

THE PHOTOCHEMICAL STABILIZATION OF BLOCK COPOLYMER MICELLES

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Conditions of the polymolecular micellization of a linear three-block copolymer—polystyrene-*block*-polybutadiene-*block*-polystyrene in a binary solvent tetrahydrofuran–ethanol were determined. Photochemical stabilization of micelles by the crosslinking of polybutadiene chains in the cores induced by intense UV radiation was carried out in a tetrahydrofuran–ethanol mixture (34.5 vol. %), in which compact micelles with the polybutadiene core are formed and, at 25°C, the micellization equilibrium is markedly shifted in favour of micelles containing a large number of associated copolymer chains. The kinetics of crosslinking of the micellar cores and the behaviour of stabilized micelles in solution were investigated.

In dilute solutions in selective solvents (i.e. thermodynamically good for one type of blocks and poor for another type) block copolymers associate, giving rise to spherical micelles, the core of which consists of insoluble blocks and the shell, of soluble ones¹. Usually, these micelles consist of copolymer molecules ranging from several tens to several hundreds. The typical average volume fraction of polymer chains in the micellar core is 0.8, while in the shell it is 0.1 (ref.²).

Similarly to micelles of soaps and surfactants in water, those of block copolymers (M) are virtually monodisperse with respect to molar mass and size, and under given conditions they usually are in a dynamic equilibrium with the unimer (U), i.e. with the molecularly dissolved copolymer:



where K_m is the equilibrium constant of micellization which depends on the thermodynamic quality of the solvent. For the given type of the copolymer, the association number n , and thus the molar mass of the micelles depend on the type (selectivity) of the solvent and on temperature. With varying concentration and at a given temperature the association number does not vary in the given system: there is only a shift in the equilibrium. Such type of association is called a “closed” one.

The fact that micelles dissociate on dilution often impedes the determination of their static and dynamic parameters (molar mass, size, unimer/micelles mass ratio, diffusion coefficient etc.) by employing methods which require extrapolation of the measured values to infinite dilution. Also, it is evident that micelles existing under given conditions (i.e. in a given solvent at a given temperature) cannot be transposed into other conditions without a change in their association number and molar mass. In an attempt to circumvent this problem, some time ago we tried to prepare stabilized micelles by the chemical crosslinking of chains in their cores. Micelles with cores consisting of polybutadiene or polyisoprene chains and containing potentially reactive bonds and groups appeared to be particularly well suited for this purpose. In our study dealing with this problem we described the stabilization of micelles of the styrene-butadiene type induced by UV radiation in the presence of dibenzoyl peroxide as the initiator of chemical crosslinking³. Later on, we also investigated the crosslinking of aliphatic cores irradiated with fast electrons⁴.

This paper is dealing with an investigation of the kinetics of direct photochemical stabilization of micelles of the polystyrene-*block*-polybutadiene-*block*-polystyrene copolymer in the selective solvent of polystyrene, induced by UV radiation in the absence of peroxidic or other initiators of radical reactions.

EXPERIMENTAL

Chemicals

The linear three-block copolymer, polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS), prepared by the anionic polymerization (Czechoslovak product, Kralupy; 70 wt. % polybutadiene) was reprecipitated from toluene three times by adding methanol in the presence of BHT as the stabilizer. The middle fraction was used in the measurement. The weight-average molar mass, M_w , determined by the light scattering measurement in good solvents (tetrahydrofuran and toluene) was $(1.53 \pm 0.05) \cdot 10^5 \text{ g mol}^{-1}$. The elution volume, V_{e1} , obtained by means of size-exclusion chromatography (SEC) in tetrahydrofuran using polystyrene standards was $1.6 \cdot 10^5 \text{ g mol}^{-1}$. The elution SEC curve (Fig. 7) shows that the sample had a relatively narrow molar mass distribution (M_w/M_n c. 1.4).

The solvents (with the exception of ethanol) were commercial products of Lachema, Brno, Czechoslovakia. Tetrahydrofuran, reagent grade, was dried with Na and CaH₂ and column distilled prior to use; the middle fraction was collected under reflux 1/30, and its purity was checked refractometrically. Ethanol, an undenatured aqueous azeotrop containing 4 vol. % H₂O, was obtained by the column distillation of aqueous ethanol. Toluene, reagent grade, and methanol, reagent grade, were used in the fractionation of the copolymer without further purification. 4-Methyl-2,6-ditert-butylphenol, reagent grade (BHT as stabilizer), was a commercial product of Lachema, Brno.

