Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Bahadur, P. and Sastry, N. V.(1986) 'Temperature Effect on the Micelle Behavior of Styrene-Isoprene Block Copolymers in Selective Solvents', Journal of Macromolecular Science, Part A, 23: 8, 1007 — 1023

To link to this Article: DOI: 10.1080/00222338608081107

URL: http://dx.doi.org/10.1080/00222338608081107

J. MACROMOL. SCI.–CHEM., A23(8), pp. 1007-1023 (1986)

Temperature Effect on the Micelle Behavior of Styrene-Isoprene Block Copolymers in Selective Solvents

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ABSTRACT

Micelle formation by several styrene-isoprene two-block copolymers in selective solvents, viz., n-heptane, n-dodecane, N,N'-dimethylformamide, and N,N'-dimethylacetamide, was studied by viscometry and photon correlation spectroscopy (PCS). Aggregation number and micellar weight were deduced by combining viscosity and PCS data. The temperature effect on the viscosity behavior of micellar solutions of block copolymers in different selective solvents is examined and explained. ^{1}H-NMR spectra of the copolymer in n-heptane were recorded at different temperatures to explain the characteristic features of micellar solutions.

INTRODUCTION

Dilute solutions of block copolymers in selective solvents are known to form colloidal particles. Colloidal behavior of block copolymer solutions has been a subject of several studies, which are reviewed ex-

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0022-233X/86/2308-1007$3.50/0

tensively by Tuzar and Kratochvil [1], Price [2], and Riess, Bahadur, and Hurtrez [3]. Depending upon the molecular characteristics of the block copolymers, the nature of solvent, and the temperature, the block copolymers were observed to exhibit the presence of unimolecular micelles [1], large particles [4-10], aggregation of molecules through an open association process [11], or aggregation through a close association process [3]. The latter results in polymolecular micelles with a narrow size distribution in analogy to conventional surfactant micelles in aqueous solution and is found to be the most favorable case.

Viscometry [6, 7, 11-24] has been used in the study of block copolymer micelles in solution and has provided useful data, mostly in conjunction with other techniques such as light scattering. A few authors have studied the effect of temperature on the colloidal behavior of block copolymers in solution [6, 7, 17, 18, 21, 26]. The thermodynamics of micellization of styrene-block-(ethylene/propylene) copolymer in dilute solution has been discussed by Price et al. [25].

A systematic study of the viscosity of different block copolymers in various selective solvents at different temperatures was expected to provide useful information. This communication is in continuation of our earlier work on block copolymer micelles [20, 23]. In this paper the effect of temperature on the micellar characteristics of diblock styrene-isoprene copolymers in each type of solvent is examined. Detailed viscometric measurements were carried out in order to get a clearer insight into the micellar solutions at different temperatures. Homologous series of well-defined block copolymers with identical polyisoprene sequences and polystyrene blocks of different molecular weight were used in such solvents as n-heptane and n-dodecane, selectively good solvents for polyisoprene, and dimethylacetamide, DMA, and dimethylformamide, DMF, selectively good solvents for polystyrene, varying in solubility parameters. The effect of temperature on micellar solutions of block copolymer in n-heptane was examined by ^{1}H-NMR spectra. Photon correlation spectroscopy was used for the determination of the size of micelles.

EXPERIMENTAL

Materials

The copolymers were prepared by anionic polymerization of styrene and isoprene and characterized by NMR and GPC in the laboratory of Professor G. Riess in Mulhouse, France; their characteristics are summarized in Table 1.

All the solvents used in this study were Fluka (purum grade) or BDH (AnalaR grade) and were used as such.

The block copolymers in good as well as in selective solvents were easily dissolved at about 45°C to make stable transparent solutions.

TABLE 1. Characteristics of Block Copolymers

Sample	$\overline{M}_n \times 10^{-3}$, g/mol	Styrene, wt%
SA-3	29	31
SA-4	36	45
SA-5	39	49
SA-6	49	59
SA-7	53	62

Micellar solutions of block copolymers, characterized by a bluish tint, did not spoil even on prolonged storage for several weeks.

Fresh solutions were always used for the measurements.

Methods

Viscosity measurements were made using Ubbelohde suspended-level viscometers. Solvent flow times in the range 120-360 s were obtained. Thus, no kinetic corrections were necessary. When at least three consecutive flow times agreeing within ± 0.2 s were recorded, the average flow time was taken. Shear corrections were not taken because the intrinsic viscosities obtained were less than 3 dL/g. The flow volume of the viscometer used was greater than 5 mL, making drainage errors unimportant. The intrinsic viscosities were evaluated by the procedures developed by Huggins, Kraemer, Martin, and Schulz-Blaschke. The appropriate relations are shown in Eqs. (1)-(4).

$$\eta_{sp}/c = [\eta]\ \{1 + k_H[\eta]c\} \tag{1}$$

$$(\ln \eta_r)/c = [\eta]\ \{1 - k_H[\eta]c\} \tag{2}$$

$$\ln\ (\eta_{sp}/c) = \ln\ [\eta] + k_M[\eta]c \tag{3}$$

$$\eta_{sp}/c = [\eta]\ \{1 + k_{SB}\eta_{sp}\} \tag{4}$$

where η_{sp} = specific viscosity, η_r = relative viscosity, and $[\eta]$ = intrinsic viscosity.

