Macromolecules **1985**, *18*, 1693–1696

Dipole Moments of Several Para-Substituted Polystyrenes and Poly(α-methylstyrenes) in Various Solvents over a Wide Range of Temperature

Bahattin M. Baysal*

Department of Chemistry, Istanbul Technical University, Istanbul, Turkey

Leylâ Aras

Department of Chemistry, Middle East Technical University, Ankara, Turkey.
Received May 22, 1984

ABSTRACT: Dipole moments of poly(*p*-chlorostyrene), poly(*p*-bromostyrene), poly(*p*-fluorostyrene), poly(*p*-methoxystyrene), poly(*p*-fluoro-α-methylstyrene), poly(*p*-bromo-α-methylstyrene), and poly(*N*-vinylcarbazole) were obtained from dielectric and refractive index measurements performed on their dilute benzene solutions over a wide range of temperature. Experimental results are expressed in terms of the dimensionless dipole moment ratio, $D_x = \langle\mu^2\rangle/x\mu_0^2$. The temperature coefficients, d ln $\langle\mu^2\rangle/\mathrm{d}T$, were calculated. The results were tabulated with our earlier values which were obtained in toluene and CCl_4. These results are compared with previous dipole moment measurements performed on poly(*p*-chlorostyrene) in a variety of solvents and with the dipole moments calculated by using a conformational model appropriate to polystyrene. The existence of specific solvent–segment interactions is suggested.

Introduction

The dipole moment of a macromolecule in solution is the vectorial sum of dipoles located along the chain. Conformational analysis and in particular the use of the rotational isomeric state model provide a direct method of estimating a measurable quantity which is an average square vector parameter, $\langle\mu^2\rangle$.[1-3] Consequently, dipole moment measurements provide information on the configuration of chains and insight into the sequence distribution in copolymers.

The advantages of dipole measurements are presented in many articles.[4-6] One of these is that the mean-square dipole moment of a chain in which each group moment is perpendicular to the main-chain axis could not be greatly affected by long-range interactions. Also, the magnitudes of group dipole moments vary over a much wider range than do bond lengths.

Experimental papers have appeared on the dipole moments of polymer solutions and their temperature coefficients in various solvents. Most of the dipole moment measurements have been carried out on poly(*p*-chlorostyrene) (PPCS)[7-13] and the results have been compared to those calculated for PPCS using the conformational model for polystyrene (PS). Recently, dipole moment studies of other para-halogenated derivatives of PS have been reported.[13] Such observations show an apparent sensitivity of the mean-square dipole moment, as well as its temperature coefficient, d ln $\langle\mu^2\rangle/\mathrm{d}T$, to the solvent in which the dipole moment measurements are performed.

In the present study we report further experimental results on dipole moment measurements of para-substituted polystyrenes and para-substituted poly(α-methylstyrene) chains in various solvents over a wide range of temperature.

Experimental Methods

Polymers of para-substituted styrenes, including poly(*p*-chlorostyrene) (PPCS), poly(*p*-fluorostyrene) (PPFS), poly(*p*-bromostyrene) (PPBS), and poly(*p*-methoxystyrene) (PPMOS), were prepared by standard free radical polymerization methods. Commercially available monomers were freshly distilled under reduced pressure before use. Poly(*N*-vinylcarbazole) (PNVC) was prepared by purely thermal polymerization of the monomer. The polymers were dissolved in toluene and reprecipitated with methanol. For all the polymeric samples mentioned above, the range of viscosity-average molecular weights was 5×10^4 to 5×10^5.