Stabilization of Micelles by UV Radiation

Solutions of the copolymer were irradiated in quartz ampoules, 50 cm³ in volume, by means of a high-pressure mercury lamp (500 W). In the range of optical transmission of the solvents used,

the mercury lamp has several rather weak bands in the range 250–300 nm, two intense maxima about 310 and 320 nm and an intense band at 355 nm. During the measurement, the samples were thermostated to $25 \pm 0.2^\circ\text{C}$ and vigorously stirred. The samples were irradiated while observing a constant geometry of the optical arrangement.

Measurement

Light scattering. The Rayleigh light scattering values were recorded by means of a SOFICA 40 200 instrument in unpolarized light at the wavelength 546 nm in the angular range, θ , $30\text{--}150^\circ$. During the measurement the cells were thermostated to 25°C with an accuracy of $\pm 0.05^\circ\text{C}$.

Measurements of the reversible micellization were carried out in the concentration range $5 \cdot 10^{-4}\text{--}5 \cdot 10^{-3} \text{ g cm}^{-3}$ (the solutions were filtered under pressure through a G5 glass filter) and the values thus obtained were extrapolated to zero concentration and zero scattering angle. In the case of good solvents the extrapolation was carried out using the Zimm method and the relation

$$Kc(\text{dn}/\text{dc})_{\mu}^2/R_{\theta,\text{cor}} = (1/M_w + 2A_2^{(\text{LS})}c) P_{\theta}^{-1}, \quad (1)$$

in which K is the optical constant, c is the polymer concentration, $(\text{dn}/\text{dc})_{\mu}$ is the refractive index increment under the condition of dialysis equilibrium of low-molar mass components of the mixture, $R_{\theta,\text{cor}}$ is the corrected Rayleigh ratio corresponding to dissolved polymer particles, $A_2^{(\text{LS})}$ is the second virial coefficient, P_{θ} is the scattering function. Extrapolation gave the weight-average molar mass of polymer components, M_w . In micellar systems the $Kc(\text{dn}/\text{dc})_{\mu}^2/R_{\theta,\text{cor}}$ vs concentration dependences are S-shaped, with a steep decrease of the measured values in the region of critical micelle concentration (c.m.c.), i.e. a shape typical of closed association. The measured values extrapolated to zero scattering angle give concentration-dependent apparent values $M_{w,\text{app}}$, which depend on the molar mass of the unimer (copolymer), M_w^{U} , and on the molar mass of the micelles, M_w^{m} , according to the relation

$$M_{w,\text{app}} = w_{\text{U}}M_w^{\text{U}} + (1 - w_{\text{U}})M_w^{\text{m}}, \quad (2)$$

in which w_{U} is the mass fraction of the unimer at the given total concentration of the copolymer. In the case where the micellization equilibrium is markedly shifted in favour of the micelles, the c.m.c. values are too low compared with the concentration range used in the light scattering measurement, and extrapolation of experimental values to infinite dilution gave apparent $M_{w,\text{app}}$ values close to M_w^{m} values of the micelles.

In the investigation of the kinetics of stabilization of micelles the $M_{w,\text{app}}$ values were determined at a finite, sufficiently low concentration ($c \cdot 5 \cdot 10^{-4} \text{ g cm}^{-3}$) and extrapolated to zero scattering angle. Prior to measurement, the solutions were filtered under pressure through a G4 glass filter.

The refractive index increments, $(\text{dn}/\text{dc})_{\mu}$, of the copolymer in the mixed solvent tetrahydrofuran–ethanol were measured by using a Brice–Phoenix 5 000 V differential refractometer after the establishment of dialysis equilibrium⁵ (vol. % EtOH in the mixture are assigned in brackets: 0.169(25), 0.172(30), 0.174(33), 0.175(34.5), 0.176(35.5)).

Size-exclusion chromatography. The chromatograms were recorded in a low-pressure SEC apparatus consisting of the following parts: tank (5 dm^3) of the eluent made from stainless steel, piston pump MG 706–300 (Microtechna, Czechoslovakia), provided with a pressure pulse equalizer, dosing valve (manufactured in the Development Workshop of the Czechoslovak Academy of Sciences), four stainless steel columns 0.8 cm in diameter and 120 cm long, packed with polystyrene gels, and a differential refractometer Waters R 403, thermostated with an ac-