PCS study on micellar solutions was made by use of a Coulter N-4 (Coultronics Inc.) instrument which derives the translational diffusion coefficient (D) from the intensity fluctuations in the scattered light.

The hydrodynamic radius (R_h) of the spherical micelles was calculated by the Stokes-Einstein equation:

$$R_h = kT/6\,\Pi\eta\overline{D}_z \qquad (5)$$

where k, T, η, and $\overline{D}_z$ are the Boltzmann constant, the absolute temperature, the viscosity of the solvent, and the z-average diffusion coefficient of micelles, respectively. $\overline{D}_z$ was calculated from the mean decay constant $\overline{Q}$ of autocorrelation functions by the relationship

$$\overline{D}_z = \overline{Q}/2K^2 \qquad (6)$$

where K = $(4\Pi\eta \sin\theta/2)/\lambda$ is the scattering vector, θ is the scattering angle, η is the refractive index of the medium, and λ is the wavelength of the medium in vacuo. When the size of micelles was calculated by Eq. (5), the values of viscosity and refractive index of the solvent at that temperature were taken.

The ^{1}H-NMR spectra of Copolymer SA-6 in n-heptane at several temperatures were recorded with a Bruker WP 80 CW instrument working at 80 MHz and attached to a temperature control unit (Bruker 100/700°C). Enough time was provided for attaining temperature equilibrium of the micellar solutions.

RESULTS AND DISCUSSION

The block copolymers in both types of solvents always formed compact micelles with narrow size distribution as deduced from PCS and electron microscopy [23] results.

Figure 1 shows the temperature dependence of the reduced viscosity, η_{sp}/c, for a series of copolymers in n-heptane (selectively good solvent for polyisoprene). With increasing temperature, η_{sp}/c reached a maximum and then decreased to shallow curvature. However, a further increase in reduced viscosity was seen at higher temperatures. The sharpness in the maximum and the shallowness were most pronounced for a low molecular weight copolymer (SA-3 in this case), and they broaden gradually with increasing total molecular weight.

A similar trend in viscosity behavior was observed for various concentrations of SA-5 block copolymer at different temperatures (Fig. 2).

The viscosity behavior of block copolymers in DMA (selective solvent for polystyrene) is shown in Figs. 3 and 4. The η_{sp}/c versus temperature curve showed two maxima before decreasing gradually at higher temperatures. Only one maximum was seen with a high concen-

