Macromolecules 1985, *18*, 1995-1999 1995

Solution Properties of Ultrahigh Molecular Weight Polymers. 5. Conformational Changes of Butyl Methacrylate-Styrene Copolymers in Dilute Solution

Cristofor I. Simionescu,† **Bogdan C. Simionescu,***† **and Silvia Ioan**‡

Department of Organic and Macromolecular Chemistry, Polytechnic Institute of Jassy, 6600 Jassy, Romania, and "P. Poni" Institute of Macromolecular Chemistry, 6600 Jassy, Romania. *Received June 1, 1984*

ABSTRACT: The conformational changes appearing in dilute solutions of ultrahigh molecular weight ($\bar{M}_w \simeq 2.4 \times 10^7$–$3.0 \times 10^7$) butyl methacrylate–styrene copolymers of different compositions are investigated. The influence of solvent nature (CCl_4, dimethylformamide, and cyclohexane) and temperature (19–55 °C) is considered. Light scattering and viscometry are used as investigation methods.

Introduction

Until recently, synthetic polymers of ultrahigh molecular weight have been only of limited interest. However, the extension of the molecular weight scale might provide a sensitive experimental test for many currently used theoretical equations.

In previously published papers[1-4] we have reported the synthesis, through a plasma-induced polymerization technique, of different macromolecular compounds. This new method of polymer synthesis was proved to proceed through a "living" radical mechanism[5,6] and to yield, under adequate experimental conditions, ultrahigh molecular weight macromolecular compounds with narrow polydispersity[7] and copolymers with small compositional heterogeneity.[8]

To underline the specific characteristics of such extremely high molecular weight polymers, the term "pleistomers" ("pleistos": very many; so "very many mers") was proposed to designate them.[9]

The systematic characterization of ultrahigh molecular weight polymers involves a number of problems. As for copolymers, the investigation of conformational changes appearing in dilute solutions for different molecular weights, solvents, temperatures, and copolymer compositions becomes interesting not only from the point of view of the results obtained but also when the experimental difficulties to be faced are considered.

The present paper continues our work on solution properties of ultrahigh molecular weight polymers and is concerned with the study of dilute solutions of butyl methacrylate (BuMA)–styrene (St) random copolymers of different compositions at different temperatures in three solvents.[10] Light scattering and viscometry were used as investigation methods.

Experimental Section

BuMA–St random copolymers were obtained by plasma-induced copolymerization. The conversions were kept low and never exceeded 6%. The composition of the copolymers was determined from ^1H NMR spectra registered on a JEOL C60 HL spectrometer.

Light scattering studies were performed on a P.C.L. Peaker apparatus, at scattering angles ranging from 30 to 90°, using unpolarized light of wavelength 436 nm at 19–55 °C in CCl_4, dimethylformamide (DMF), and cyclohexane (C_6H_{12}). The concentration range was 10^{-4}–5×10^{-4} g·cm^{-3}; all solutions were kept in the dark at 40 °C for 5 days in order to promote complete dissolution of the polymer and were then made optically clean by centrifugation at $\simeq$11000*g* for about 1 h in a Janetzki centrifuge. No mechanical stirring was applied to the solutions at any stage, in order to prevent shear degradation.

Table I
Experimental Data on Butyl Methacrylate–Styrene Ultrahigh Molecular Weight Copolymers

	copolym comp		$\bar{M}_w \times 10^{-7}$		
sample	% BuMA	% St	CCl_4	DMF	C_6H_{12}
1	26	74	2.54	2.25	2.58
2	38	62	2.50		2.54
3	47	53	2.54		2.43
4	57	43	2.43		2.46
5	72	28	2.85	2.54	2.87

Table II
$\langle S^2\rangle^{1/2}$ Values for Copolymer 1 in C_6H_{12} at Different Temperatures As Determined by Berry's Method and Fujita's Method

	$\langle S^2\rangle^{1/2}$, Å	
temp, °C	Berry's method	Fujita's method
20	1193	1204
25	1314	1308
30	1595	1544
35	1749	1644
40–50	1821	1732

Weight-average molecular weights ($\bar{M}_w$) obtained in CCl_4, DMF, and C_6H_{12} were determined according to Berry's method.[11] Figure 1 presents the dependence of the reciprocal square root of reduced scattering intensity on concentration for copolymer 1 (Table I) in C_6H_{12} at 20 °C. The minimum concentration was selected and limited by the scattering by pure solvent over the 30–40° range of scattering angles. The extrapolations to zero concentration become extremely difficult when measurements are made for concentrations and scattering angles higher than those presented in Figure 1.