curacy $\pm 0.01^\circ\text{C}$. The gels were prepared in the Synthetic Rubber Research Institute, Kralupy, Czechoslovakia, and had the following elution limits: one column up to $2.5 \cdot 10^4$, two columns up to 10^6 and one column up to 10^7 g mol^{-1} . The flow rate of the eluent (tetrahydrofuran) was $0.8 \text{ cm}^3 \text{ min}^{-1}$, the concentration range was $5 \cdot 10^{-4} - 10^{-3} \text{ g cm}^{-3}$. The apparatus was calibrated with polystyrene standards having a narrow molar mass distribution ($M_w/M_n < 1.25$), and the following values of the peak maxima of the individual standards were determined ($V_{el}, \text{cm}^{-3}/M_w \cdot 10^4, \text{g mol}^{-1}$): 161/1.75, 140/10, 133/15, 121/30, 112/86, 111/90, 104/230.

Ultracentrifugation. The sedimentation measurements were carried out in an analytical ultracentrifuge MPM 3 170, Hungary, in a one-sector cell 10 mm long, at 45 000 rpm and $25^\circ\text{C} \pm 0.2^\circ\text{C}$. The movement of the concentration boundary was investigated by using the cylinder lens schlieren optics and recorded on a photographic film.

Infrared spectroscopy. The infrared spectra were recorded with a Perkin-Elmer 684 apparatus. The dried amorphous samples at slightly elevated temperature and pressure were shaped into films $c. 0.03 \text{ mm}$ thick.

RESULTS AND DISCUSSION

Micellization Conditions of the Copolymer SBS

Preliminary measurements showed that the SBS sample forms polymolecular micelles with a polybutadiene core and polystyrene shell in THF-EtOH mixtures containing 30–36 vol. % alcohol at 25°C . The dependence of the apparent molar mass on the composition of the solvent can be seen in Fig. 1. In mixtures with 33–35 vol. % EtOH the $M_{w,app}$ values were obtained by the extrapolation of light scattering data

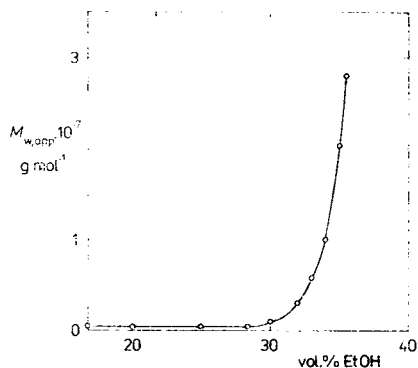


FIG. 1

Dependence of the apparent weight-average molar masses, $M_{w,app}$, of the copolymer SBS on the composition of the mixed solvent THF-EtOH

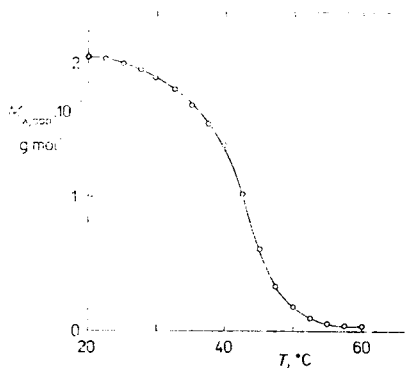


FIG. 2

Effect of temperature on $M_{w,app}$ of reversible micelles in the mixture THF-EtOH (34.5 vol. %)

to infinite dilution from the concentration range in which the unimer \rightleftharpoons micelles equilibrium was markedly shifted in favour of the micelles. In this range of composition of the mixed solvent the values in Fig. 1 can be regarded as close to those of the particle molar mass of the micelles. We chose micelles in the mixture containing 34.5 vol. % EtOH for the photochemical stabilization for the following reasons: (i) The unimer micelles equilibrium is shifted in favour of the micelles within a broad concentration range. (ii) The molar mass of the micelles is sufficiently high and its changes can be readily detected by light scattering. (iii) The $M_{w,app}$ value remains virtually unchanged in the range 20–30°C. Gradual decomposition of the micelles, i.e. a simultaneous decrease of the association number and a shift of the equilibrium towards the unimer take place in the range 30–50°C (Fig. 2); for this reason, the effect of temperature on the kinetics of photochemical stabilization can also be studied in the given mixture. (iv) At 25°C, the mixture is still a relatively good solvent for polystyrene, and therefore one need not be afraid of macroscopic phase separation which might occur at an accidental cooling of solutions with solvents having an alcohol content higher than 35 vol. %.