Polymers of para-substituted α-methylstyrenes were prepared by cationic polymerization with Friedel–Crafts catalysts. The preparation by poly(*p*-fluoro-α-methylstyrene) (PPFαMS) has been described[9,14] earlier ($M_w = 1.2 \times 10^5$). Poly(*p*-bromo-α-methylstyrene) (PPBαMS) was kindly given to us by Professor R. W. Lenz of the University of Massachusetts ($M_w = 5.4 \times 10^4$).[15]

A General Radio Co. Type 1620-A capacitance measuring assembly was used to measure dielectric constants at low frequencies (1 and 10 kHz). The solutions were confined in a Balsbaugh Laboratories Model 350-G three-terminal cell of two coaxial cylinders, which requires about 55 mL of solution. The three-terminal cell was mounted into a plastic vessel and immersed in a thermostat. Solvent escape was prohibited and the temperature of the cell was controlled to ±0.1 °C during capacitance measurements. All solutions were prepared by weighing both components. In calculating volume concentrations from these weights, it was assumed (since the solutions were dilute) that the thermal expansion of all solutions was the same as that of the pure solvent. After extrapolation to infinite dilution this causes no errors. Solvents were middle fractions from two successive distillations. Refractive index increments were obtained with standard Brice-Phoenix equipment.

Results

Low-frequency dielectric increments were measured at several concentrations in the range 1–3%, over a range of temperature from about 1 to 70 °C.

The mean-square dipole moments per repeat unit of the polymer chain were calculated from an appropriate form of the Guggenheim–Smith equation[16,17]

$$\langle\mu^2\rangle/x = \frac{27kTM_0}{4\pi N_A}\left[\frac{\mathrm{d}\epsilon/\mathrm{d}c}{(\epsilon_1 + 2)^2} - \frac{2n_1(\mathrm{d}n/\mathrm{d}c)}{(n_1^2 + 2)^2}\right] \quad (1)$$

in which M_0 is the molar weight of a repeat unit, N_A is Avogadro's number, k is Boltzmann's constant, T is the absolute temperature, ϵ is the static dielectric constant, n is the refractive index for visible light (546 nm for the increments), and subscript 1 refers to values for pure solvent.

All results are expressed in terms of the dimensionless dipole moment ratio

$$D_x = \langle\mu^2\rangle/x\mu_0^2 \quad (2)$$

in which μ_0 is the dipole moment of the repeat unit in the

0024-9297/85/2218-1693$01.50/0

Table I
Dipole Moments of Various Vinyl Polymers at 25 °C

polymer	solvent	μ_0, D	$\langle\mu^2\rangle/x\mu_0^2$	$-\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T \times 10^3$, °C^{-1}	ref
PPCS	benzene	2.00[a]	0.67	~8	this work
			0.64	~6	9
PPCS	CCl_4	1.88[b]	0.57	~4	9
PPCS	toluene	1.88[b]	0.47	~0	24
PPFS	benzene	1.82[c]	0.62	~8	this work
			0.51		9
PPBS	benzene	2.08[d]	0.72		this work
PPMOS	benzene	1.21[e]	0.94	~11	this work
PNVC	toluene	3.21[f]	0.36	~4	24
PPFαMS	benzene	1.82[c]	0.23	~11	this work
	benzene	1.82[c]	0.27		9
	CCl_4	1.82	0.23		9
PPBαMS	benzene	2.08[d]	0.28	~15	this work

[a] *p*-Chloroethylbenzene in benzene. [b] *p*-Chlorotoluene in CCl_4. [c] *p*-Fluorotoluene in benzene. [d] *p*-Bromoethylbenzene in benzene. [e] *p*-Methoxytoluene in benzene. [f] *N*-Vinylcarbazole in benzene.