The experimental data for copolymer 1 in C_6H_{12} at 20–50 °C for 30–40° scattering angles were analyzed by using both Berry's square root method and Fujita's method[12] (Figure 2). The latter method expresses the particle scattering factor $P(\theta)$ starting from the Debye function, according to

$$1/y(u) = (1/\bar{M}_w) + bZ(u) + \text{higher terms in } Z \qquad (1)$$

where $y(u) = \lim_{c\to 0} (R_\theta/Kc)$, $u = \sin^3(\theta/2)$, $b = (32\pi^2/3\lambda^2)\cdot(\langle S^2\rangle/\bar{M}_w)$, and

$$Z(u) = [y(u)u^{4/3}]^{-1}\int_0^u y(u)\,du \qquad (2)$$

Figure 3 represents the experimental values of $y(u)u$ as a function of u at different temperatures for copolymer 1. The data were used to evaluate the integral in eq 2.

According to Figure 2, when the square root method is applied, a more pronounced curvature appears for scattering angles higher than 35°. Fujita's method allows a more precise extrapolation to zero scattering angle by reducing the curvature appearing at higher angles. The treatment of the experimental data by use

---

† Polytechnic Institute of Jassy.

‡ "P. Poni" Institute of Macromolecular Chemistry.

0024-9297/85/2218-1995$01.50/0

Table III
Refractive Index Increments of Butyl Methacrylate-Styrene Copolymers (Samples 1-5) at Different Temperatures

	20 °C			25 °C			30 °C			40 °C			50 °C		
sample	CCl_4	DMF	C_6H_{12}	CCl_4	DMF	C_6H_{12}	CCl_4	DMF	C_6H_{12}	CCl_4	DMF	C_6H_{12}	CCl_4	DMF	C_6H_{12}
1	0.121	0.142	0.148	0.126	0.144	0.149	0.127	0.146	0.152	0.130	0.149	0.156	0.133	0.153	0.159
2	0.105	0.128	0.133	0.110	0.130	0.135	0.112	0.132	0.138	0.116	0.136	0.143	0.118	0.140	0.146
3	0.093	0.117	0.122	0.097	0.119	0.124	0.099	0.121	0.128	0.104	0.126	0.133	0.107	0.130	0.137
4	0.079	0.104	0.109	0.084	0.107	0.112	0.087	0.110	0.116	0.092	0.114	0.121	0.095	0.119	0.126
5	0.059	0.086	0.091	0.064	0.089	0.094	0.067	0.092	0.099	0.073	0.098	0.104	0.077	0.103	0.109

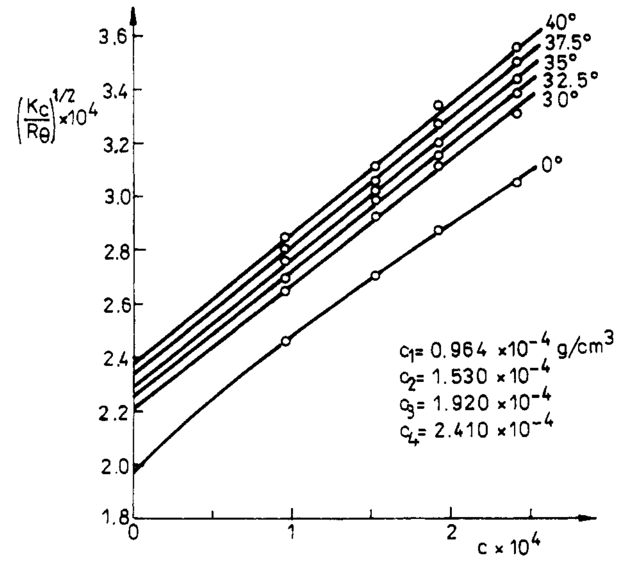

Figure 1. Square root of reduced scattering intensity $(Kc/R_\theta)^{1/2}$ as a function of concentration for copolymer 1 in C_6H_{12} at 20 °C.

