, USA

and L. Karásek and J. Pokorný*
Department of Polymers, Prague Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

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Micelle formation, thermodynamic equilibrium and compactness of chromophore-labelled styrene–(hydrogenated isoprene) diblock and styrene–(hydrogenated butadiene)–styrene three-block copolymers in selective solvent systems have been investigated using nonradiative energy transfer and fluorescence quenching techniques. Donor (carbazole) or acceptor (anthracene) chromophores were randomly attached to the polystyrene part of block copolymers. The relaxation behaviour of micellar solution and the kinetics of micelle dissociation in various solvent composition and temperature were studied. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Block copolymers in selective solvents (i.e., thermodynamically good solvents for one type of blocks and poor solvents for the other type of blocks) form multimolecular micelles[1,2] with a relatively high association number (tens to hundreds of associated polymer chains). Micellization of block copolymers obeys the scheme of a closed association, characterized by a reversible equilibrium:

$$nU \overset{K}{\rightleftharpoons} M$$

where U represents unimers (nonmicellized, molecularly dissolved copolymer chains). M represents micelles (with a core and a shell formed of the insoluble and soluble blocks, respectively), n is the association number and K is the equilibrium constant. The association number, n, depends on copolymer composition, solvent quality and temperature. The micelles are usually nearly monodisperse in mass and size.

A scaling theory for the structure of micelles formed by A–B diblock copolymers in a highly selective solvent was investigated by Halperin[3]. He found correlations between core and overall micelle radii and polymerization degrees of the A and B blocks. Munch and Gast elaborated a theory of influences on a formation of lamellar and spherical micelles[4].

A theory of micellization of A–B diblock copolymer molecules in a selective solvent was developed by Nagarajan and Ganesh[5]. The micelles are assumed to have a completely segregated core region consisting only of the A block and a shell region consisting of the solvent compatible B block swelled with the solvent. The theory allows one to predict the critical micelle concentration (CMC), the micelle size distribution, the average aggregation number, as well as the core radius and the shell thickness of micelles. A theoretical model[6] was also proposed for micellization of a three-block copolymer B–A–B in solvents selective for outer blocks B.

Relaxation experiments in solutions of polymeric micelles were theoretically analysed by Halperin and Alexander[7]. Polymeric micelles are expected to grow or dissolve primarily via the Aniansson–Wall mechanism, which allows the micellar size distribution to adjust in steps consisting of single-chain insertion/expulsion. The relaxation behaviour was expected to be characterized by two relaxation times.

Nonradiative energy transfer (NET) can be observed in systems containing two fluorescent species, such that the emission spectrum of the donor overlaps the absorption spectrum of the acceptor. The efficiency of NET is inversely proportional to the sixth power of the distance between donor and acceptor, which depends on the overall concentration of both chromophores in the absence of any association effects. In the last decade, the NET between fluorescent labels attached to polymers has been frequently used to study properties of macromolecules in solution and also in the solid state[8,9].

Dilute solutions of fluorescently labelled block copolymers in selective solvents represent interesting and suitable systems for NET studies, because of the vast difference of the NET efficiency between molecularly dissolved copolymers and associates caused by different local label concentration in both systems. Detailed

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*To whom correspondence should be addressed. Present address: Kaučuk Group a.s., Synthetic Rubber Research Institute VUSK, 27852 Kralupy nad Vltavou, Czech Republic

Table 1 Average numbers of fluorophores per chain, c_f

Polymer	c_f
G-1701-A	1.31
G-1701-C	1.06
G-1650-A	0.24
G-1650-C	1.22
PS-1-C	6.85

steady-state fluorescence measurements in such systems reveal new information on polymer chain dynamics, micellar compactness and the kinetics of micelle dissociation.

While numerous studies have been devoted to the kinetics of micellization of soaps and surfactants[10], kinetic data on block copolymer micelles are scarce. In spite of extensive experimental data on the micellization equilibrium, little is known about the dynamics of unimer–micelle exchange under equilibrium conditions or the kinetics of micelle dissociation. Direct data on block copolymer micelle formation and dissociation are very rare. Stopped flow measurements[11] confirmed the important role of the copolymer structure. However, it must be kept in mind that stopped flow data refer to large perturbations of the equilibrium conditions. Recently, a comprehensive theoretical summary and a few experimental data[12] were published concerning the equilibrium mass exchange.

The aim of this work is to study the nonradiative energy transfer between attached carbazole and anthracene moieties in a block copolymer–micellar system in the mixed solvent 1,4-dioxane/*n*-heptane at various temperatures, and to present data concerning unimer exchange rate at equilibrium and micelle dissociation.