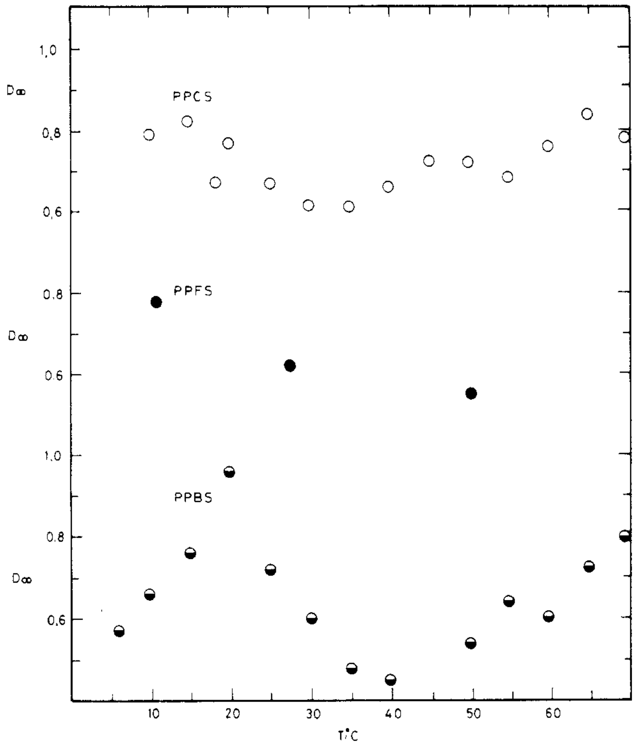

Figure 1. Dependence of the dipole moment ratio on temperature in benzene solutions: (○) poly(*p*-chlorostyrene) (PPCS); (●) poly(*p*-fluorostyrene) (PPFS); (◒) poly(*p*-bromostyrene) (PPBS).

polymeric chain. The values of D_x are independent of x for the high molecular weights (>5 × 10^4) studied in this work and are thus assumed to equal their limiting value.[18]

Results of dipole moment measurements at 25 °C for various para-substituted polystyrene and poly(α-methylstyrene) chains, poly(*p*-methoxystyrene), and poly(*N*-vinylcarbazole) are given in Table I. Values of the repeat-unit moments μ_0 were selected from those found in McClelan's tables and other literature[19,20] for the indicated model compounds.

Figures 1 and 2 show the dependence of D_∞ values in benzene on temperature for para-substituted polystrene and poly(α-methylstyrene) chains, respectively. The D_∞ values decrease and reach a minimum around 35–40 °C for nearly all the polymeric chains studied in this work. However, the D_∞ values then increase over the approximate temperature range 40–70 °C.

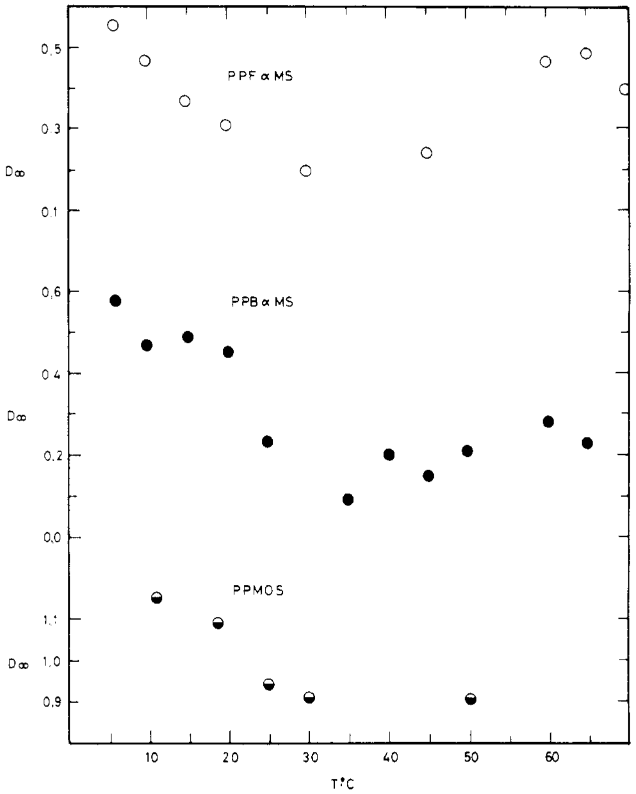

Figure 2. Dependence of the dipole moment ratio on temperature in benzene solutions: (○) poly(*p*-fluoro-α-methylstyrene) (PPFαMS); (●) poly(*p*-bromo-α-methylstyrene) (PPBαMS); (◒) poly(*p*-methoxystyrene) (PPMOS).