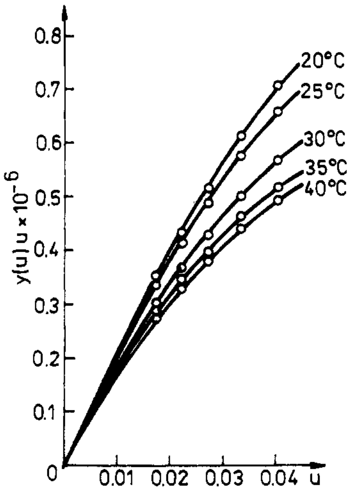

Figure 3. Plots of $y(u)u$ against u for copolymer 1 in C_6H_{12} at 20–50 °C.

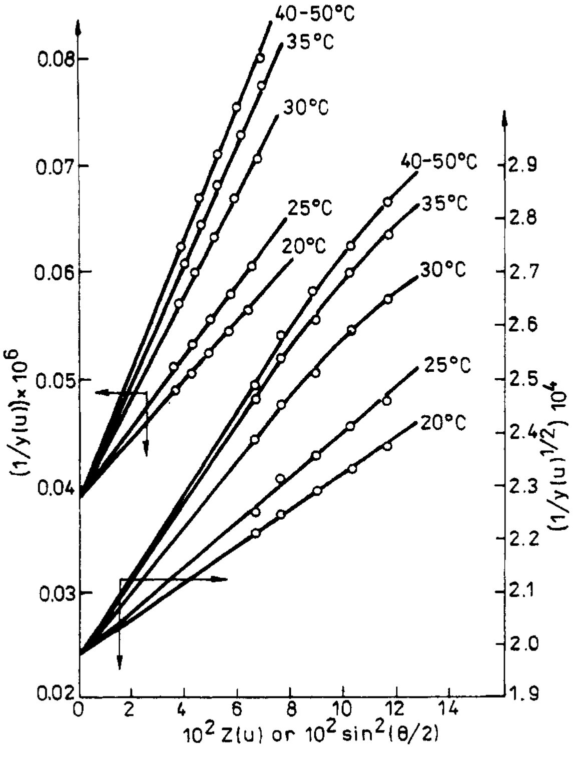

Figure 2. Tests of the methods of Berry and Fujita for copolymer 1 in C_6H_{12} at 20–50 °C.

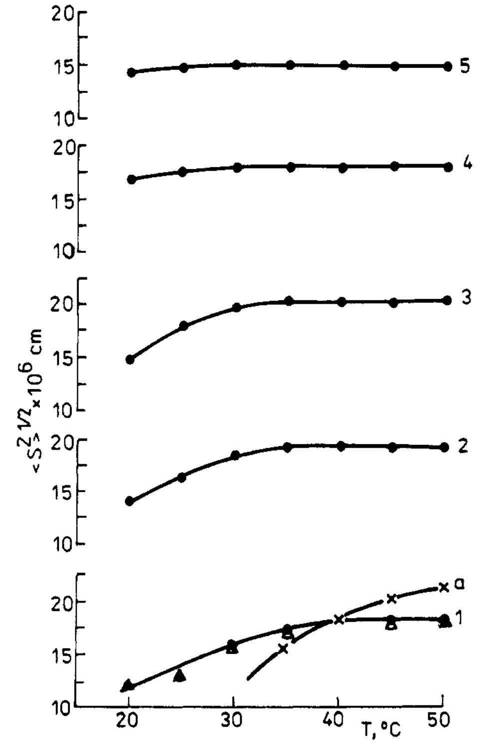

Figure 4. Root-mean-square radii of gyration $\langle S^2 \rangle^{1/2}$ of copolymers 1-5 and polystyrene ($\bar{M}_w = 2.50 \times 10^7$) (curve a) in C_6H_{12} as a function of temperature: (●) Berry's method; (△) Fujita's method.

of both methods in the 30–40° scattering angle range (Figure 2) led to very similar values for $\bar{M}_w$ (Berry's method, $\bar{M}_w = 2.58 \times 10^7$; Fujita's method, $\bar{M}_w = 2.63 \times 10^7$) and $\langle S^2 \rangle^{1/2}$ values (Figure 4 and Table II).