Stabilization of Micelles

In contrast to our preceding paper³, it was found that the block copolymer SBS with a high polybutadiene content can be stabilized by sufficiently intense UV radiation without using peroxidic or other initiators of radical reactions. However, the stabilization is effective only in solutions containing dissolved O₂. Degassing of the solutions reduced the efficiency of stabilization. A higher amount of dissolved oxygen enlarges not only the rate of stabilization, but also the fraction of the microgel in the resulting product. Since the objective of the study has been a reproducible stabilization of micelles (with the fraction of side products being as small as possible), solutions containing the equilibrium concentration of dissolved air oxygen were used in the measurement.

Fig. 3 shows the kinetic curves of stabilization of micelles in the mixture THF–EtOH (34.5 vol. %) depending on the irradiation time for various temperatures in the range 20–40°C and for the copolymer concentration, $c \cdot 10^{-2} \text{ g cm}^{-3}$. The plot shows an increase in $M_{w,app}$ of stable particles formed in solution during the irradiation. Experimental data were obtained as follows: In chosen time intervals small volume quantities (1 cm³ – to prevent an important change in volume, and thus in the conditions of irradiation) were taken from the solution during irradiation. After dilution with tetrahydrofuran the resulting mixture (1.7 vol. % EtOH) became a good solvent for both blocks, and polymer chains which were not bound mutually in the cores of micelles could be released from the micellar cores; the mixture was stirred for 2 h, to disentangle all “entanglements” in the core of partly stabilized micelles and to release all unbound chains (after two hours the $M_{w,app}$ values did not vary any more). Thus, the $M_{w,app}$ data given here obtained by the light scattering

measurements are those at the finite, sufficiently low concentration ($5 \cdot 10^{-4} \text{ g cm}^{-3}$) and extrapolated to zero scattering angle.

The dependences in Fig. 3 having a typical form of kinetic conversion curves with the induction period resemble curves obtained in our preceding paper⁶. After the initial slow increase (c. 1.5 h) the stabilization process accelerates, and roughly after six hours of irradiation the $M_{w,app}$ values approach a certain limiting value which, however, is slightly less than one half of that obtained for irreversible micelles before the stabilization in a mixture containing 34.5 vol. % alcohol. A rise in temperature has an accelerating effect on the stabilization process; in particular, the induction period is shorter. Nevertheless, curves recorded at higher temperatures have lower $M_{w,app}$ values of the irradiated mixtures, because the $M_{w,app}$ values of reversible micelles are also lower (cf. Fig. 2).

The dependence of the dissymmetry of light scattered from stabilized particles after transfer into a good solvent (cf. the determination of $M_{w,app}$ for plots in Fig. 3) on the irradiation time at 25°C is represented by a curve in Fig. 4. The curve is S-shaped, similarly to that in Fig. 3, thus differing from the case of the stabilization of copolymers with a lower content of polybutadiene caused by peroxidic initiators^{3,6,7}. In earlier cases the increasing crosslinking of polybutadiene cores caused a limited swelling of samples irradiated for a longer time, and the dissymmetry had a maximum at irradiation times about 2 h. Some deviations compared with copo-

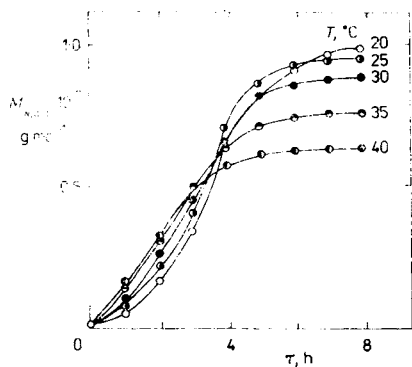


FIG. 3

Stabilization of micelles of the copolymer SBS ($c 10^{-2} \text{ g cm}^{-3}$) in the mixture THF-EtOH (34.5 vol. %) as a function of the time of irradiation ($M_{w,app}$ values determined from measurements of samples of the mixture after dilution with tetrahydrofuran: 1.7 vol. % EtOH, $c 5 \cdot 10^{-4} \text{ g cm}^{-3}$)

