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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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

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bottles capped with self-sealing rubber septums. A 0.20 M solution of sec-butyllithium was prepared in similar fashion, by diluting with heptane a 1.47 M stock solution in hexane, from Foote Mineral Company. All solutions were transferred by hypodermic syringes.

Polymerizations

An appropriate solution of α-methylstyrene in cyclohexane was prepared and passed through a chilled (< 10°C) silica gel column under nitrogen pressure. It was collected in a receiver flask, sparged with and stored under nitrogen. One master portion of solution was used for all runs carried out at a given temperature.

Polymerizations were run in 4 oz, screw-capped bottles. 40 ml of solution were charged into a bottle under a blanket of nitrogen, and sparged 10 sec with nitrogen. Three bottles were randomly selected for analyses by gas chromatography. The triplicate results were averaged to determine the α-methylstyrene concentration.

All other bottles were initiated with 2.5 ml each of sec-butyllithium solution and the appropriate ether solution. (The α-methylstyrene concentrations were corrected for this dilution.) They were sealed with a metal screw-cap lined with a polyethylene gasket. For runs at 5° and 10°C, bottles were chilled to these temperatures before initiation; for the other runs, initiation was done at ambient temperature (~24°C), and bottles were quickly placed in a water bath at the desired temperature.

Initiation was instantaneous in all cases; the deep red colour of the α-methylstyryl anion appeared at once. A few drops of methanol were added to terminate polymerization after various intervals. Polymer was isolated by precipitation in methanol, and dried *in vacuo.*

Determination of $[M]_e$

α-Methylstyrene polymerizes very slowly in hydrocarbon media, especially when compared to styrene[4]. For the experimental conditions reported herein, it was not possible to attain the monomer–polymer equilibrium with sec-butyllithium initiator alone. Small amounts of an ether strongly accelerate this polymerization[9], so four combinations of sec-butyllithium and an ether modifier, at different molar ratios, were used as initiators: diethyl ether/Li = 2 or 3, and tetrahydrofuran/Li = 1 or 2. With all of these, polymer yields became constant in 72 h, and often within 24 h, i.e. no further increases after extended reaction times of 10–11 days. This was taken as evidence that equilibrium had been attained. (No attempt was made to approach equilibrium from the other side, by depolymerization of a 'living' polymer. This has been demonstrated in tetrahydrofuran solvent[1].)

Since a series of polymerizations was run with each of the four initiator combinations, quadruplicate determinations of equilibrium polymer yield were made at each temperature. These were converted to mol/l of α-methylstyrene polymerized, $[M]_p$. The initial α-methylstyrene concentration, $[M]_0$, was determined from the gas chromatographic analyses of the starting solution (see above). The concentration of unreacted α-methylstyrene remaining at equilibrium was determined by $[M]_0 - [M]_p = [M]_e$. Thus four sets of values were determined for $[M]_e$. No significant trends were noted in the $[M]_e$ values for the different initiator combinations, and agreement between the four values at each temperature was fairly good (see *Table 1*). Hence they were averaged to determine $[M]_e$ at each respective temperature.

RESULTS AND DISCUSSION

The equilibrium monomer concentrations found at the various temperatures are given in *Table 1.* Several authors have shown that $[M]_e$ is affected by the polymer concentration[3,5,6]. Attempts were made in this study to maintain the amount of polymer, $[M]_p$, reasonably constant to minimize any affect it might have on $[M]_e$.

Dainton and Ivin defined the relation between temperature and equilibrium monomer concentration by the equation:

Table 1 Equilibrium monomer concentrations

T(°C)	$[M]_0$ (mol/l)	$[M]_p$ (mol/l)	$[M]_e$ (mol/l)
5	2.09	1.72	0.37 (±0.03)
10	2.09	1.57	0.52 (±0.02)
20	2.22	1.19	1.03 (±0.04)
20	2.33	1.22	1.11 (±0.04)
30	3.41	1.32	2.09 (±0.07)
40	5.13	1.60	3.53 (±0.07)

All values are averages of results from the four sec-butyllithium/modifier combinations; average errors are included with $[M]_e$ values to show their reproducibility

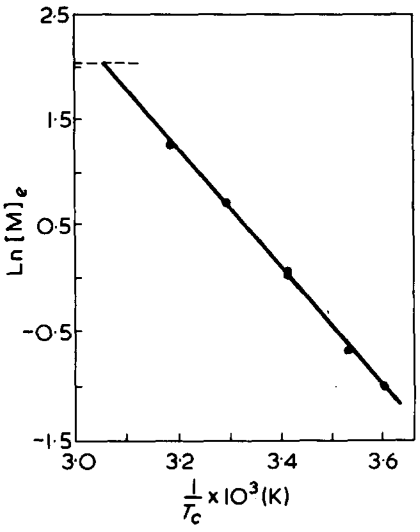

Figure 1 Logarithm of equilibrium monomer concentration (M/L) as a function of reciprocal temperature (K x 10³). – – –, represents concentration of neat α-methylstyrene