Table III presents the refractive index increments of BuMA-St copolymers for different temperatures. The experimental precision in the determination of $\bar{M}_w$ values was ±10%, and in the determination of refractive index increments (Zeiss interferometer), ±1.7%. The composition of the copolymers and the $\bar{M}_w$ values are given in Table I.

Considering that the copolymerization yields were lower than 6%, one can conclude that the copolymers have very small compositional heterogeneity. In addition, as observed in Table I, only small differences, within the experimental errors, appear among the molecular weights determined in the different solvents. The determination of molecular weight heterogeneity according to the existing methods is difficult for ultrahigh molecular weight polymers or copolymers. Our previous studies on poly(methyl methacrylate) and 1:1 methyl methacrylate–styrene copolymers[8,10] by use of the light scattering method have shown that a plasma-induced polymerization technique yields low-polydispersity polymers.

Viscometric measurements were performed with a capillary viscometer of the Ubbelohde type requiring no corrections for flow kinetics or hydrostatic pressure in C_6H_{12} solutions. The temperature control of the bath was better than ±0.1 °C. Flow times were reproducible to within ±0.05 s.

Results and Discussion

Nonpolar copolymers, in general, exhibit large expansion in solution as a result of repulsive interactions between unlike monomer units in the chain. These repulsive interactions influence both the short- and long-range parameters, depending on the nature of the solvent.

The conformational changes with temperature were followed through the reciprocal reduced scattering intensity at zero concentration $(Kc/R_\theta)_{c=0}$, the variation of the radius of gyration $(\langle S^2\rangle^{1/2})$, and the variation of the intrinsic viscosity $[\eta]$. The interpretation of conformational changes was based on the chemical structure of the copolymers and on the modification of the physical interactions under the influence of both temperature and solvent. As solvents, DMF, which exhibits a preferential affinity for polystyrene, CCl_4, a good solvent for both polystyrene and poly(butyl methacrylate), and C_6H_{12}, a poor solvent for both homopolymers ($[\eta]$ increases with temperature) were selected.

In a copolymer chain, the interaction parameter Z is a linear combination of three terms

$$Z = C_{11}Z_{11} + C_{22}Z_{22} + C_{12}Z_{12} \tag{3}$$

where Z_{11}, Z_{22}, and Z_{12} are proportional to the interaction energy for each type of contact in a given solvent and C_{11}, C_{22}, and C_{12} are the frequency factors for each type of contact. These interaction parameters are related to the expansion of the copolymer chain according to

$$\alpha^2 = 1 + (134/105)Z + ... \tag{4}$$

where Z_{11}, Z_{22}, and Z_{12} imply the effect of the solvent

$$Z_{11} = (3/2\pi b^2)^{3/2}N^{1/2}V_s(1 - 2\chi_{1s}) \tag{5}$$

$$Z_{22} = (3/2\pi b^2)^{3/2}N^{1/2}V_s(1 - 2\chi_{2s}) \tag{6}$$

$$Z_{12} = (3/2\pi b^2)^{3/2}N^{1/2}V_s[1 - (\chi_{1s} + \chi_{2s} - \chi_{12})] \tag{7}$$

where b is the length of a statistical segment, N the number of segments, and V_s the specific volume of the solvent.

An increase of Z_{11} and Z_{22} indicates the existence of small χ_{1s} and χ_{2s} repulsive interactions, while an increase of Z_{12}, characteristic for heterocontact interactions, indicates the existence of important χ_{12} repulsive interactions. The rise of the number of heterocontacts in the copolymer results in an increase of incompatibility and an additional expansion of the macromolecular chain. On the other hand, when the solvent exhibits a preferential affinity for one of the components of the copolymer, the incompatibility increases. Usually, an increase of temperature results in a decrease of the incompatibility, this effect determining a corresponding decrease of the expansion of the copolymer chain in a given solvent with increasing temperature.