EXPERIMENTAL

Polymers

Two commercial Shell copolymers were used, a diblock copolymer Kraton G-1701 [polystyrene-*block*-poly(hydrogenated isoprene), $\bar{M}_w = 1.05 \times 10^5\,\mathrm{g\,mol^{-1}}$, 42 wt% polystyrene, narrow distribution of molar masses[11,12]] and a three-block copolymer Kraton G-1650 [polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene, $\bar{M}_w = 7.4 \times 10^4\,\mathrm{g\,mol^{-1}}$, 28 wt% polystyrene, narrow distribution of molar masses[11,12]]. Both copolymers were labelled by anthracene (G-1701-A, G-1650-A), or by carbazole (G-1701-C, G-1650-C) by chemical bonding via short side chains. Anthracene and carbazole were covalently attached to the aromatic ring of polystyrene via $-CH_2-O-CH_2-$ and $-CH_2-$ bridge, respectively. First, 9-anthraldehyde was synthesized[13], then it was reduced to 9-anthracenemethanol[14]. The polystyrene block was chlormethylated[15] to a low degree and tagging was achieved by reacting the potassium salt of either 9-anthracenemethanol or carbazole with the chlormethyl[16] group.

In order to remove unreacted fluorescent residues, the polymer was precipitated three times from a good solvent 50/50 (v/v) 1,4-dioxane/*n*-heptane into methanol. The tagging was random and the extent of labelling was determined by u.v.-vis. absorption spectroscopy. The average number of fluorophores per chain are summarized in *Table 1*.

Polymer PS-1 was prepared by an anionic polymerization in toluene initiated with partially hydrolysed $NaAlH_2(OCH_2CH_2OCH_3)_2$, Synhydrid (Synthesia Kolín, Czech Republic). The resulting polystyrene was atactic (according to ^{1}H n.m.r.) with $\bar{M}_n = 3.6 \times 10^4\,\mathrm{g\,mol^{-1}}$ and $\bar{M}_w = 5.4 \times 10^4\,\mathrm{g\,mol^{-1}}$. The sample was labelled by carbazole using the method described above (PS-1-C). Polymer PS-2 was prepared by radical polymerization using AIBN initiator ($\bar{M}_n = 4.0 \times 10^3\,\mathrm{g\,mol^{-1}}$, $\bar{M}_W = 1.1 \times 10^4\,\mathrm{g\,mol^{-1}}$). Molecular weights of polystyrenes were obtained by g.p.c. technique in tetrahydrofuran using Waters 150 ALC/GPC instrument equipped with μ-Bondagel E-linear 60 Å columns. The calibration was made using polystyrene standards with narrow distribution of molecular weights.

Model

N-benzyl carbazole was prepared by reaction of carbazole with benzyl bromide in the presence of $NaNH_2$[17].

Solvents

1,4-Dioxane and *n*-heptane, u.v. spectroscopy grade, were used.

Fluorescence measurements

The nonradiative energy transfer was studied in binary solvents 1,4-dioxane/*n*-heptane with different ratios of components and at different temperatures. In most measurements, the overall mass copolymer concentration was kept constant, $c = 5 \times 10^{-3}\,\mathrm{g\,mol^{-3}}$, and the molar ratios of anthracene/carbazole in diblock and three-block copolymer systems were $x_{AC} = 1.0$ and 3.0, respectively. All steady-state spectra were measured in 1 cm quartz cuvettes with a Spex-Fluorolog 2 fluorometer (Spex. Ind., USA). Samples were prepared by dilution to the desired concentration, sealed in vials and thermostatted for 1 h at 100°C in order to ensure a dissolution. The samples were purged with nitrogen before any fluorescence spectra were taken. The excitation and emission spectra of anthracene- and carbazole-labelled Kraton copolymers were shown and discussed elsewhere[12]. Excitation of carbazole at 295 nm was used and the emission intensities at 348 nm for carbazole and at 414 nm for anthracene were monitored.

The fluorescence quenching experiments were carried out with carbazole-labelled polymers using CCl_4 as a quencher. The fluorophore emission intensities at 348 nm were measured in the dependence on a quencher concentration in the range $0 - 7 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$ and quenching rate constants were evaluated by linear regression of the Stern–Volmer equation from at least seven measurements. The addition of a proper amount of quencher was accomplished by direct injection into a cuvette containing a fluorophore solution using a micropipette.

The kinetic experiments were performed by a stepwise addition of nitrogen purged solutions (either two solutions of carbazole- and anthracene-labelled copolymers in a proper solvent in the case of unimer–micelle mass exchange or a mixed solution of carbazole-/anthracene-labelled copolymers and pure dioxane in the case of micelle dissociation) in a cuvette. After rapid