Table II
Dipole Moments of PPCS

solvent	T, °C	$\langle\mu^2\rangle/x$, D^2	$\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T \times 10^3$, °C^{-1}	ref
benzene	25	2.68 ± 0.03	-8	this work
benzene	25	2.55	-6	9
benzene	25	1.93		7
benzene	0	4.06[a]	+9	11
toluene	25	1.65	~0	24
toluene	30	1.82	~0	26
toluene	25	2.10	-4	8
toluene	30	2.08	~0	12
isopropylbenzene	25	1.54	-4	8
isopropylbenzene	30	2.07	~0	12
isopropylbenzene	25	1.87	-1.6	26
CCl_4	25	2.00	-4	9
p-dioxane	20	2.11		13
p-xylene	20	1.99		8
p-xylene	0	3.25[a]	+9	11
none	159	3.22[a]	+0.9	31

[a] See Discussion.

Table II presents the dipole moments and temperature coefficients measured for PPCS in various solvents by previous workers, together with our own experimental values.

Discussion

Several interesting observations may be drawn from inspection of the data given in Tables I and II. First, the values of dipole moment ratios are all different for *p*-halo-substituted polystyrenes and *p*-halo-substituted poly(α-methylstyrenes) as well as for other vinyl polymeric chains (PPMOS and PNVC) studied in this work. Second, the values of both $\langle\mu^2\rangle/x$ and d ln $\langle\mu^2\rangle/\mathrm{d}T$ are sensitive to the solvent in which the dipole moment measurements are performed; values of $\langle\mu^2\rangle/x$ differ as much as 30%, depending on the solvent. A negative temperature coefficient, d ln $\langle\mu^2\rangle/\mathrm{d}T$, is observed for all polymeric chains studied in benzene solutions around room temperature.

However, we find relatively large positive temperature coefficients for the dipole moments over the temperature interval 40–70 °C, again in benzene solutions.

The change in sign observed at 50 °C for the temperature coefficient of the dipole moments of PPCS in toluene, *p*-xylene, and isopropylbenzene was first reported by Burshtein and Stepanova.[8] Positive temperature coefficients for D_∞ were reported earlier for isotactic poly(methyl methacrylate) in toluene,[21] for poly(methyl acrylate) in benzene,[22] and for styrene–*p*-chlorostyrene copolymers in toluene.[23]

Figure 1 shows that a change in sign of d ln $\langle\mu^2\rangle/\mathrm{d}T$ of PPCS in benzene occurs around 35 °C. Similar behavior is observed for other *p*-halo-substituted polystyrene and poly(α-methylstyrene) chains studied in this work. In our dipole moment measurements loss of solvent (benzene) is minimized, and reproducible dipole moment results are obtained with increasing and decreasing temperature of the same solution in the dielectric capacitance cell. However, positive temperature coefficients reported for PPCS in benzene (Kotera[7]) and for PPCS and PPBS in *p*-dioxane (Tonelli and Belfiore[13]) may be confusing, since the calculated results were based on dipole moment measurements performed at only two temperatures widely separated from each other, such as 20 and 50 °C.

Over the temperature interval T = 20–60 °C Saiz et al.[18] calculated d ln $\langle\mu^2\rangle/\mathrm{d}T$ as -3×10^{-4} °C^{-1} for atactic (w_m = 0.5) PPCS chains and as -2.4×10^{-3} °C^{-1} for syndiotactic (w_m = 0.0) PPCS chains. We have found much larger, negative temperature coefficients for PPCS and other polymeric chains in benzene solutions for temperatures lower than about 35–40 °C. However, our earlier observations show that the temperature coefficient is close to zero for PPCS in toluene.[14] This result recently has been confirmed by Blasco and Riande[12] for the temperature interval 30–70 °C.