To explain the conformational changes of copolymers **1**–**5** (Table I) with temperature, the corresponding homopolymers were studied (Figures 4–6). It appears that in DMF and CCl_4 the conformation of polystyrene chains is only slightly affected by increasing temperature, the expansion showing a small decrease. In C_6H_{12} (Θ solvent for

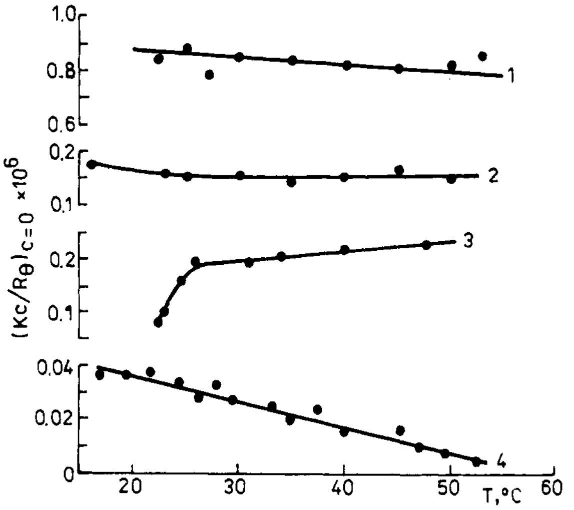

Figure 5. Plots of reciprocal reduced scattering intensity at zero concentration against temperature for the two homopolymers in CCl_4 and DMF: polystyrene ($\bar{M}_w = 2.50 \times 10^7$) in DMF (1) and CCl_4 (2); poly(butyl methacrylate) ($\bar{M}_w = 1.21 \times 10^7$) in DMF (3) and CCl_4 (4).

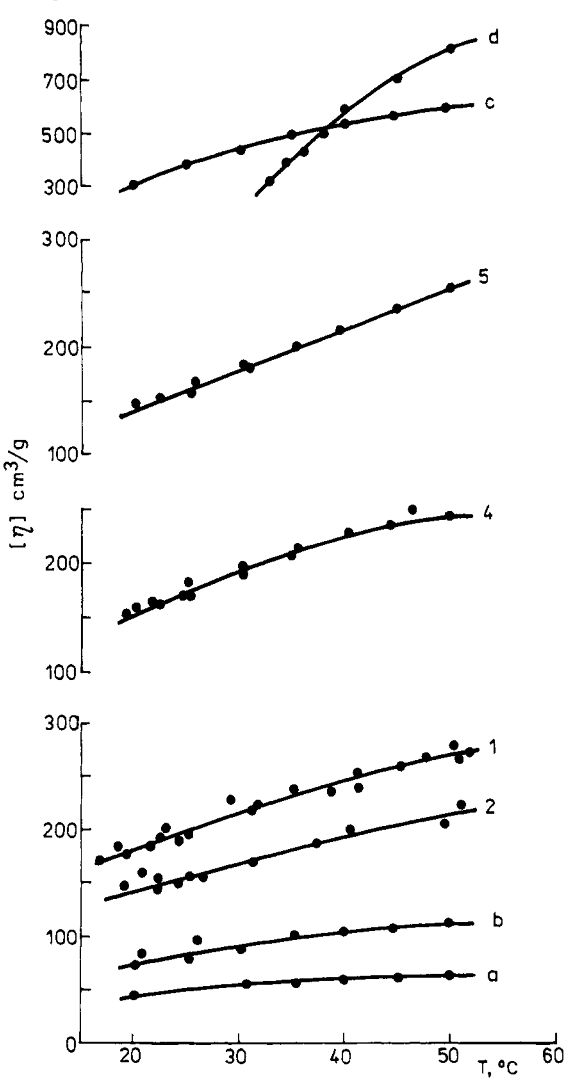

Figure 6. Plots of intrinsic viscosity in C_6H_{12} against temperature for copolymers **1**, **2**, **4**, and **5** (see Table I), 28% BuMA–72% St ($\bar{M}_w = 5.23 \times 10^5$) copolymer (curve a), 68% BuMA–32% St copolymer ($\bar{M}_w = 7.02 \times 10^5$) (curve b), poly(butyl methacrylate) ($\bar{M}_w = 1.21 \times 10^7$) (curve c), and polystyrene ($\bar{M}_w = 2.50 \times 10^7$) (curve d).