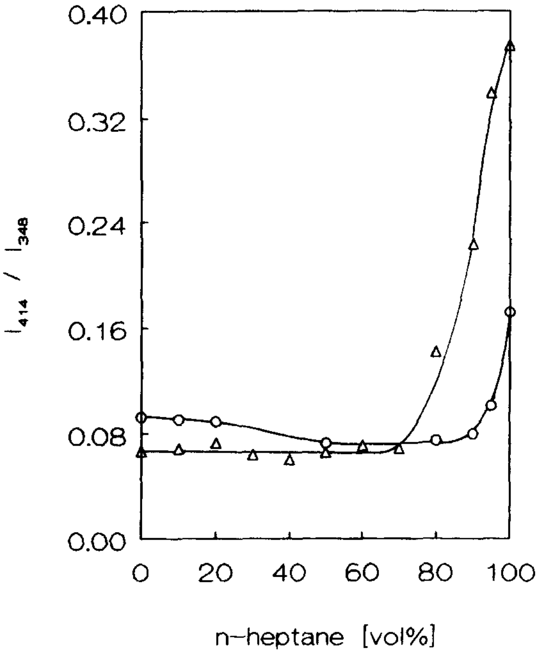

Figure 1 The dependence of I_{414}/I_{348} on the composition of 1,4-dioxane/n-heptane solvent mixture for (△) G-1701 and (○) G-1650 (copolymer concentration $c = 0.005\,\mathrm{g\,cm^{-3}}$)

mixing, the time dependent change of anthracene emission intensity at 414 nm was followed during carbazole excitation. Since the addition of solutions had to be carried out manually, the measurement began 5 s after the instant of mixing. Thus, the values of relaxation times might be somewhat distorted in the case of fast relaxation processes, particularly in less selective solvents or at higher temperatures.

The time-resolved fluorescence measurements were carried out using a 299T Multiplexed Single Photon Fluorometer (Edinburgh Instruments Ltd., UK). Concentrations of N-benzyl carbazole and G-1701-C were $3 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$ and $1 \times 10^{-2}\,\mathrm{g\,cm^{-3}}$, respectively.

RESULTS AND DISCUSSION

Polymer labelling

An attachment of labels to the polymer was accomplished by two chemical reactions from which in the first chlormethylation step complications with an increase of polymer molecular weight and crosslinking may arise. In preliminary experiments it was found that chlormethylation of Kraton G-1701 in CCl_4 at room temperature for 60 min ($SnCl_4$ catalyst) provided sufficient quantity of chlormethylation for an attachment of a proper amount of label while it still kept the copolymer molecular weight in the range of g.p.c. experimental error. The molecular weight parameters reported in the Experimental section were obtained for unlabelled polymers. It is probable that a small portion of lower molecular weight macromolecules was removed during the reprecipitation. One may suppose that this is more significant for PS-1-C, because of its lower molecular weight and broader distribution when compared with block copolymers.

Nonradiative energy transfer in micellar solutions

The binary solvents 1,4-dioxane/n-heptane are of particular interest in micellization studies of Kraton block copolymers because it is possible to find three ranges of solution behaviour according to the solvent composition, providing that the overall copolymer concentration exceeds that of the CMC[18]. Pure 1,4-dioxane and 1,4-dioxane-rich mixtures (with up to 40 vol% of n-heptane) are selective precipitants for aliphatic blocks. In this range, multimolecular micelles with cores of aliphatic blocks and shells of polystyrene blocks are formed and they are in equilibrium with molecularly dissolved block copolymer molecules. In the second range (30–60 vol% of 1,4-dioxane in the mixed solvent) only molecularly dissolved copolymer molecules exist in the solution.

In the third range, n-heptane and n-heptane-rich mixtures (with up to 30 vol% of 1,4-dioxane) are selective precipitants for polystyrene blocks. Solutions of diblock copolymer show the presence of spherical micelles with cores composed of polystyrene blocks and shells composed of hydrogenated polyisoprene blocks. Also three-block copolymers are known to form associates in selective solvents for their middle block. The morphology of these associates usually differs from spherical micelles and it is dependent on the nature of the selective solvent. It is supposed that a successive aggregation of the insoluble blocks causes the formation of highly branched or even network-like structures[19].

Figure 1 shows anthracene/carbazole fluorescence emission intensities ratio I_{414}/I_{348} for labelled copolymers G-1701 and G-1650 as a function of solvent composition. It is obvious that no significant change of NET is indicated for the diblock copolymer up to 70 vol% of n-heptane in the mixed solvent. This means that the used technique cannot distinguish between molecularly dissolved copolymer and micelles with labelled polystyrene blocks in their shells. However, when n-heptane content is increased above 70 vol%, the nonradiative energy transfer increases rapidly. The experimental curve indicates a gradual shift of the unimer–micelle equilibrium towards micelles as well as an increase of the compactness of associates with increasing n-heptane content.

The values I_{414}/I_{348} for the three-block copolymer are slightly higher in the solvents containing 0–30 vol% of n-heptane than those for the diblock copolymer. In this case the formation of micelles with polystyrene shells is probably indicated. In the range 40–90 vol% of n-heptane in the solvent composition, the ratio I_{414}/I_{348} does not reveal any association behaviour. If the n-heptane content exceeds 90 vol%, NET increases rapidly and indicates the formation of aggregates with associated polystyrene blocks, but does not reach the value for the diblock copolymer. This may be due to different structure and/or compactness of the three-block copolymer associates. However, the main obstacle for quantitative comparison of the behaviour of both block copolymers is the difference in the label concentration and the donor/acceptor ratio.