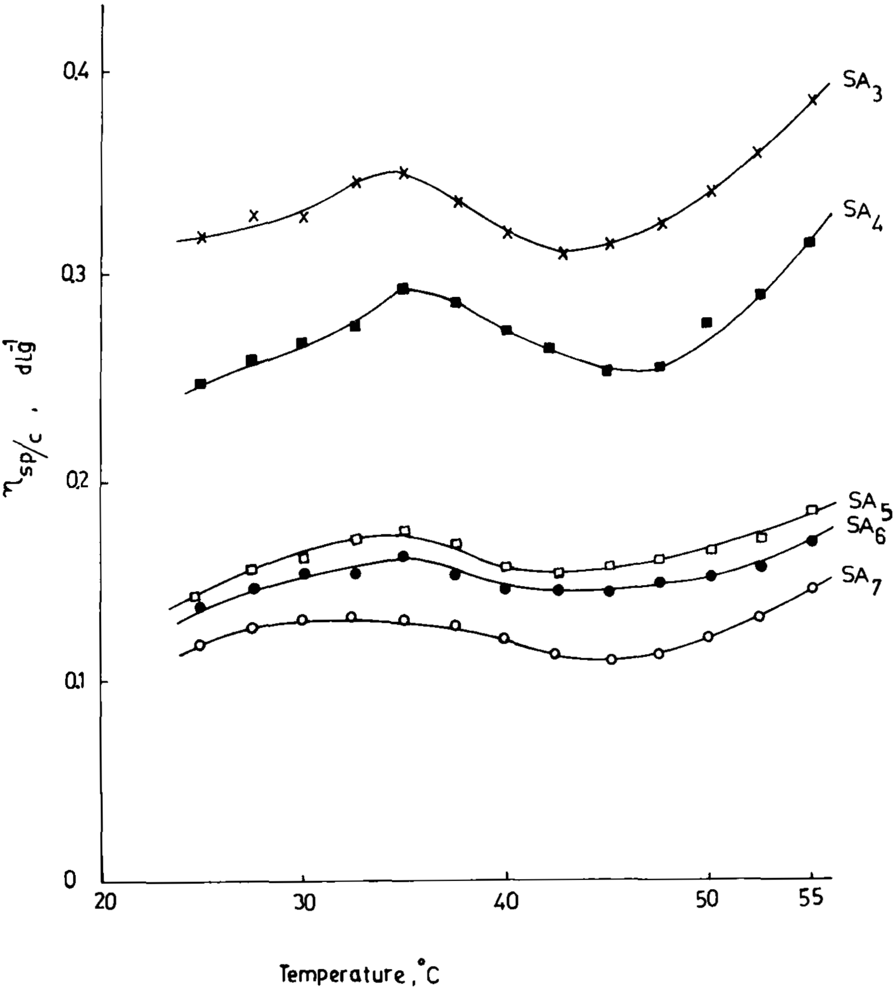

FIG. 1. Reduced viscosity in n-heptane at 0.3 g/dL copolymer concentration.

tration of low molecular weight and a low concentration of high molecular weight copolymers.

Figure 5 displays the temperature dependence of η_{sp}/c for a fixed concentration (0.3 g/dL) of Copolymer SA-4 in DMA, DMF, and methyl ethyl ketone (MEK). In the temperature and concentration range studied, perhaps no micelles were formed in MEK due to its good solvent power. It is interesting to see that the values of η_{sp}/c

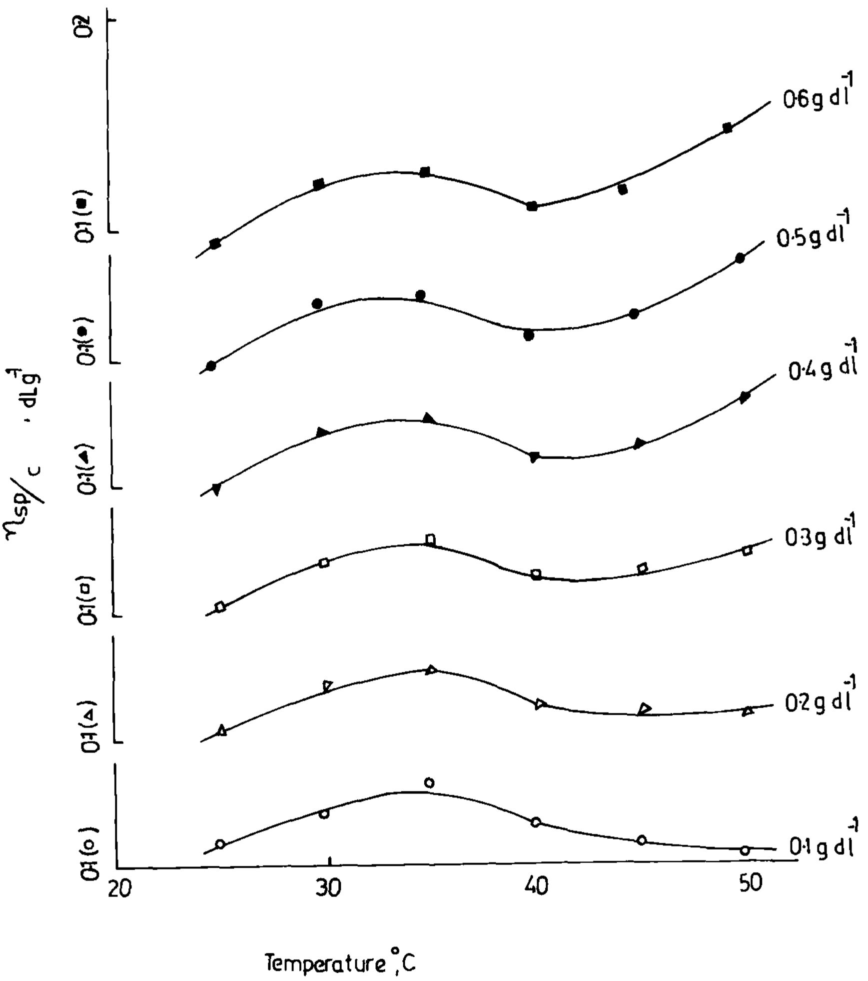

FIG. 2. Reduced viscosity in n-heptane at various copolymer concentrations.