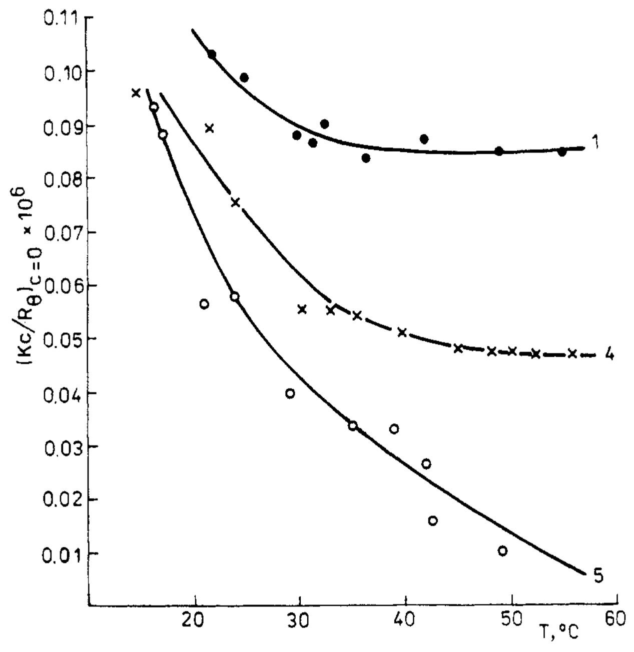

Figure 7. Plots of reciprocal reduced scattering intensity at zero concentration against temperature for copolymers 1, 4, and 5 (Table I) in CCl_4.

this polymer at 34.5 °C[13]), an increase of $[\eta]$ with temperature is noted (Figure 6); this behavior indicates an improvement of solvent quality.

As previously observed by Fujita et al.,[14] the variation of the root-mean-square radius of gyration with temperature shows a relatively rapid increase up to the Θ temperature and a less pronounced increase for higher temperatures (Figure 4). Thus, DMF and CCl_4 behave as good solvents for polystyrene, while C_6H_{12} is a poor solvent whose quality is improved by increasing temperature.

As for poly(butyl methacrylate), with increasing temperature, the expansion decreases in CCl_4 (Figure 5), while it increases, following the improvement of solvent quality, in C_6H_{12} (Figure 6). In DMF, as also observed for polystyrene in C_6H_{12}, a modification of the slope of the curve representing the variation of $(Kc/R_\theta)_{c=0}$ with temperature appears in the 23–27 °C interval, where the system is in the vicinity of the Θ point (Figure 4).

The interactions occurring for both homopolymers explain the conformational changes noted for the studied ultrahigh molecular weight BuMA-St copolymers. Figure 7 presents the $(Kc/R_\theta)_{c=0}$ vs. temperature variation for samples **1**–**5** in CCl_4. No matter what the composition, increase of temperature leads to a decrease of the expansion and thus of the incompatibility, this behavior being mainly due to the presence of BuMA units (see Figure 4).

In DMF, where poly(butyl methacrylate) passes through the Θ point (23.6 °C[15]) in the studied temperature range, the changes are imposed by copolymer composition (Figure 8). This solvent exhibits a preferential affinity for one of the monomers, and an increased incompatibility between the two unlike comonomers occurs. This incompatibility is more pronounced with increase of BuMA content in the copolymer, as well as the expansion of the chain. At the same time, for copolymer **5**, characterized by a very high probability of existence of BuMA–BuMA type contacts, a conformational transition occurs around 28 °C.

For an approximately 1:1 composition of copolymers **3** and **4**, the magnitude of chain expansion appearing as a consequence of the improvement of solvent quality toward BuMA units is compensated by the contrary effect manifested by St units in DMF. Thus, the macromolecular chain exhibits a slight expansion, but important conformational changes are absent.

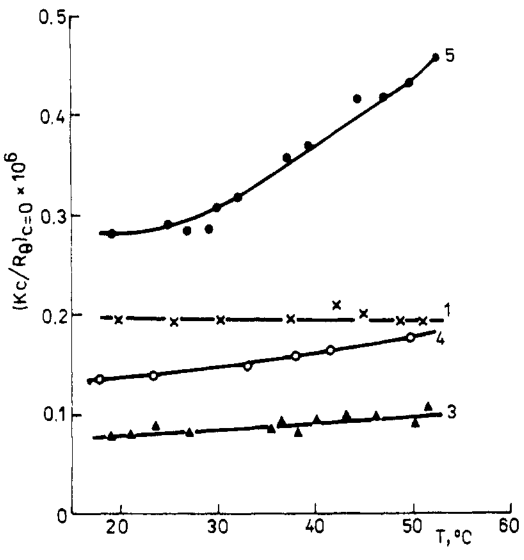

Figure 8. Plots of reciprocal reduced scattering intensity at zero concentration against temperature for copolymers 1, 3, 4, and 5 (Table I) in DMF.