Fluorescence quenching

The kinetics of the fluorescence quenching of an energy donor is described by the Stern–Volmer equation[20]

$$I_0/I = 1 + k_q\tau_0[Q] \qquad (1)$$

where I_0 and I are fluorescence emission intensities of an

Table 2 The fluorescence liftimes of carbazole fluorophore in 1,4-dioxane/*n*-heptane mixtures

Sample	*n*-Heptane (vol%)	*A*	τ_1 (ns)	τ_2 (ns)
N-Benzyl carbazole	0	1	13.1	-
	50	1	12.7	-
	100	1	11.8	-
G-1701-C	0	0.972	13.1	0.7
	50	0.981	13.2	1.2
	80	0.973	12.6	1.7
	90	0.973	13.3	1.3
	100	0.966	12.2	1.5

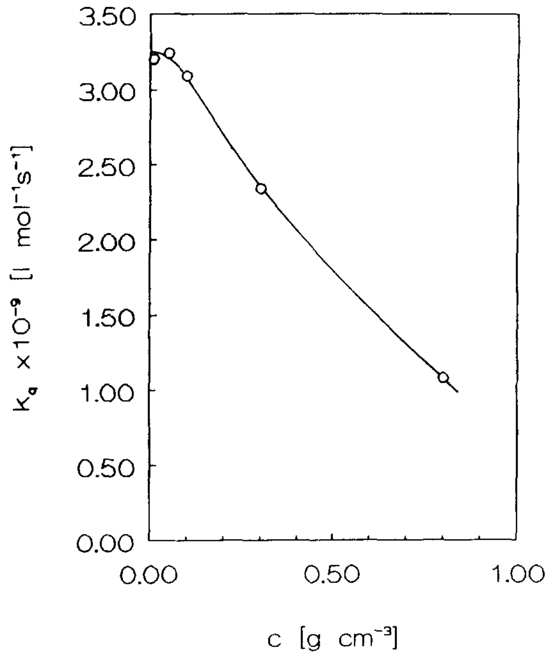

Figure 2 The dependence of CCl_4 quenching rate constant k_q on polystyrene concentration (in grams per ml of solvent) in 1,4-dioxane

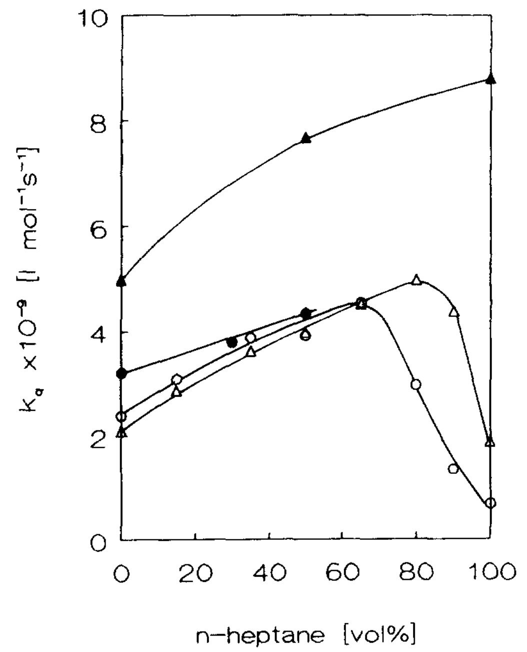

Figure 3 The dependence of k_q constant on the solvent composition for (▲) *N*-benzyl carbazole, $c = 10^{-4}$ mol l^{-1}, (●) PS-1-C, $c = 0.01$ g cm^{-3}, (○) G-1701-C, $c = 0.01$ g cm^{-3}, and (△) G-1650-C, $c = 0.01$ g cm^{-3}

energy donor in the absence and presence of a quencher (or an energy acceptor), respectively, k_q is the quenching rate constant, τ_0 is the fluorescence lifetime of an unquenched energy donor and $[Q]$ is the concentration of a quencher.

The observed quenching rate constant, k_q, is affected by a number of processes involved in the quenching reaction and the magnitude of this constant is strongly influenced by the rate of fluorophore and quencher diffusion under certain conditions[20]. Thus, the observed k_q values should be sensitive to the local viscosity in the fluorophore environment.

Table 2 contains values of unquenched carbazole fluorescence lifetimes under different experimental conditions. As expected, the time-resolved fluorescence of the model compound *N*-benzyl carbazole exhibits a single exponential decay. The experimental values of its fluorescence lifetimes differ only slightly with the solvent composition. The relative fluorescence decay, $F(t)$, of carbazole covalently attached to the block copolymer was fitted with a double exponential decay curve in the form

$$F(t) = A\exp(-t/\tau_1) + (1-A)\exp(-t/\tau_2) \qquad (2)$$

where τ_1 and τ_2 are the lifetimes of the slow and fast fluorescence decay processes, respectively, and A is the fraction of the slow process. The first, relatively slow process, comparing its lifetime with that of *N*-benzyl carbazole under the same conditions should be the proper fluorescence emission of the label; the values τ_1 were used for the evaluation of k_q from equation (1). The second, very fast deactivation process, whose fraction appears to be influenced slightly by the association process of block copolymer, is probably caused by the energy migration along the polystyrene chain.