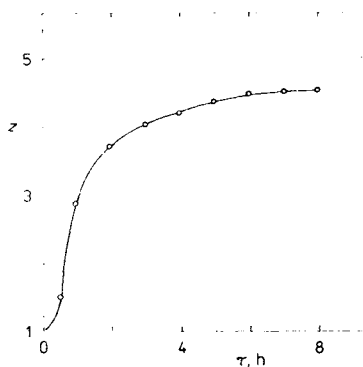


FIG. 4

Dependence of the dissymmetry of scattered light, z , on the time of irradiation of a solution of the copolymer SBS ($c 10^{-2} \text{ g cm}^{-3}$) in the mixture THF-EtOH (34.5 vol. %) at 25°C. Measurements performed with samples diluted with tetrahydrofuran: 1.7 vol. % EtOH, $c 5 \cdot 10^{-4} \text{ g cm}^{-3}$)

lymers studied earlier⁴ are also indicated in plots in Figs 5 and 6. A decrease of $M_{w,app}$ values was observed for micelles irradiated in the THF-EtOH system (34.5 vol. %) for 2 and 6 h after dilution of the original irradiated solution to the copolymer concentration $5 \cdot 10^{-4} \text{ g cm}^{-3}$ in different solutions with increasing THF content. The plot (Fig. 5) shows a sudden decrease in $M_{w,app}$ on transition to a good solvent, due to the release of chemically non-bound polymer chains. The dependence of the dissymmetry of light scattered under the same conditions implies, however (Fig. 6), that stabilized micelles swell strongly also in selective precipitants of polybutadiene (especially at a significant dilution of the solution). Such surprising behaviour can be explained, on the one hand, by the solubilization of fragments of photodegradation rich in polybutadiene into the cores of micelles⁸, and, moreover, on the basis of the photooxidation behaviour of polybutadiene⁹, which can also be partly demonstrated by IR spectra.

Due to partial degradation⁹, irradiation of copolymer samples with a relatively high polybutadiene content may lead to the formation of smaller fragments richer in polybutadiene than the original copolymer. In a selective solvent for polystyrene these fragments are then solubilized in the cores of the micelles⁸, which is accompanied by the formation of a certain fraction of heavier and very bulky micelles. After the stabilization, the resulting effect is reflected in a partial increase in $M_{w,app}$ and in a considerable rise in dissymmetry.

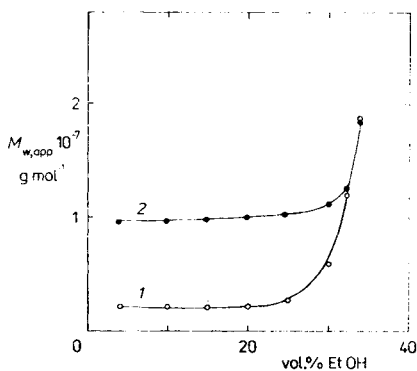


FIG. 5

Dependence of $M_{w,app}$ of irradiated micelles on the composition of the solvent THF-EtOH at 25°C after dilution to constant concentration $5 \cdot 10^{-4} \text{ g cm}^{-3}$. Time of irradiation: 1 2 h, 2 6 h

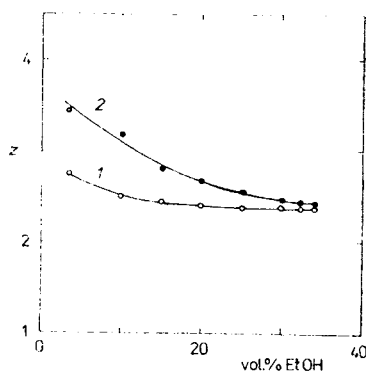
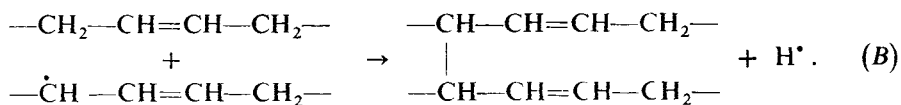


FIG. 6

Dependence of the dissymmetry of light scattered from irradiated micelles on the composition of the solvent THF-EtOH at 25°C after dilution to constant concentration $5 \cdot 10^{-4} \text{ g cm}^{-3}$. Time of irradiation: 1 2 h, 2 6 h

The other photooxidative process, which may contribute to an increase in the dissymmetry of scattered light (and thus to the formation of bulkier particles), consists in the fact that, in the presence of O_2 in solutions of polybutadiene and of copolymers with an important fraction of polybutadiene, a minor amount of hydroperoxides is formed, which absorb in the near UV range by two or three orders of magnitude more strongly than polybutadiene¹⁰. Since the solvent mixture used is optically transparent by 90%, already starting from the wavelength 275 nm and more (at 285 nm, the transparency reaches 99%), these chromophores are operative as photosensibilizing radiation receptors. The absorbed energy is partly transferred to $-CH_2-$ groups in the α -position with respect to the double bonds $C=C$, on which both hydrogen atoms¹¹ and the adjacent carbon atoms are bound by a very labile bond. Hence, the crosslinking proceeds according to the scheme⁹



