Notes to the Editor

Formation of ABA poly(styrene-b-butadiene) copolymer micelles in methyl ethyl ketone and other solvents

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(Received 29 December 1977)

INTRODUCTION

It is well known[1-5] that block copolymers of the ABA poly(styrene-b-butadiene) type form micelles when solutions are prepared utilizing either single or mixed solvents which are selective for the polystyrene end blocks. These multimolecular micelles are envisaged as consisting of cores formed by aggregation of precipitated polybutadiene blocks which are surrounded by solubilized fringes of the end blocks. The core may be envisaged as being swollen or unswollen depending on the solvent power of the liquid medium. Some evidence[6] exists to show that the solid state aggregates formed in ethyl acetate have a more complex structure. This work[6] also indicates that for the one sample studied there seems to be a distribution of sizes of micelles ranging from monomolecular micelles up to some very large supramolecular structures. In other words, the open system proposed by Elias[7] seems to be correct.

In this paper an attempt has been made to estimate the average number of SBS molecules per micelle ($\bar{N}_m$) in methyl ethyl ketone from light scattering studies. It is, of course, the case that light scattering data for a copolymer polydisperse with respect to composition, does not lead to a true value of the weight-average molecular weight ($\bar{M}_w$)[8,9], but to an apparent molecular weight ($\bar{M}_a$). However, the samples used in this work had a composition (*Table 1*) which was homogeneous enough to justify the assumption[4] that $\bar{M}_a$ is approximately equal to $\bar{M}_w$, thus permitting the calculation of $\bar{N}_m$.

Krause and Reismiller[5] have reported a similar study also in methyl ethyl ketone. They argue that the number of molecules per micelle ought to be proportional to the butadiene mid-block molecular weight (M_B) to the power 1.5

if the micellar cores are unswollen. Using this approach, they calculated the value of $\bar{N}_m$ to be expected for an SBS copolymer sample used by Pleštil and Baldrian[2] claiming excellent agreement with the reported experimental value. This concept has been tested further using our own and literature data.

An alternative, non-rigorous approach to the calculation of $\bar{N}_m$ may also be adopted. Consider the SBS micelles in a solution to be aggregated into a region of volume V such that the density (σ) of this region is that of the copolymer in the bulk state. This is what is considered to happen[6] when a micellar solution is allowed to evaporate to dryness during a casting operation. The number of molecules per unit volume (N) of the condensed region is given by equation (1):

$$N = \frac{\sigma}{M} N_A \qquad (1)$$

Here M is the molecular weight of the copolymer and N_A is Avogadro's number. If N_T is the total number of molecules in volume V, then

$$V = N_T M / N_A \sigma \qquad (2)$$

The average volume of a micelle ($\bar{V}_m$) is given by equation (3):

$$\bar{V}_m = N_T M / n N_A \sigma \qquad (3)$$

where n is the number of micelles. Equation (3) may be rewritten as:

$$\bar{V}_m = \bar{N}_m M / N_A \sigma \qquad (4)$$

If the assumption is made that the individual micelles are spherical with a mean radius ($\bar{R}$), then:

$$\bar{V}_m = 4\pi\bar{R}^3/3 = \bar{N}_m M / N_A \sigma \qquad (5)$$

Therefore:

$$\bar{R} = (3\bar{N}_m M / 4\pi N_A \sigma)^{1/3}$$
$$= 0.075(\bar{N}_m M)^{1/3} \qquad (6)$$

In equation (6) where $\bar{R}$ is in nm, an experimentally determined density value of 0.94 g/cm^3 (ref 6) was taken. This relation has been applied to the data available in the literature.

EXPERIMENTAL

The characterization data for the two samples kindly supplied by the Shell Chemical Company are shown in *Table 1*. The number-average molecular weights ($\bar{M}_n$) were determined at 37°C in toluene using a model 501 Mecrolab membrane osmometer. A Waters Associates GPC apparatus (model 502) was used to determine the $\bar{M}_w/\bar{M}_n$ ratio, whilst the styrene content and the polybutadiene microstructure were obtained from 100 and 220 MHz proton n.m.r. spectra, respectively.

Table 1 Characterization data

Sample code	FC1	FA2
$\bar{M}_n \times 10^{-3}$	141	84
$\bar{M}_w/\bar{M}_n$	1.08	1.08
A—B—A[a]	18 700—103 600—18 700	10 700—62 600—10 700
Styrene (wt %)	26.5	25.5
Microstructure (%):		
trans 1,4-	46	46
cis 1,4-	38	39
1,2-	16	15

[a] Block molecular weights calculated using the measured styrene content

The methyl ethyl ketone was redistilled (x3) prior to use. The solvent and solutions for light scattering were clarified by pressure filtration through sintered glass filters directly into the light scattering cells. The specific refractive index increment (0.201 ml/g) for the SBS/methyl ethyl ketone system was determined at 25°C and at a wavelength of 546 nm using a Brice—Phoenix differential refractometer. The refractive index of methyl ethyl ketone at the same temperature and wavelength was taken as 1.3780[10]. The light scattering experiments were performed on dilute solutions using a Sofica light scattering photometer (model 701). Measurements were made for four concentrations over a range of angles between 30° and 150°. The data were simultaneously double extrapolated to zero angle and zero concentration in the conventional way[11].