The dependence of k_q on the polystyrene concentration in 1,4-dioxane at room temperature is shown in *Figure 2*. Samples were prepared by adding unlabelled polystyrene PS-2 to the solution of PS-1-C with the concentration 0.01 g cm^{-3} to get the final concentration, c, in grams of PS per ml of the solvent. The plot clearly indicates the decrease of k_q values with increasing polystyrene concentration due to reduced diffusion rates.

Figure 3 shows Stern–Volmer k_q constants for *N*-benzyl carbazole, PS-1-C and block copolymers G-1701-C and G-1650-C in different solvents. *N*-benzyl carbazole was used as a model of polymer-bound label, which is affected neither by the covalent linkage to the polymer chain nor by the micellization process. The steady increase of k_q value with increasing *n*-heptane content in the mixed solvent is caused by a decrease of solvent viscosity only.

Polystyrene with covalently attached carbazole, PS-1-C, models the behaviour of polystyrene blocks in block copolymers. However, it is not affected by the micellization. The k_q values for PS-1-C are lower than those for N-benzyl carbazole due to reduced diffusion rate of the label covalently linked to the polymer chain. Thus, the fastest diffusion process which controls the carbazole fluorescence quenching is the diffusion of CCl_4 quencher. An increase of *n*-heptane content in the mixture decreases the solvent viscosity and enhances the k_q value, which will probably rise up to the moment, when precipitation of polystyrene coils begins.

Both block copolymers, G-1701-C and G-1650-C,

Table 3 Quenching constant k_q and accessible label fraction f_a for G-1701-C in *n*-heptane ($c = 0.01\,\mathrm{g\,cm^{-3}}$)

Temperature (K)	$k_q \times 10^{-9}$ ($\mathrm{l\,mol^{-1}\,s^{-1}}$)	f_a
296	2.34	0.58
303	2.47	0.57
313	2.24	0.63
320	2.19	0.71
329	2.79	0.70

show similar behaviour in *Figure 3*. The k_q values in 1,4-dioxane-rich solvents are lower than those of PS-1-C and indicate the enhanced local polystyrene segment concentration in micelles with polystyrene shells as compared to the random coil of PS-1-C. The k_q values for the three-block copolymer in this range are somewhat lower than those for the diblock one, thus again confirming higher compactness of micelle shells as suggested from NET measurements. In principle, by comparing k_q values for both block copolymers in pure 1,4-dioxane with k_q concentration dependence for PS-1-C quenching (see *Figure 2*), a rough estimation of an average polystyrene segment concentration in micelle shells can be obtained. In this way, one can deduct values (in grams of PS per ml of the solvent) 0.30 and 0.37 for the diblock and the three-block copolymers, respectively.

In the range of molecularly dissolved copolymers the values of k_q for both block copolymers approach that of PS-1-C. As in the case of PS-1-C a steady increase of quenching rate is observed when *n*-heptane content is increased. The reason is in the shift of the micelle–unimer equilibrium towards molecularly dissolved copolymer and in a gradual change of solvent viscosity. In the range 70–100 vol% of *n*-heptane for G-1701-C and 80–100 vol% of *n*-heptane for G-1650-C, the formation of associates with polystyrene cores is evidenced by a rapid decrease of the Stern–Volmer quenching rate constant. The final k_q values in pure *n*-heptane demonstrate higher compactness of the cores of the diblock copolymer associates when compared to those of the three-block one.

Some complications arose with the evaluation of the k_q constants for G-1701-C in pure *n*-heptane and in the mixture with 10 vol% of 1,4-dioxane. In these solvent systems, curved Stern–Volmer kinetics were found; the k_q values in *Figure 3* were, however, obtained by the evaluation of data in the usual way according to equation (2). Curved Stern–Volmer dependence could be treated in terms of a fractional quenching model[21], which considers that only a fraction of fluorophores, f_a, is accessible for the quencher during the fluorescence lifetime.

$$I_o/(I_o - I) = (1/f_a) + (1/f_a k_q \tau_o [Q]) \qquad (3)$$

Table 3 contains f_a and k_q values obtained for carbazole labelled diblock copolymer G-1701-C in *n*-heptane at various temperatures. The values of the quenching rate constant do not show any significant temperature dependence, but they are considerably higher when compared to the same values calculated from equation (2). The reason is that according to the fractional quenching model the k_q value indicates the diffusion to the accessible label only. On the other hand, f_a rises with increasing temperature. This demonstrates continuous micelle swelling which decreases the local polystyrene chain concentration, and thus allows higher fraction of labels to be quenched. On the basis of these results, one may deduce a rather high inhomogeneity of the polystyrene segment concentration inside the cores of the diblock copolymer micelles in highly selective solvents.