Considering that $[\eta]$ increases with temperature for both homopolymers in C_6H_{12} (Figure 6), this solvent appears to be a poor one.[16] On the other hand, polystyrene reaches its Θ point in the studied temperature range. Samples **1**–**5** exhibit, in C_6H_{12}, an increase of $[\eta]$ with temperature, as well as a slight modification of the slope for high St content samples around 35–40 °C. By comparing curves a and b with curves for **1**–**5** one can see an easier stabilization of chain dimensions (expressed as $[\eta]$ variation) for lower molecular weight chains. This phenomenon is normal considering the important lengths of copolymers **1**–**5**; for these copolymers, the influence of solvent appears at higher temperatures.

The same conclusion is apparent from the behavior of the radius of gyration as a function of temperature (Figure 4). An increase of the expansion and the appearance of a conformational transition near 35 °C for the copolymers with high St content are observed; this transition is shifted to lower temperatures with the increase of BuMA content.

Thus, in C_6H_{12} the increase of temperature leads to an increase of incompatibility, a tendency to stabilization of incompatibility at high temperatures being observed.

Conclusions

Ultrahigh molecular weight BuMA-St random copolymers of different compositions were studied, the conformational changes for different solvents and temperatures being considered. The increase or decrease of incompatibility as a consequence of the presence of unlike monomer units was discussed.

The experimental results led to the following conclusions:

(1) In DMF, which manifests a preferential affinity for one of the components of the copolymers, an increase of incompatibility with temperature and/or with BuMA content in the copolymer occurs.

(2) In CCl_4, a good solvent for both components of the copolymer, a decrease of incompatibility with increasing temperature appears.

(3) In C_6H_{12}, a poor solvent for both components, an increase of incompatibility with temperature is observed. This behavior is more pronounced for ultrahigh molecular weight copolymers. A stabilization of chain dimensions

at higher temperatures is noted, as well as the appearance of some conformational transitions occurring at temperatures related to the BuMA content of the copolymers.

Acknowledgment. We are indebted to Professor W. H. Stockmayer, Dartmouth College, for encouragement and helpful discussions and for careful reading of the manuscript.

References and Notes

(1) Simionescu, B. C.; Natansohn, A.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1980**, *2*, 809.
(2) Simionescu, B. C.; Natansohn, A.; Leancă, M.; Ananiescu, C.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1980**, *3*, 247.
(3) Simionescu, C. I.; Simionescu, B. C. *Chem. Zvesti* **1983**, *37*, 685.
(4) Simionescu, C. I.; Simionescu, B. C. *Rev. Roum. Chim.* **1982**, *27*, 141.
(5) Simionescu, C. I.; Simionescu, B. C.; Leancă, M.; Ananiescu, C. *Polym. Bull. (Berlin)* **1981**, *5*, 61.
(6) Simionescu, B. C.; Popa, M.; Ioan, S.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1982**, *6*, 415.
(7) Simionescu, C. I.; Simionescu, B. C. *Pure Appl. Chem.* **1984**, *56*, 427.
(8) Simionescu, B. C.; Ioan, S.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1981**, *6*, 87.
(9) Simionescu, C. I.; Simionescu, B. C.; Ioan, S. *J. Macromol. Sci., Chem.* **1985**, *A22*, 765.
(10) For previous papers in this series, see, e.g.: Simionescu, C. I.; Simionescu, B. C.; Ioan, S. *Makromol. Chem.* **1983**, *184*, 829. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 549.
(11) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(12) Fujita, H. *Polym. J. (Tokyo)* **1970**, *1*, 537.
(13) Reiss, C.; Benoit, H. *J. Polym. Sci., Part C* **1968**, *16*, 3079.
(14) Miyaki, Y.; Fujita, H. *Polym. J. (Tokyo)* **1981**, *13*, 749.
(15) Nakajima, A.; Okazaki, K. *Chem. High Polym.* **1965**, *22*, 791.
(16) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; pp 622–626.