RESULTS AND DISCUSSION

The Zimm plots for both samples were distinctly curved unlike those reported by Lally and Price[4] for an SBS copolymer in ethyl acetate. This lack of linearity precluded the calculation of radii of gyration. The values of $\overline{M}_a$ obtained for sample FC1 and FA2 were 23×10^6 and 3.8×10^6, respectively. Using calculated values (Table 1) of $\overline{M}_w$ for the copolymer samples, the $\overline{N}_m$ values for samples FC1 and FA2 are 151 and 42, respectively.

There are two papers[2,5] in the literature concerned with the estimation of $\overline{N}_m$ for SBS block copolymers in methyl ethyl ketone. For a sample containing about 50% by wt of polystyrene (Table 2) Krause and Reismiller[5] calculated $\overline{N}_m$ to be about 60, whilst for a higher molecular weight sample (Table 2) Pleŝtil and Baldrian[2] found a value of around 300. For the purpose of this paper a value of 276 molecules per micelle (Table 3) will be taken as the best value of $\overline{N}_m$ from the Pleŝtil and Baldrian[2] data. The Pleŝtil and Baldrian[2] sample had a mid-block molecular weight of about 55 000 as opposed to 28 000 for the Krause and Reismiller[5] sample. Thus, it is to be expected that the Pleŝtil and Baldrian[2] polymer should form the larger micelles.

As stated earlier, Krause and Reismiller[5] suggested that $\overline{N}_m$ should be proportional to $M_B^{1.5}$. They claim, using their own data ($\overline{N}_m$ equal to 60) to calculate the proportionality constant, that this relation predicts that the Pleŝtil and Baldrian[2] sample should yield micelles containing about 200 molecules

and comment that the agreement is excellent. From the data presented in Table 4, it can be seen that the agreement is not particularly good as the best experimental value for the Pleŝtil and Baldrian[2] work, as mentioned earlier, is thought to be 276, whilst the value calculated using the Krause and Reismiller[5] data predicts a value of 171. When this approach of using a particular set of data to calculate the proportionality constant which is then used to predict $\overline{N}_m$ values for other SBS samples in methyl ethyl ketone is applied to the first four systems in Table 3 the data in Table 4 are produced. It is clear that this approach is not successful as the experimental and predicted $\overline{N}_m$ values are often vastly different. It seems that the Krause and Reismiller[5] proposal that $\overline{N}_m$ is proportional to $M_B^{1.5}$ is not confirmed in practice. When this approach is applied irrespective of solvent, to all the systems detailed in Tables 2 and 3, the observed differences between experimental and calculated $\overline{N}_m$ values do not become any worse.

The values of $\overline{R}$ from equation (6) apply to the average micellar radius in a solid, solvent cast sample, but a micelle in solution may have a somewhat swollen core and will have a solubilized fringe of polystyrene end blocks. In order to check whether $\overline{R}$ is an approximate measure of the micellar radius of gyration, equation (6) was used both for samples FC1 and FA2 and for the four literature samples[1-5] already discussed. The results of this excercise are shown in Table 5 along with the corres-

ponding radius of gyration literature values. Unfortunately, there are only three such values reported. In two cases there is very good accord between the literature radius of gyration and the calculated $\overline{R}$ value, but in the other case the results differ by a factor of two. It was thought that a possible explanation for this dramatic difference might be that the micellar cores are significantly more swollen in ethyl acetate than they are in methyl ethyl ketone or dioxane/ethanol. To check this possibility a polybutadiene sample with a number-average molecular weight of 100×10^3 and with a microstructure virtually identical to samples FC1 and FA2 was swollen in both methyl ethyl

Table 2 Characterization data for literature samples

Authors (reference)	Sample code	$\overline{M}_n$ (X 10^{-3})	A—B—A	Styrene (wt %)
Pleŝtil and Baldrian[2]	SBS	112	28 600—54 900—28 600	51
Krause and Reismiller[5]	68	56.1	14 500—27 900—13 700	50.3
Lally and Price[4]	TR-41-1469	97.9	13 600- 69 800—14 500	28.7
Tuzar and Kratochvil[1]	SBS-2	140[a]	36 400—67 200—36 400	52
Tuzar, Petrus and Kratochvil[3]	SBS-2	Same sample as Tuzar and Kratochvil[a]		