The hydrogen atoms thus released may react further with the $-CH_2-$ groups. In addition, a cleavage of the $C-C$ bonds also occurs here¹². Reactions of the peroxides give rise to labile $C-O-O-C$ bonds, which during intense irradiation are again partly destroyed, while giving rise to relatively stable $C-O-C$ bonds. Great many reactions may occur in this case, because the $\cdot OH$ radicals formed by the decomposition of hydroperoxide groups may again initiate reactions of the $-CH_2-$ groups. In the final photooxidation product, carbonyl groups are formed to quite a considerable extent. Measurement of IR spectra in the range around $1\,000\text{ cm}^{-1}$ (by following the ratio of intensity of the deformation vibration of $C-H$ in the *cis* double bond $-CH=CH-$ at 967 cm^{-1} and the vibration intensity of $C-H$ in the aromatic ring of polystyrene at $1\,030\text{ cm}^{-1}$) indicated a significant loss in the double $C=C$ bonds (by 25% on the average after eight hours of irradiation). In the sample after irradiation, there is a broad band of $-C-O-$ vibrations ($1\,000-1\,200\text{ cm}^{-1}$) with a maximum about $1\,100\text{ cm}^{-1}$, vibrations of the $C=O$ groups about $1\,700\text{ cm}^{-1}$ and vibrations of the $-O-H$ groups in the range below $3\,600\text{ cm}^{-1}$. In view of the fact that the crosslinking occurs preferentially on carbon atoms of the $-CH_2-$ groups in the α -position to the double bond $C=C$ (ref.¹¹) and that a strong tendency towards swelling suggests a low density of crosslinking, it may be assumed that, in particular, carbonyl groups are formed in the polybutadiene chain^{13,14} (simultaneously with the decay of the original double bonds), which change the character of the chain and its interaction with the solvent. This is why the cores of the micelles undergoing crosslinking swell already during the irradiation in the selective solvent.

The kinetic curves shown in Figs 3, 4 indicate only an increase in the apparent weight-average molar mass or dissymmetry of all particles existing in solution for

a certain irradiation time, but do not provide any information as to the mass distribution of sizes and molar masses of the particles in solution. These changes in the distribution of sizes and molar masses during the irradiation were investigated by SEC chromatography and sedimentation.

In order to estimate the effect of photooxidative processes on the molar mass distribution of the molecularly dissolved copolymer SBS, first an SBS sample in a good solvent (THF) was irradiated for 8 hours. Under the same conditions as in the preceding and subsequent experiments, samples for measurements of the elution curves in THF as the eluent were extracted from the irradiated solutions at certain time intervals.

A comparison of chromatograms of the untreated copolymer and of a sample irradiated for eight hours (Fig. 7) shows that, except for the broadening of the elution curve towards lower and higher elution volumes, there is no significant change in the distribution (in the sense of changes investigated in the stabilization of micelles). The maximum of the peak of the irradiated sample is slightly shifted to higher elution volumes, thus suggesting a partial degradation of the chains. This fact is not surprising, because in dilute solution the sample is present in the form of free coils.

Fig. 8 shows distribution changes after the irradiation of the copolymer SBS in the THF-EtOH mixture (20 vol. %). Although this mixture is a poor solvent for polybutadiene, the untreated copolymer under study is molecularly dissolved in it. Already after two hours of irradiation the formation of a non-negligible fraction of markedly larger particles can be observed (Fig. 8a). After eight hours there is an indication of two maxima on the elution curve. This finding may be explained in the following way: Due to the degradation process, subchains with a markedly predominating, or even a hundred-per-cent content of polybutadiene are split off. During their clustering (which in systems not containing the block copolymer would precede the phase separation), induced micellization takes place⁸, i.e. the precipitated chains are surrounded by undegraded copolymer molecules which impede their macroscopic separation. The cores of these micelles which contain solubilized chains with a high content of polybutadiene units may be readily crosslinked. A rather pronounced shift of the maximum of the peak of small particles towards higher V_{e1} values (especially at a shorter irradiation time) corresponds to the higher degree of coiling of polybutadiene blocks in the molecularly dissolved copolymer and with the increased probability of their intramolecular crosslinking. After being transferred into THF, these blocks cannot swell so readily. The broadening of the peak towards high V_{e1} values is also supported by the degradation products with a higher polystyrene content or with photooxidatively modified polybutadiene sequences.