showed an increase with temperature without any maxima or minima. This behavior is almost the same for block copolymer in CCl_4 and toluene, which are good solvents for both the blocks of copolymer. Similar differences between viscosity behavior in selectively good solvent for one block and for solvents selectively good for both the blocks were reported by Price et al. [26]. Because DMF is a poorer

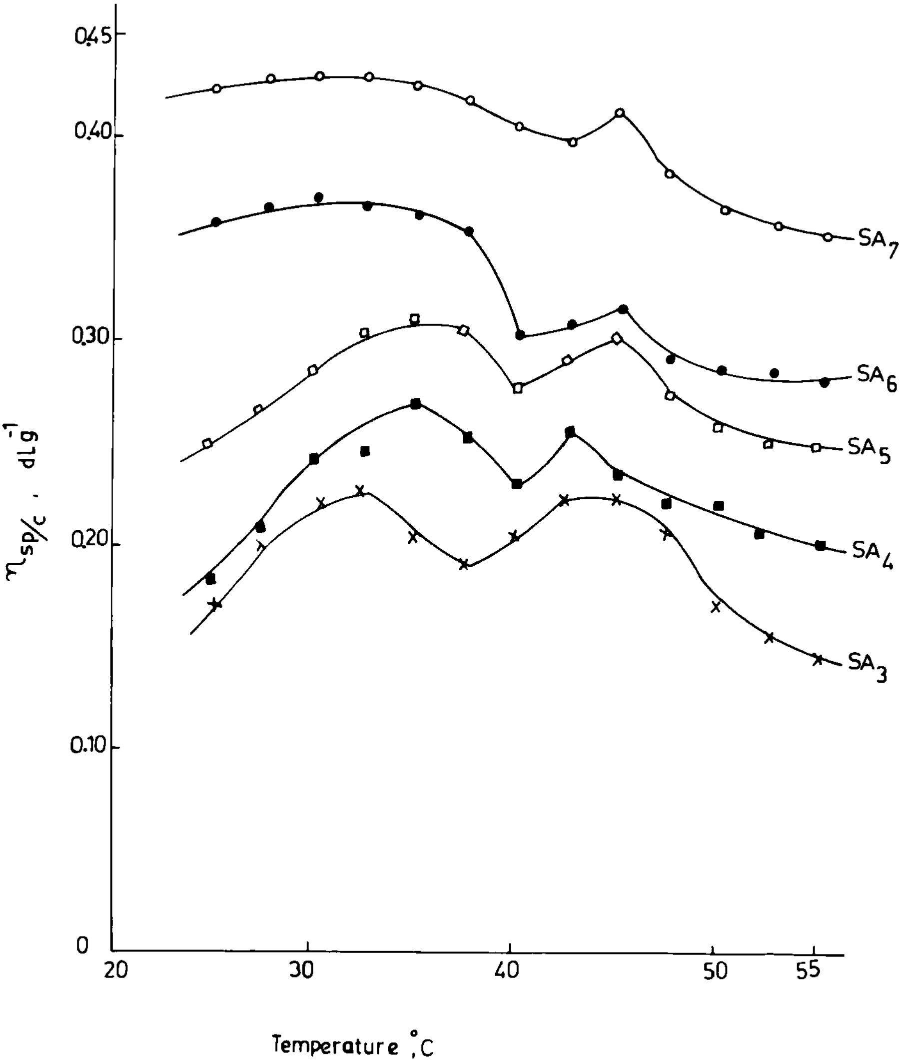

FIG. 3. Reduced viscosity in DMA at 0.3 g/dL copolymer concentration.