Polymerized Surfactant Vesicles. Determinations of Rates and Degrees of Polymerization in Vesicles Prepared from Styrene-Containing Surfactants

Juan Serrano,[1] Sergio Mucino,[1] Sonia Millan,[1] Rocio Reynoso,[1] Luz Alicia Fucugauchi,[1] Wayne Reed,[2] Faruk Nome,[3] Pietro Tundo,[4] and Janos H. Fendler*[2]

Department of Chemistry and Institute of Colloid and Surface Science, Clarkson University, Potsdam, New York 13676, and Instituto Nacional de Investigaciones Nucleares, Quimica Del Positronio, Agricultura 21, 11800 Mexico, D.F., Mexico.

Received November 28, 1984

ABSTRACT: Rate constants (η/E values) for laser pulse initiated photopolymerization have been determined for 1200–2700-Å-diameter bilayer surfactant vesicles prepared from dioctadecylmethyl(2-[(4-vinylbenzoyl)oxy]ethyl)ammonium bromide (**3**), from mixtures of dioctadecyldimethylammonium bromide (DODAB) and vinylbenzoic acid, from mixtures of **3** and DODAB, and from mixtures of **3** and vinylbenzoic acid. η/E values were 1.35 J^{-1} for 1650-Å-diameter **3** vesicles, were 0.059 J^{-1} for mixed vesicles prepared from vinylbenzoic acid and DODAB (0.25:1 mole fraction), varied between 0.123 and 1.46 J^{-1} for vesicles prepared from different mixtures of DODAB and **3**, and varied between 0.16 and 0.314 J^{-1} for different mixtures of vinylbenzoic acid and DODAB. Plots of polymerization rate constants against the mole fraction of **3** in vesicles prepared by cosonicating **3** + DODAB were found to increase curvilinearly to a plateau value, indicating domain formation. Subsequent to vesicle polymerizations, cumulants, weight- and number-average molecular weights of the separated poly(vinylbenzoates) and, hence, the average chain lengths were determined by gel exclusion chromatography. The average chain lengths varied from 10 in laser-polymerized **3** vesicles, through 20 in laser-polymerized vesicles prepared from mixtures of DODAB and vinylbenzoic acid, to 40 in laser-polymerized vesicles prepared from mixtures of **3** and vinylbenzoic acid. These relatively small chain lengths were discussed in terms of the restricted geometries prevailing at intravesicular surface polymerizations. Fluorescence measurements and a Monte Carlo based computer simulation of the photopolymerization were used to substantiate the proposed mechanism of vesicle polymerization.

Introduction

Polymerized surfactant vesicles[5-9] have become the most sophisticated systems in the armory of membrane mimetic chemists.[10,11] Vesicles are smectic mesophases of surfactants containing water between their bilayers. Prepared by sonication from such simple surfactants as dioctadecyldimethylammonium bromide (DODAB) or dihexadecylphosphate (DHP), they are single bilayer spherical aggregates with diameters of 500–1000 Å and bilayer thickness of ca. 50 Å.[12] Once formed, vesicles, unlike micelles, do not break down on dilution. Nevertheless, they are dynamic structures. They undergo phase transition, fuse, and are osmotically active. Molecular motions of the individual surfactants in the vesicles involve rotations, kink formation, lateral diffusion on the vesicle plane, and transfer from one interface of the bilayer to the other (flip-flop). Vesicles are capable of organizing a large number of molecules in their compartments. Hydrophobic molecules can be distributed among the hydrocarbon bilayers of vesicles. Polar molecules may move about relatively freely in vesicle-entrapped water pools, particularly if they are electrostatically repelled from the inner surface. Small charged ions can be electrostatically attached to teh oppositely charged vesicle surfaces. Species having charges identical with those of the vesicles can be anchored onto the vesicle surface by a long hydrocarbon tail. These organizational abilities of surfactant vesicles have been exploited in reactivity control, catalysis, transport, drug delivery, and artificial photosynthesis.[10-12]

The need for increased stabilities, controllable sizes, and permeabilities led to the development of polymerized surfactant vesicles.[5-9] Vesicle-forming surfactants have