Equilibrium mass exchange

The block copolymers exist in dilute solution of a good solvent as separated coils and the donor and acceptor are separated enough for significant NET. In a selective solvent, multimolecular micelles are in a reversible equilibrium with a certain fraction of unimer molecules[2] (very small in mass, but comparable in number with micelles). As a consequence of a reversible equilibrium, there is a continuous exchange of individual copolymer chains between different micelles and molecularly dissolved unimer molecules. In *n*-heptane-rich solvents, micelles with fluorophore-labelled polystyrene cores are formed.

By mixing two solutions, one containing micelles labelled by carbazole, the other micelles labelled by anthracene, and following the time-dependent increase in acceptor emission when the donor is excited, one can obtain information on the rate of equilibrium unimer–micelle mass exchange and the kinetics of micelle formation[12].

In this work, the exchange of unimers between micelles and molecularly dissolved unimer molecules in various selective solvent composition systems and at various temperatures were studied.

The experimental time dependence of the acceptor emission fluorescence intensity, I_t, can be transformed into normalized relaxation decay curves by plotting $(I - I_t)/I$ vs. t, I being the limiting value of I_t for high values of time. The decay curves could be best fitted by a double exponential function

$$S(t) = a_1 \exp(t/\tau_{r1}) + a_2 \exp(t/\tau_{r2}) \qquad (4)$$

where a_1 and a_2 are the normalized amplitudes ($a_2 = 1 - a_1$), τ_{r1} and τ_{r2} are relaxation times and $S(t)$ is $(I - I_t)/I$. The double exponential function was used as a reasonable approximation of a probably continuous spectrum of relaxation times. The mean value, $\bar{\tau}_e$,

$$\bar{\tau}_e = a_1\tau_{r1} + a_2\tau_{r2} \qquad (5)$$

can be considered as the relaxation time for mass exchange. The quantity V, defined by[22]

$$V = (a_1{\tau_{r1}}^2 + a_2{\tau_{r2}}^2 - {\bar{\tau}_e}^2)^{0.5}/\bar{\tau}_e \qquad (6)$$

was calculated as a measure of the width of the distribution of relaxation times.

Experimental dependence of the relaxation time $\bar{\tau}_e$ on the selective solvent composition for the diblock copolymer is shown in *Figure 4*. The rate of unimer exchange between micelles and molecularly dissolved copolymer chains depends significantly on the compactness of the micelle core which is strongly dependent on the solvent thermodynamical quality. In strong selective precipitants for polystyrene, the micelles with compact cores are formed and the insoluble blocks in the micellar cores are entangled and interpenetrated. In a consequence of this core compactness, all disentanglement motions as

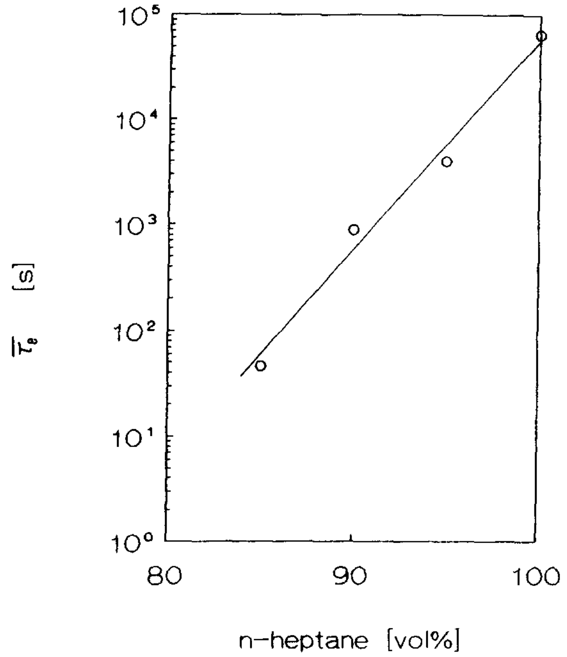

Figure 4 The dependence of the mass exchange relaxation time $\bar{\tau}_e$ on the selective solvent composition (diblock copolymer Kraton G-1701, 298 K, 1,4-dioxane/*n*-heptane)