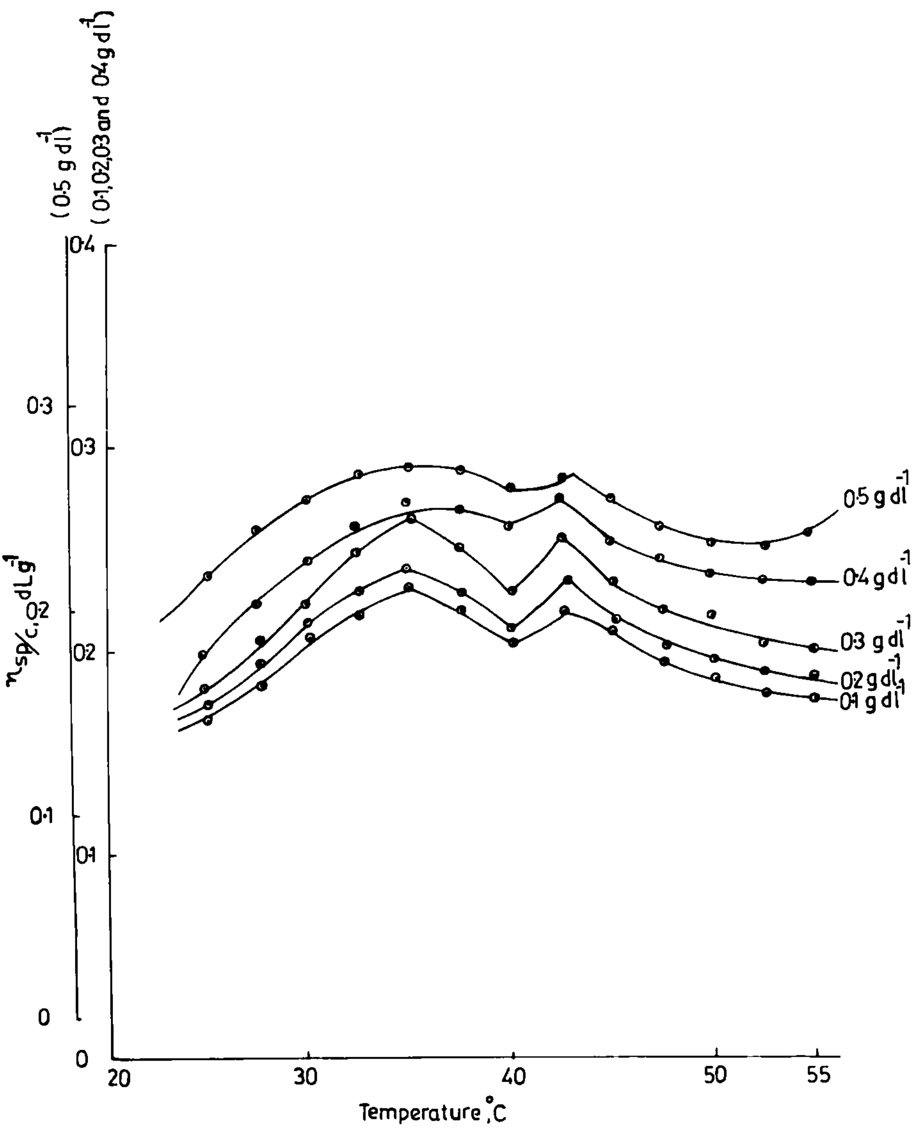

FIG. 4. Reduced viscosity in DMA at various copolymer concentrations.

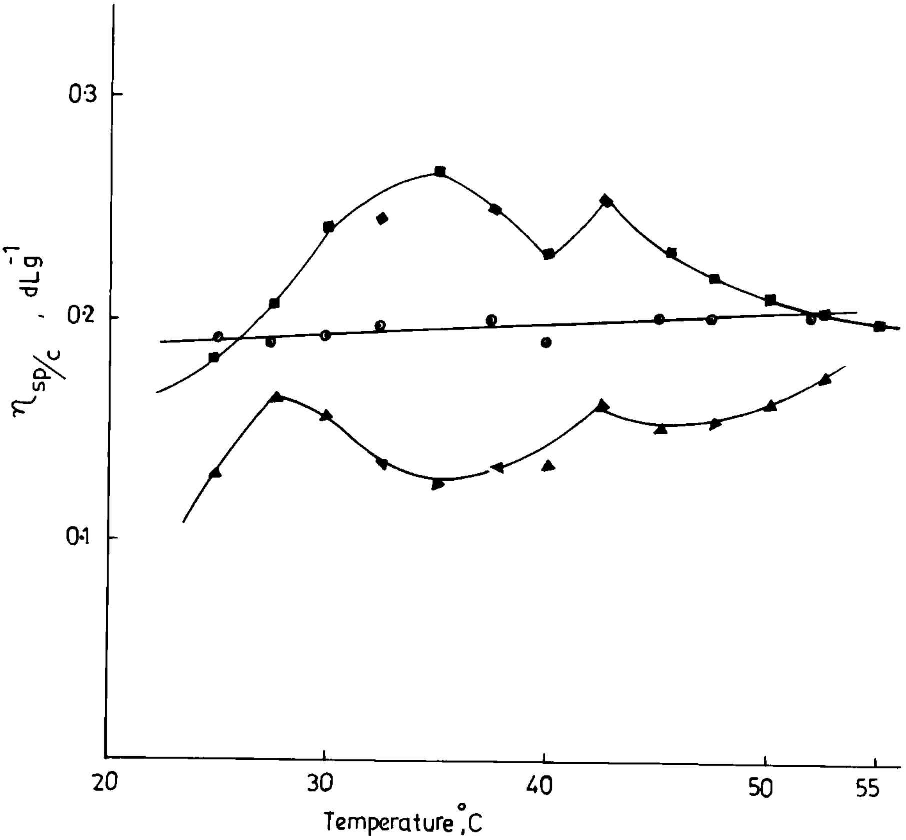

FIG. 5. Reduced viscosity in various solvents at 0.3 g/dL copolymer concentration.

solvent (δ = 12.1) than DMA (δ = 10.8) for polystyrene (δ = 9.2), a sharp increase in η_{sp}/c was observed at higher temperatures.