Changes in the distribution which occur in the stabilization of micelles in the THF-EtOH mixture (34.0 vol. %) at the copolymer concentration 10^{-2} g cm⁻³ are shown in Fig. 9. Already after two hours (Fig. 9b) the contribution of large particles can be seen; after three hours the distribution has two distinct peaks (Fig. 9c). After

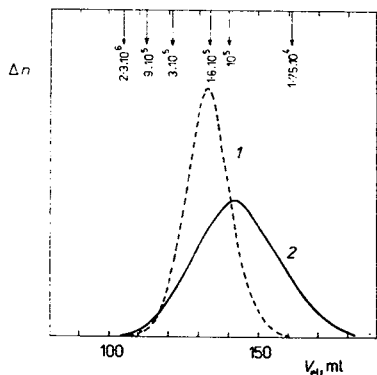


FIG. 7

SEC chromatogram of the copolymer SBS in tetrahydrofuran: 1 untreated sample, 2 after two hours of irradiation (in the upper part of the figure the positions of the peak maxima of polystyrene standards are indicated)

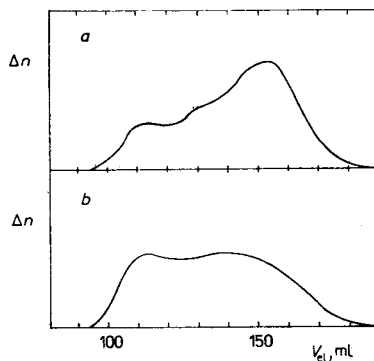


FIG. 8

SEC chromatogram of the copolymer SBS ($c 10^{-2} \text{ g cm}^{-3}$) irradiated in the mixture THF-EtOH (20 vol. %) at 25°C for 2 h $\frac{a}{b}$, 6 h $\frac{b}{a}$

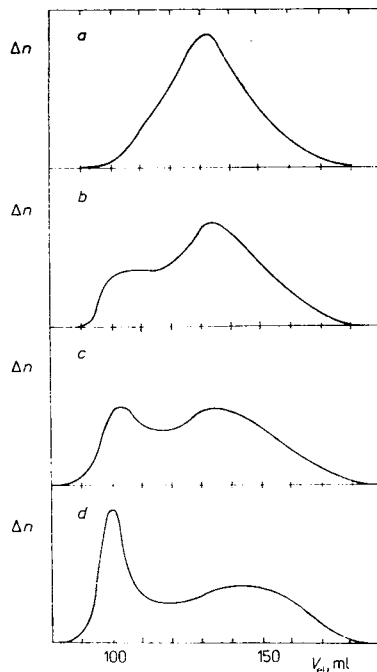


FIG. 9

SEC chromatogram of the copolymer SBS ($c 10^{-2} \text{ g cm}^{-3}$) irradiated in the mixture THF-EtOH (34.0 vol. %) for 1 h (a), 2 h (b), 3 h (c), and 6 h (d)