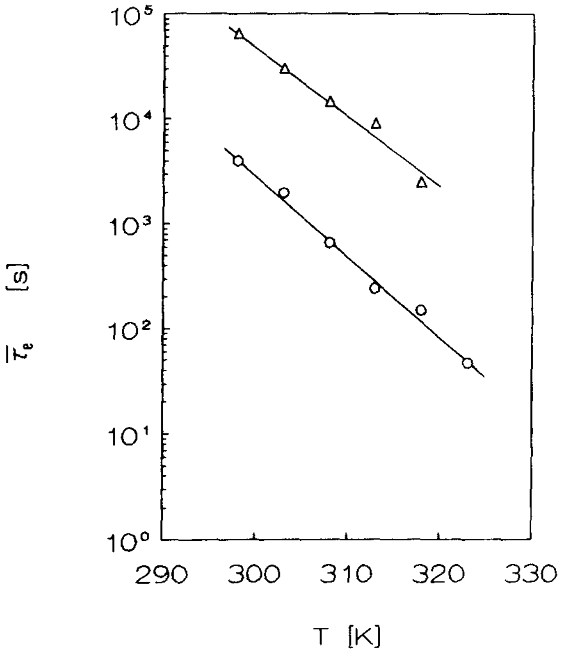

Figure 5 The mass exchange relaxation time $\bar{\tau}_e$ as a function of temperature (diblock copolymer Kraton G-1701), (Δ) 100/0 (v/v) *n*-heptane/1,4-dioxane, (O) 95/5 (v/v) *n*-heptane/1,4-dioxane

Table 4 Activation enthalpy $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$ values of mass exchange in micellar equilibrium systems of diblock copolymer Kraton G-1701

n-heptane (vol%)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
100	118	59
95	143	165

well as the release of unimer molecules from micelles are more hindered than in micelles with more swollen cores in weaker precipitants for PS. The V value ranged from 0.2 to 1.1. The situation of the equilibrium mass exchange of unimers for the three-block copolymer is more complicated. In highly selective solvent (pure *n*-heptane) and at a copolymer concentration 0.01 g cm^{-3} the value of the relaxation time $\bar{\tau}_e$ was only about 530 s. This value reflects the difference in the diblock and the three-block copolymer micelle structure.

The solvent quality also improves for both blocks with increasing temperature. The micellar cores swell, and the micelles partially dissociate, while the unimer–micelle mass exchange should accelerate at higher temperatures. The significant decrease of the relaxation time $\bar{\tau}_e$ with increasing temperature for diblock copolymer in two selective solvents with different thermodynamical quality is demonstrated in *Figure 5*. The increase of temperature plays a similar role to the improvement of solvent thermodynamical quality.

The linear dependences of $\ln \bar{\tau}_e$ on the temperature were treated according to the Eyring equation

$$k = (k_T T/h) \exp(\Delta S^{\neq}/R) \exp(-\Delta H^{\neq}/RT) \qquad (7)$$

where k is the rate constant ($k = 1/\bar{\tau}_e$), k_T is the Boltzmann constant, h is the Planck constant, R is the gas constant, T is the temperature, $\Delta S^{\neq}$ is the activation entropy, and $\Delta H^{\neq}$ is the activation enthalpy. The values of the activation entropy and the activation enthalpy were calculated and the results are listed in *Table 4*.

Experimental measurements of the equilibrium mass exchange of unimers with various overall mass copolymer concentrations were also carried out. A decrease of mass exchange relaxation time with increase of copolymer concentration was observed.

Dissociation of block copolymer micelles

Rates of dissociation of block copolymer micelles using light-scattering stopped-flow measurements were studied by Bednář *et al.*[11]. Dissociation of the micelles was achieved by mixing a micellar solution in 1,4-dioxane with an equal volume of *n*-heptane, so the authors used a large perturbation of the micellization equilibrium. In the case of Kraton G-1701, a value of relaxation time below 1 ms was measured.

In this study we focused on much smaller perturbations of the micellization equilibrium. Pure 1,4-dioxane was added to the *n*-heptane micellar solution with both anthracene and carbazole labels in micelle cores and the final solvent composition was in the range between 95/5 (v/v) and 80/20 (v/v) *n*-heptane/1,4-dioxane.

By mixing the pure 1,4-dioxane solvent with the *n*-heptane micelle solution, following the rapid time-dependent decrease in acceptor emission when the donor is excited, one can achieve information on the rate of the micelle partial dissociation and on the kinetics of this process.

Experimental time-dependent decay curves of the dissociation were again best fitted by a double exponential function [equation (4)] with $S(t) = I_t/I_{t0}$, I_{t0} being the value of I for $t = 0$. The mean value of partial dissociation relaxation time $\bar{\tau}_d$ was calculated in the same way as $\bar{\tau}_e$ according to equation (5).

The dependences of micelle partial dissociation

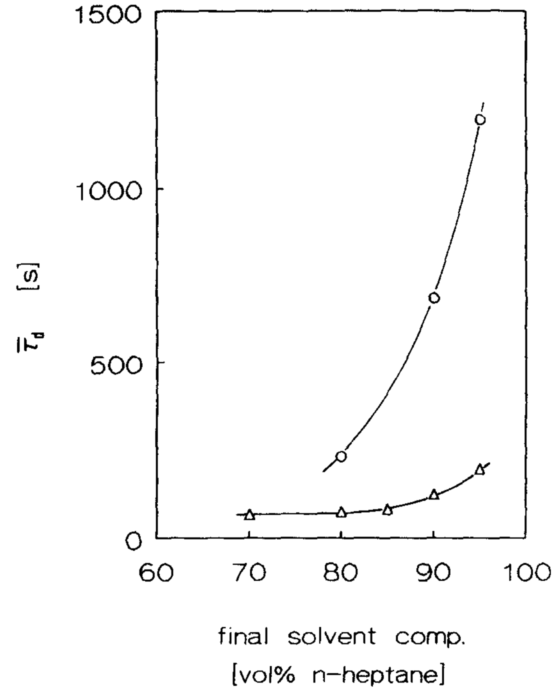

Figure 6 The partial dissociation relaxation time $\bar{\tau}_d$ as a function of final composition of selective solvent (298 K, 1,4-dioxane/*n*-heptane), (△) diblock copolymer Kraton G-1701, (○) three-block copolymer Kraton G-1650