Several factors will be considered here for interpretation of viscosity behavior of micelle-generating block copolymers.

Micellization of block copolymers is a complex phenomenon, and a better explanation of behavior in dilute solution can be given by studies using different methods of investigation. Elias et al. [27], in their model calculations on the concentration dependence of the reduced viscosity, η_{sp}/c, for closed association systems, assumed that the shape of individual curves of η_{sp}/c versus c may be affected by the values of seven independent parameters: the molar mass of unimer, the intrinsic viscosities and Huggins coefficients of both the unimer and the n-mer, the aggregation number, and the equilibrium constant of the association. Since all these parameters are sensitive to temperature, the η_{sp}/c versus temperature curve at fixed copolymer concentration may show a maximum or minimum depending on the dominance of one parameter over the other in the given temperature range. Depending on the relative molecular weights and hydrodynamic radii of the micelles and unimers for micellar solutions of fixed copolymer concentration, η_{sp}/c for some systems has been observed to increase on passing from predominantly micellar to unimer solution [26]. However, a decrease in η_{sp}/c with increasing temperature was reported by Mandema et al. [6]. Based on these arguments, it is not unreasonable to assume that multimolecular micelles dissociate to unimolecular solutions at higher temperatures, and maxima and minima in viscosity curves can be attributed to the shift in micelle unimer equilibrium in favor of unimers at higher temperatures.

Table 2 displays intrinsic viscosity values at 25°C of copolymers in both types of solvents, computed by different extrapolation techniques. In n-heptane (selectively good solvent for polyisoprene) the intrinsic viscosities decrease with increasing total molecular weight of copolymer and in DMA (a selectively good solvent for polystyrene), the intrinsic viscosities increased with increasing total molecular weight of copolymer. In both solvents the Schulz-Blaschke method yielded higher intrinsic viscosities than in other methods [28].

The influence of temperature on intrinsic viscosity is shown in Table 3. The intrinsic viscosities show a maximum over a temperature range, and at high temperatures a considerable decrease was observed. In Table 4 are shown the micelle size of block copolymers in selective solvents, where micelle size increases with increasing molecular weight of the block copolymer. Table 5 displays the influence of temperature on micellar characteristics of Block Copolymer SA-5 in n-heptane. The micelle size is found to decrease with increasing temperature. Similar temperature dependence of micelle size for styrene-isoprene copolymer in n-decane was observed by Mandema et al. [7]. Plestil and Baldrian [31] studied the micelle size of styrene-butadiene copolymer in n-heptane as a function of temperature by small-angle x-ray scattering. They assumed that the increase in roughness of the surface region of micellar core causes a drop in micelle size with increasing temperature. The aggregation number N, calculated as the ratio of micellar weight to copolymer initial molecular weight, also decreased with increasing temperature. Tuzar et al. [32], using small-angle x-ray scattering, sedimentation analysis, and light scattering studies, observed that micellar weight decreased with increasing temperature because the weight fraction of micelles decreased considerably at elevated temperature. Price et al. [26] also reported a similar dependence of aggregation number on temperature for a styrene-g-

TABLE 2. Intrinsic Viscosities of Block Copolymers in Selective Solvents Obtained by Different Extrapolation Techniques at 25°C

	Copolymer				
Solvent $[\eta]$, dL/g	SA-3	SA-4	SA-5	SA-6	SA-7
n-Heptane:					
$[\eta]_H$	0.154	0.128	0.113	0.106	0.104
$[\eta]_K$	0.152	0.128	0.114	0.106	0.104
$[\eta]_M$	0.160	0.136	0.117	0.107	0.113
$[\eta]_{SB}$	0.156	0.130	0.119	0.114	0.110
DMA:					
$[\eta]_H$	-	0.140	0.230	0.245	0.260
$[\eta]_K$	-	0.145	0.225	0.245	0.260
$[\eta]_M$	-	0.145	0.236	0.254	0.269
$[\eta]_{SB}$	-	0.145	0.240	0.260	0.268

TABLE 3. Influence of Temperature on Intrinsic Viscosities of Block Copolymer Micelles

Polymer/ solvent	Intrinsic viscosity, dL/g	Temperature, °C					
		25	30	35	40	45	50
SA-5/heptane	$[\eta]_H$	0.113	0.130	0.140	0.122	0.108	0.094
	$[\eta]_K$	0.114	0.130	0.140	0.120	0.100	0.098
	$[\eta]_M$	0.117	0.135	0.140	0.121	0.108	0.100
	$[\eta]_{SB}$	0.119	0.130	0.140	0.122	0.108	0.106
SA-4/DMA	$[\eta]_H$	0.140	0.188	0.220	0.180	0.175	0.160
	$[\eta]_K$	0.145	0.192	0.220	0.180	0.196	0.166
	$[\eta]_M$	0.143	0.194	0.220	0.184	0.193	0.168
	$[\eta]_{SB}$	0.145	0.190	0.220	0.180	0.192	0.165