[a] Weight-average molecular weight

Table 3 Own and literature data on micelles in single and mixed solvents

Authors (sample)	Solvent	$\overline{M}_a$ (X 10^{-6})	$\overline{N}_m$
Enyiegbulam and Hourston (FC1)	Methyl ethyl ketone	23	151
Enyiegbulam and Hourston (FA2)	Methyl ethyl ketone	3.8	42
Pleŝtil and Baldrian (SBS)	Methyl ethyl ketone	37	276[a]
Krause and Reismiller (68)	Methyl ethyl ketone	4	62[b]
Lally and Price (TR-41-1469)	Ethyl acetate	12	123
Tuzar and Kratochvil (SBS-2)	Dioxane/ethanol (39% by vol)	15.5	110
Tuzar, Petrus and Kratochvil (SBS-2)	THF/allyl alcohol (52% by vol)	23	164

[a] Based on the determined molecular weight (134 000) of a disintegrated micellar solution;
[b] Based on an $\overline{M}_a$ value (64 500) for the sample cyclohexane

Table 4 Experimental and calculated values of $\overline{N}_m$ for SBS samples in methyl ethyl ketone

	$\overline{N}_m$	$\overline{N}_m$
This work (FC1)	151	89[b]
		716[c]
		444[d]
This work (FA2)	42	71[a]
		336[c]
		208[d]
Pleŝtil and Baldrian (SBS)	276	35[b]
		58[a]
		171[d]
Krause and Reismiller (68)	62	13[b]
		21[a]
		100[c]

* Superscripts indicate the data used to calculate the proportionality constants: [a] this work using sample FC1; [b] this work using sample FA2; [c] Pleŝtil and Baldrian[2]; [d] Krause and Reismiller[5] using sample 68

Table 5 Data calculated using equation (6) and the equivalent sphere model

Authors (reference)	Sample	Radius of gyration (literature) (nm)	$\bar{R}$ (nm)	D (nm)	σ_s (kg/m^3)
This work	FC1		21	54	460
This work	FA2		11	28	550
Pleštil and Baldrian[2]	SBS	25.3	24	62	490
Krause and Reismiller[5]	68		11	28	580
Lally and Price[4]	TR-41-1469	35	17	44(90)[a]	450(52)[a]
Tuzar and Kratochvil[1]	SBS-2	20	19	49	420
Tuzar, Petrus and Kratochvil[3]	SBS-2		21	54	460

[a] Calculated using the value of radius of gyration give in ref 4

ketone and ethyl acetate. In fact, the sample in methyl ethyl ketone absorbed 0.72 g of solvent/g of polybutadiene whilst the value in ethyl acetate was 0.64 g of solvent/g of polybutadiene. It is difficult to see an explanation other than an association of micelles for this discrepancy as the molecular weights of the mid-blocks (*Table 2*) of the three polymers[1,2,4] are roughly equivalent and as the Lally and Price[4] sample has much shorter end blocks (*Table 2*) it would seem improbable that they are able to dominate the magnitude of the radius of gyration to the observed extent even if ethyl acetate is a significantly better solvent than methyl ethyl ketone for polystyrene. Clearly it is necessary to test equation (6) much further before any claim that it is widely applicable can be justified.

If it is assumed that $\bar{R}$ is equal to the radius of gyration, the diameters of the equivalent hard spheres (D) can be calculated[12] from equation (7):

$$\bar{R}^2 = 3D^2/20 \tag{7}$$

The values are shown in *Table 5* along with the densities (σ_s) of the equivalent spheres. These were calculated on the assumption that the micelles were of uniform density and are an order of magnitude higher than would be the case for a randomly coiled macromolecule of the same molecular weight[2]. The values in methyl ethyl ketone and other solvents do differ from sample to sample, but it is not possible at this stage to place any significance on these variations. It was noted (*Table 5*) that the Lally and Price[4] sample gave a

density which was similar to the others, but when the quoted radius of gyration (35 nm) is used, a density value results which is an order of magnitude lower than for any of the other samples.

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Equilibrium monomer concentration for the anionic polymerization of α-methylstyrene in cyclohexane

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(Received 14 October 1977; revised 16 January 1978)

INTRODUCTION

The anionic equilibrium polymerization of α-methylstyrene has been the object of several studies[1-8]. Most of these were carried out in tetrahydrofuran or p-dioxane solvent. Two were carried out in neat α-methylstyrene[4,7]. There was evidence for a solvent effect on the equilibrium monomer concentration, $[M]_e$, at various temperatures,

with $[M]_e$ being smaller in less polar solvents[4,6,7]. It was of interest in these laboratories to determine $[M]_e$ values in cyclohexane for this polymerization system. The temperature range studied was from 5°C (below which the solution freezes) to 40°C (above which polymer yield becomes very small unless the polymerization is run in neat α-methylstyrene).

EXPERIMENTAL

Materials

Cyclohexane was 99.5% grade obtained from Phillips Petroleum Company. It was passed through a water-cooled silica gel column under nitrogen pressure and stored under nitrogen. Source and purification of the α-methylstyrene and diethyl ether were described previously[9,10]. Tetrahydrofuran was stored over and distilled from sodium wire, then stored over fresh sodium wire until used. Heptane solutions of 0.40 and 0.60 M diethyl ether, and 0.20 and 0.40 M tetrahydrofuran were prepared under nitrogen in