relaxation time $\bar{\tau}_d$ on the final solvent composition for both diblock and three-block copolymer are shown in *Figure 6.* As compared with the experiments using a relatively large perturbation of the micellization equilibrium[11], the values of relaxation time obtained here are several orders of magnitude higher. The dissociation relaxation time $\bar{\tau}_d$ decreases with increasing fraction of 1,4-dioxane in the final solvent composition. In this case of mixing micelles with a good solvent for the core blocks, the small solvent molecules penetrate rapidly into the micellar cores and cause a rapid swelling and disentanglement of PS macromolecules. The higher the amount of good solvent, the more rapid micelle dissociation. From *Figure 6*, the large difference in the values of $\bar{\tau}_d$ for diblock and three-block copolymer micelles is evident. This can be explained by different structures of diblock and three-block copolymer micelles.

The influence of molecular weight parameters

Molecular weight and distribution of molecular weights as well as the length of individual blocks have significant influence on the association behaviour of block copolymers in selective solvents. A change of these parameters affects the equilibrium properties of micellar solutions – CMC, aggregation number, radius of a micelle core and thickness of a micelle shell.

Let us consider, for example, a diblock copolymer (such as G-1701) in *n*-heptane. In this case, the micelle cores consist solely of polystyrene blocks. Since *n*-heptane is a strong selective solvent for aliphatic blocks, the unimer–micelle equilibrium is shifted towards micelles and the fluorescence from unimers can be neglected. Let us consider, for simplicity, the effect of labelled polystyrene block length on the NET and the fluorescence quenching rate. Taking into account a similarity with polystyrene–polybutadiene in *n*-heptane[5], an increase of polystyrene block length increases significantly the core radius and the aggregation number, decreases the CMC, but affects only very slightly the shell thickness of micelles. Since the labels are randomly located throughout the micelle core, the average equilibrium properties of the micelle core – mainly a chain segment concentration and a local viscosity of a label environment – should be of most significance for the NET and the fluorescence quenching measurement. These properties, however, do not seem to change substantially with insoluble block length. Thus, we do not suppose a significant change of I_{414}/I_{348} and k_q, if the label concentration per styrene monomer unit is kept equal for all samples.

This might not be true in systems with very short (probably oligomeric) insoluble blocks particularly in combination with relatively long soluble blocks. The unimer concentration is high under such conditions. Moreover, because a low aggregation number is expected, the micelle core exhibits relatively high surface-to-volume ratio and the difference of properties of a local environment of labels inside the core and close to the core-shell interface might become more evident. Both of these effects should decrease I_{414}/I_{348} and increase k_q relatively to copolymers with longer insoluble blocks.

The influence of molecular weight parameters could be more significant considering the dynamical behaviour of micellar solutions such as the equilibrium unimer–micelle mass exchange. Since the micelle cores are very compact and polystyrene blocks are probably tightly interlaced, a release of a unimer molecule with longer insoluble block from the micelle (according to the Aniansson–Wall mechanism) should be more time consuming and the relaxation time of such a system should be longer. It seems reasonable to expect the same tendency for the partial micelle dissociation, even if this process is solvent-assisted. This conclusion has been made on the basis of a very simple assumption. For a more rigorous prediction, it is necessary to apply the conclusions of Halperin and Alexander[7], who investigated theoretically the dependence of the relaxation times on the rate constants for expulsion of a single chain from a micelle, on equilibrium properties, such as the mean and the variance of the aggregation number distribution, and on copolymer concentration.

The likely impact of insoluble block length on experimental measurements has been discussed. We suppose that similar assumptions allow one to estimate the effects of other parameters including overall copolymer molecular weight, molecular weight distribution, or soluble block length.

CONCLUSIONS

Fluorescence techniques are powerful tools for the study of micellization behaviour of block copolymers in selective solvents. They offer valuable characteristics of micellar systems, even if we are not able to derive quantitative data like the apparent molecular weight.

Fluorescence quenching provides information on the compactness of micellar cores as well as shells on a semiquantitative level. On the other hand, NET with energy donor and acceptor labelled copolymers demonstrates a unique way for characterization of rates of unimer–micelle mass exchange under equilibrium conditions and the rates of dissociation of block copolymer micelles.

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