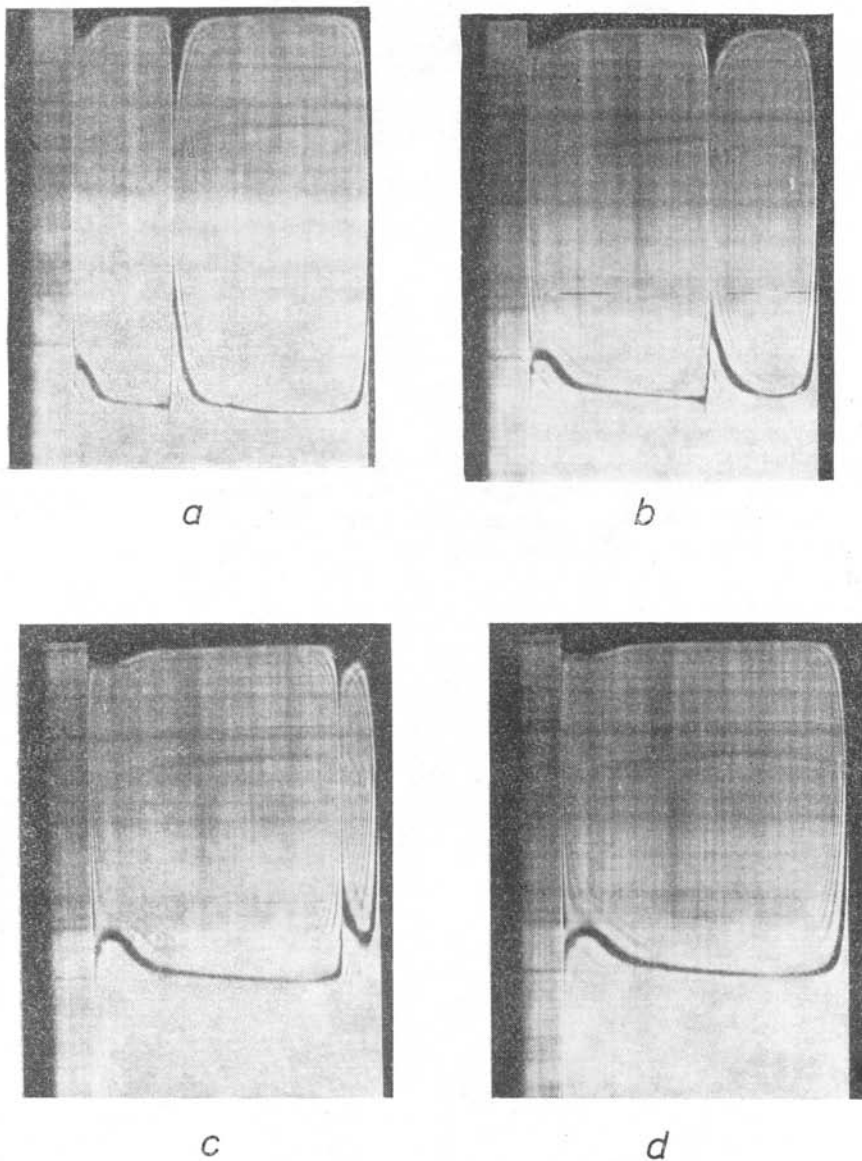


FIG. 10
Sedimentation diagrams of the copolymer SBS ($c 1.0 \cdot 10^{-2} \text{ g cm}^{-3}$) irradiated 8 h in the mixture THF-EtOH (34.5 vol. %) after dilution of the system with tetrahydrofuran ($c 3.3 \cdot 10^{-3} \text{ g cm}^{-3}$, 11.5 vol. % EtOH). Times (min): 10 (a), 20 (b), 30 (c), 40 (d)

six hours of irradiation the mass fraction of large and heavy particles varies about 50 wt. %. The peak of small particles is very broad. The small width of the peak of stabilized micelles is mainly due to the fact that the stabilized particles approach by their size the elution limit of SEC chromatography (of the gels used). In this range of dimensions of polymer particles the resolution of the column is minimal, and the narrow width of the elution peaks does not mean a small polydispersity of sizes of polymer particles. On the contrary, sedimentation measurements (cf. below) prove that the polydispersity of the mixture is quite considerable. Chromatograms of samples stabilized in mixture with 34.5 and 35.0 vol. % EtOH are very similar to the preceding case, both by their form and by the fraction of large and small particles after completed irradiation, and are not reported here. The only difference (compare with the curve 9d) consists in the fact that the size of the stabilized particles exceeds the elution limit of the columns, and the maximum of the corresponding peak appeared each time at V_{e1} 95 cm³.

The SEC chromatography provides valuable information about changes in the distribution of non-micellized species (unimers and their fragments) and about the mass ratio of large stabilized particles to smaller ones; due to the large molar mass and size of the stabilized micelles, it cannot provide sufficient information on their polydispersity. For this reason, our study has been supplemented by preliminary sedimentation measurements (stabilization in the system THF–EtOH (34.5 vol. %), c 10⁻² g cm⁻³; the sedimentation was carried out after dilution (1 : 2 by vol.) with tetrahydrofuran, i.e. in a thermodynamically good solvent of both blocks). The rate of sedimentation of stabilized particles is so much higher, compared with the micellized fractions (Fig. 10), that both adequately developed peaks cannot be recorded in the sedimentation pattern simultaneously (either the peak of the micelles is adequately developed, but that of the unimer is still not sufficiently separated from the meniscus, or later on the peak of the micelles is deformed due to the substance concentrated at the bottom of the cell). The sufficiently long range of zero concentration gradient between the two peaks demonstrates a sufficient difference between molar masses of the stabilized micelles and of the other particles. This clearly proves the effectivity of stabilization, leading to a significant fraction of really large particles containing a large number of chemically bound chains. At high sedimentation rates, where diffusion is quite negligible, asymmetry of the peak of the micelles towards the cell bottom becomes a qualitative evidence of the considerable polydispersity of stabilized micelles.

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