TABLE 4. Hydrodynamic Radius of Block Copolymers in Selective Solvents[a]

	R_h, nm			
Copolymer	n-Heptane	n-Dodecane	DMA	DMF
SA-3	26.0	29.5	-	-
SA-4	27.5	33.5	-	-
SA-5	30.0	36.5	46.0	59.8
SA-6	38.0	45.0	55.5	70.2
SA-7	45.0	75.0	57.6	77.8

[a] Standard deviation was normally between ±5-15% of the micelle size.

TABLE 5. Hydrodynamic Radius, Intrinsic Viscosities, Aggregation Number, and Micellar Weight of Block Copolymer SA-5 in n-Heptane at Different Temperatures

Temperature, °C	R_h, nm	$[\eta]$, mL/g	N	Micellar weight, $\overline{M}^{(m)} \times 10^{-7}$, g/mol
25	30.0	11.3	386	1.50
30	29.5	13.0	319	1.24
35	29.0	14.0	281	1.09
40	27.5	12.2	275	1.07

isoprene graft copolymer in decane. Based on the above studies and our viscosity results, it is presumed that the decrease in micellar characteristics with rising temperature is due to dissociation of polymolecular micelles to unimolecular micelles at higher temperatures. Thus a maximum in intrinsic viscosity is an indication of a shift in the micelle-unimer equilibrium in favor of unimers, and the low values at higher temperatures infer the presence mainly of unimers.

The effect of temperature and molecular weight on different viscosity slope constants for copolymer micelles (SA-5 in n-heptane and SA-4 in DMA) are recorded in Tables 6 and 7. There is a change in

TABLE 6. Viscosity Slope Constants for Block Copolymers in Selective Solvents at 25°C

Solvent/viscosity slope constant	Copolymer				
	SA-3	SA-4	SA-5	SA-6	SA-7
n-Heptane:					
k_H	-0.64	-1.18	-1.89	-2.41	-2.72
k_K	1.17	2.08	2.46	2.70	2.96
k_M	-0.83	-2.08	-2.49	-2.55	-2.72
k_{SB}	-0.89	-2.96	-3.31	-3.56	-3.69
DMA:					
k_H	-	8.42	6.87	6.11	7.64
k_K	-	-6.56	-6.08	-5.84	-5.92
k_M	-	5.33	4.89	4.72	5.08
k_{SB}	-	5.00	4.51	4.10	4.66

sign in the viscosity slope constant values. A similar dependence of slope constants on temperature was reported by Tuzar et al. [5] and Gallot et al. [29, 30].

Table 8 shows micellar characteristics of SA-6 in selective solvents. The hydrodynamic radius is greater in dodecane (δ = 7.9) because the polyisoprene (δ = 8.0) segment is more extended in it than it is in n-heptane (δ = 7.4).

The influence of temperature on the ^{1}H-NMR spectrum of Block Copolymer SA-6 micelles in n-heptane is shown in Fig. 6. It is evident from Fig. 6 that only peaks due to polyisoprene segments at δ 4.7-4.9 ppm appeared and no aromatic styrenic protons were detectable at lower temperatures. At higher temperatures, however, a peak corresponding to styrenic protons is seen at 6.6-6.9 ppm and it becomes sharp at higher temperatures. Polymolecular micelles formed in n-heptane at lower temperatures consist of a polystyrene core, and its motion is restricted (no peak due to styrenic protons appeared). As the temperature is raised, the selectivity of the solvent with respect to polystyrene diminishes, and the compact micelle structure is destroyed to form mainly unimers. This enhances the mobility of polystyrene, and peaks due to its segments appear in the NMR sprectrum.