On the other hand, Chiba et al.[25] reported that the radius of gyration of PPCS in *n*-propylbenzene shows a sudden decrease (~11%) within a temperature interval of about 10 °C below the Θ-temperature (which is about 43 °C for this system). Similarly, isopropylbenzene is a Θ-solvent at 59.0 °C for PPCS.[26] It can be seen from Table II that the reported values of $\langle\mu^2\rangle/x$ for PPCS in isopropylbenzene (1.54,[8] 1.87,[26] and 2.07 D^2 [12]) are different.

Furthermore, benzene is a Θ-solvent at 20 °C for PPBS,[27] and it is probably a Θ-solvent also for PPCS at about 20 °C as manifested by Huggins' constants.[28] Negative and relatively high values of d ln $\langle\mu^2\rangle/\mathrm{d}T$ which we observe just about the Θ-temperature for PPCS, PPBS, and PPFS in benzene can be related to short-range intramolecular interactions. However, the "collapse" transition of the polymer molecule to a more compact state at temperatures lower than the Θ-temperature and the existence of positive temperature coefficients observed at higher temperatures in benzene suggest the possible influence of specific solvent–segment interactions. The quality of solvent (toluene, benzene, isopropylbenzene, etc.) and the working temperatures with respect to the Θ-condition have to be carefully considered. Before speculating further, however, one ought first to reduce some remaining experimental uncertainties, for example for measuring the dipole moment μ_0 of the chosen model compound (e.g., *p*-isopropylchlorostyrene) over the same temperature range, and in each solvent, as for the polymer.

The dipole moment ratios D_∞ for PPCS chains as a function of replication probability can be calculated by Monte Carlo methods.[29] Saiz et al. used a two-state scheme of meso and racemic diads which were distributed at random and calculated D_∞ as a function of the a priori expectation w_m of a meso diad.[18] They also calculated the dependence of D_∞ on temperature for various stereochemical compositions. Their results are shown in Figure 3 with our own experimental values for PPCS in benzene. It is seen that the dipole moments calculated by Saiz et al.[18] for atactic PPCS using the conformational description of PS derived by Yoon et al.[30] are not in agreement with those we measure for the same halogenated polystyrenes in benzene. Calculated and observed temperature coefficients are also different.

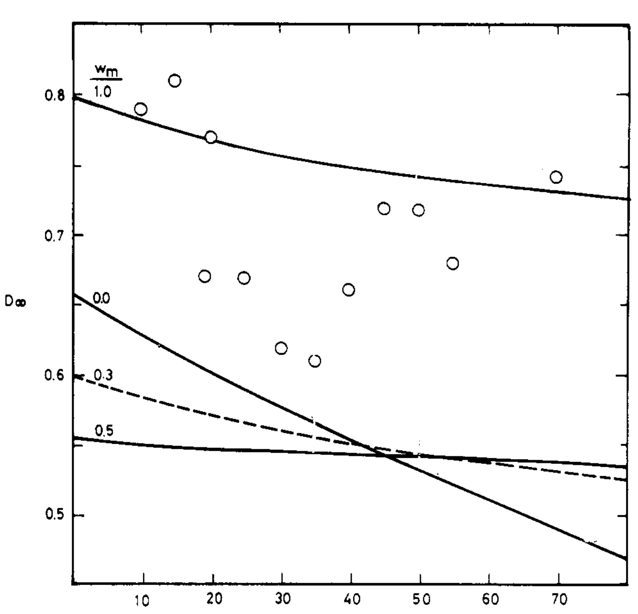

Figure 3. Dependence of the dipole moment ratio on temperature for poly(*p*-chlorostyrene). The curves are calculated[18] for various stereochemical compositions (w_m) as indicated. The circles are our experimental points.

The presence of syndiotactic triads for poly(*p*-fluoro-α-methylstyrene) was suggested by considering the NMR spectrum of this polymer.[14] The low dipole moment ratios measured for polymers para-substituted poly(α-methylstyrene) chains may be related to their highly stereoregular structures.[9]

The high dipole moment ratios for poly(*p*-methoxystyrene) may reflect the great flexibility of the polar group uninfluenced by its neighbors. On the other hand, the existence of a bulky side group and low D_∞ value observed for the poly(*N*-vinylcarbazole) chain seem to offer a proper system for configurational analysis.