$$T_c = \frac{\Delta H}{\Delta S^0 + R\ln[M]_e} \qquad (1)$$

where T_c is the ceiling temperature corresponding to a given $[M]_e$[11]. Thus the ceiling temperature is not constant but varies with the monomer concentration, and it can be raised by increasing the latter quantity. Equation (1) shows $\ln[M]_e$ is a linear function of $1/T_c$, as verified by McCormick for polymerization of α-methylstyrene in tetrahydrofuran[2]. The data of *Table 1* are plotted in *Figure 1*, showing a linear relationship for the reactions in cyclohexane. The broken line in *Figure 1* represents the concentration of neat α-methylstyrene. The graph, when extrapolated to this value, gives T_c = 54°C for the neat monomer. [Separate plots were made for each of the four sets of $[M]_e$ values from the different initiator/modifier combinations (see Experimental). These were practically overlapping, and when extrapolated gave T_c = 54.4° ± 0.6°C. Because of the magnitude of errors in $[M]_e$, and the errors introduced by extrapolation, this value was rounded to the nearest whole number. For purposes of clarity, only a single plot of the average $[M]_e$ values from *Table 1* is given in *Figure 1.*] Since this is the most concentrated solution of α-methylstyrene that can be attained, this T_c may be regarded as the 'absolute' ceiling temperature for α-methylstyrene, above which it cannot be polymerized at all to high molecular weight polymer. Several investigators have found various values for this temperature, or have provided data which can be used to estimate it. These results are summarized in *Table 2.*

Comparing the data of *Table 1* and *Figure 1* with like data obtained in tetrahydrofuran[1,2] shows that $[M]_e$ is smaller in cyclohexane, supporting previous findings[4,6,7] that equilibrium monomer concentrations are lower in less polar solvents (see Introduction). These data also permit the calculation of ΔH and ΔS^0 for this polymerization, from equation (1). The values obtained from the present work, plus those reported in the literature for polymerization in other solvents, are summarized in *Table 3.*

Table 2 'Absolute' ceiling temperature for the anionic polymerization of α-methylstyrene

Solvent	Absolute T_c(°C)	Reference
Tetrahydrofuran	51*	1
Tetrahydrofuran	61	2
Neat monomer	~55	4
Neat monomer	57	7
Cyclohexane	54	This work

*Extrapolated from data for polymerizations from 0° to −40°C

Table 3 Enthalpy and entropy for the anionic polymerization of α-methylstyrene

Solvent	Counterion	$-\Delta H$ (kcal/mol)	$-\Delta S^0$ (cal/mol/°C)	Reference
Tetrahydrofuran	Na^+	6.96	24.8	2
Tetrahydrofuran	Na^+	7.47	26.5	3
Tetrahydrofuran	Na^+	10.8	35.4	5
p-Dioxane	K^+	10.6	–	6
Cyclohexane	Li^+	11.4	39.0	This work

It was noted in all polymerizations that the deep-red colour of the α-methylstyryl anion faded as the reactions proceeded. This has been described by others, who have attributed it to a variety of possible reactions leading to termination of the 'living' polymer[4,12]. The higher the reaction temperature, the more rapidly the colour faded. It was found in this work, however, that the colour was more persistent when the ether modifiers were present; some colour always remained in the polymerization mixtures up to at least 264 h reaction time. Since maximum polymer yield was reached in 24–72 h, it is felt that a true equilibrium was attained, i.e. the $[M]_e$ values were not the result of premature termination of the polymerization. This was not the case when unmodified sec-butyllithium was the initiator. It gave such slow polymerizations that equilibrium was never reached, and colour faded almost completely in these runs after several days. Hence no results from them are included in the data reported here.

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Letter

Thermomechanical study of the hysteritic behaviour of natural rubber networks

Introduction

The deformation of a rubber-like material can be described in a simple way using thermodynamic state functions. At constant pressure and temperature the following state equation can be written:

$$\Delta H = \Delta W + \Delta Q \qquad (1)$$

where ΔH is the enthalpic change, ΔW the elastic work, and ΔQ the heat transferred from or to the sample.

All the terms of the equation (1) can be referred to the volume unit.

The elastic work ΔW, in elongational deformation, is given by the integration of the function τ vs. α, where τ is the force on the unit of undeformed cross-sectional area, and α is the strain ratio defined as L/L_0, L and L_0 being the deformed and undeformed sample length. The integration, which can be performed graphically, gives the numerical value of the integral:

$$\int_1^{\alpha} \tau \mathrm{d}\alpha$$

It follows that:

$$\int_1^{\alpha} \tau \mathrm{d}\alpha + \Delta Q = \Delta H \qquad (2)$$

If equation (2) is used to analyse the hysteretic behaviour of a sample that is stretched and relaxed in a cyclic manner, going through a maximum value of the strain, it can be rewritten:

$$\oint \Delta W + \oint \Delta Q = \oint \Delta H \qquad (3)$$

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