TABLE 7. Influence of Temperature on Viscosity Slope Constants for Block Copolymers in Selective Solvents

Copolymer/solvent	Viscosity slope constant	Temperature, °C					
		25	30	35	40	45	50
SA-5/heptane	k_H	-1.89	-1.97	-0.94	-1.16	11.64	31.19
	k_K	2.46	1.16	1.50	1.73	-1.35	-8.32
	k_M	-2.49	-1.36	-0.75	-1.751	2.26	7.87
	k_{SB}	-3.31	-1.28	-1.23	-2.20	2.24	4.86
SA-4/DMA	k_H	8.42	4.57	2.96	3.45	7.14	8.73
	k_K	-6.56	-25.0	-15.15	-41.84	-46.27	-43.54
	k_M	5.33	2.77	3.01	3.07	3.25	3.66
	k_{SB}	5.00	3.29	0.96	2.70	3.56	3.56

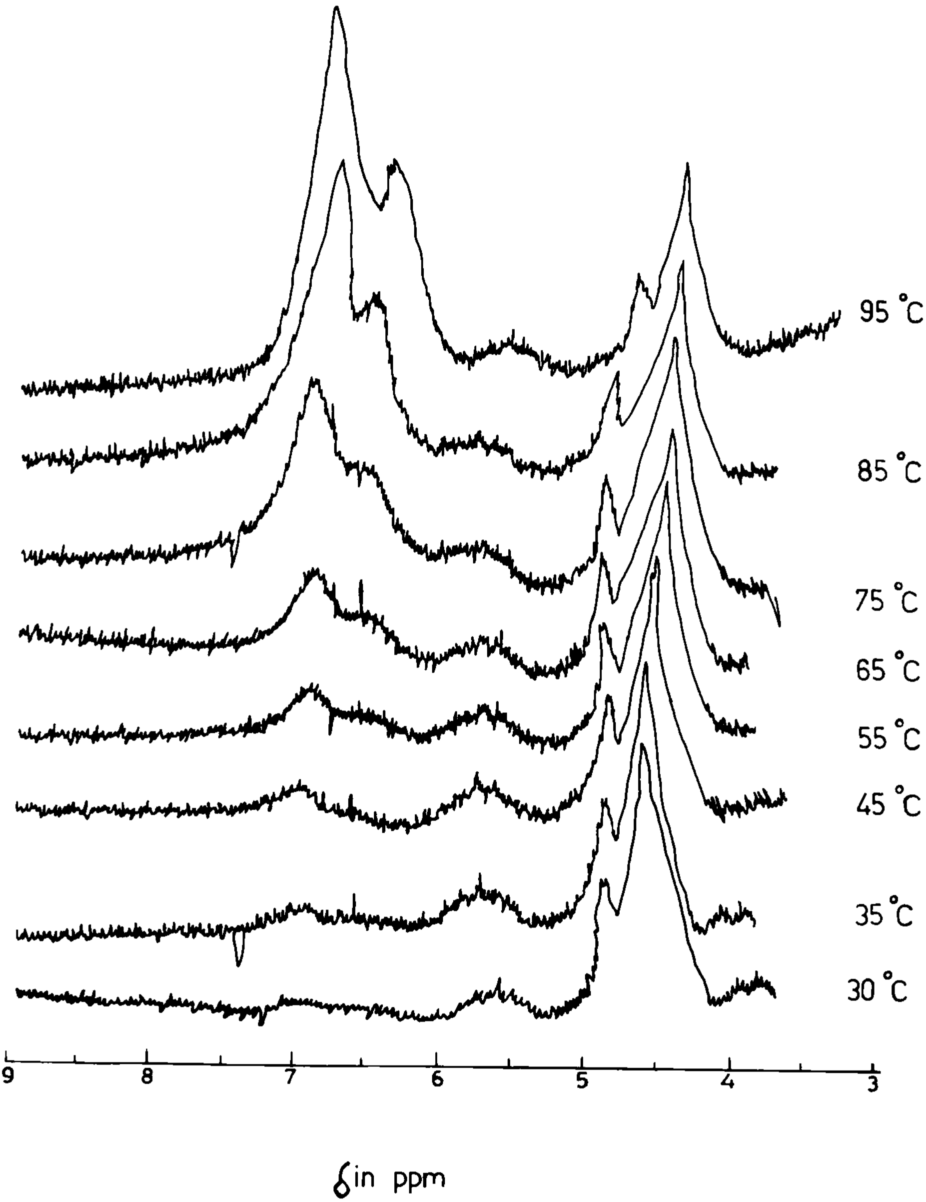

FIG. 6. Influence of temperature on proton NMR spectrum of micelles in n-heptane.

TABLE 8. Micellar Characteristics of Block Copolymers in Selective Solvents

Copolymer/solvent	R_h, nm	$[\eta]$, mL/g	N	Micellar weight, $\overline{M}^{(m)} \times 10^{-7}$ g/mol
SA-6/heptane	38.0	10.6	666	3.26
SA-7/dodecane	45.0	12.0	976	4.78
SA-6/DMA	55.5	25.8	852	4.18
SA-6/DMF	70.2	35.0	1271	6.23

ACKNOWLEDGMENTS

The authors are thankful to Professor G. Riess for the gift of block copolymer samples and for valuable suggestions. N.V.S. thanks the University Grants Commission for the award of a fellowship.

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Received June 1, 1985