It remains for us to discuss the various results of PPCS displayed in Table II. It should be realized that different equations were used by different groups of investigators in evaluating the dipole moment from the observed dielectric constants. Thus, Kotera,[7] Burshtein and Stepanova,[8] and Yamaguchi et al.[26] extrapolated to infinite dilution the specific polarization found according to the Halverstadt–Kumler[32] equation. Blasco and Riande,[12] Tonelli and Belfiore,[13] and Baysal et al.[9,24] used eq 1 or slightly modified forms[16,17] thereof. Finally, Work and collaborators[11,31] used the Onsager relation.[33] Unusually high values for the dipole moment are reported by the last-named authors for PPCS both in the melt and in solution. They do not display the equation they actually used, but we infer from their text that they employed the relation

$$\epsilon_0 - \epsilon_\infty = [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)](4\pi N_\mathrm{A}\mu_\mathrm{e}^2/3k_\mathrm{B}T) \qquad (3)$$

This omits a factor of $9/(\epsilon_\infty + 2)^2$, which would convert μ_e^2

into the equivalent quantity in vacuum and bring their results into much closer agreement with the other entries in Table II.

Registry No. PPCS, 24991-47-7; PPFS, 24936-47-8; PPBS, 24936-50-3; PPMOS, 24936-44-5; PPFαMS, 42475-56-9; PPBαMS, 86068-37-3; PNVC, 25067-59-8.

References and Notes

(1) Volkenstein, M. W. "Configurational Statistics of Polymer Chains"; Interscience: New York, 1963.
(2) Burshtein, T. M.; Ptitsyn, O. B. "Conformation of Macromolecules"; Interscience: New York, 1966.
(3) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(4) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(5) Mark, J. E. *Acc. Chem. Res.* **1974**, *7*, 218.
(6) Block, H. *Adv. Polym. Sci.* **1979**, *33*, 93.
(7) Kotera, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 750.
(8) Burshtein, L. L.; Stepanova, T. P. *Vyoskomol. Soedin., Ser. A* **1969**, *11*, 2885.
(9) Baysal, B.; Lowry, B. A.; Yu, H.; Stockmayer, H. In "Dielectric Properties of Polymers"; Karasz, F. E., Ed.; Plenum Press: New York, 1972.
(10) Roig, A.; Fuentes, I. H. *An. Quim.* **1974**, *70*, 668.
(11) Mashimo, S.; Nozaki, R.; Work, R. N. *J. Chem. Phys.* **1982**, *77*, 2663.
(12) Blasco, F.; Riande, E. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 835.
(13) Tonelli, A. E.; Belfiore, L. A. *Macromolecules* **1983**, *16*, 1740.
(14) Orhan, E. H.; Akovali, G.; Baysal, B. M. *Makromol. Chem.* **1976**, *177*, 3009.
(15) Lenz, R. W.; Westfelt, L. C. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2147.
(16) Guggenheim, E. A.; Prue, J. E. "Physico-Chemical Calculations"; Interscience: New York, 1955; p 106.
(17) Smith, J. W. "Electric Dipole Moments"; Butterworths: London, **1955**; p 60.
(18) Saiz, E.; Mark, J. E.; Flory, P. J. *Macromolecules* **1977**, *10*, 967.
(19) McClelan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963.
(20) Aroney, M. J.; Calderbank, K. E.; Le Fêvre, R. J.; Pierens, R. K. *J. Chem. Soc. B* **1969**, 159.
(21) Mikhailov, G. P.; Burshtein, L. L.; Andreyeva, T. P. *Vyoskomol. Soedin., Ser. A* **1967**, *9*, 2963.
(22) Masegosa, R. M.; Hernandez-Fuentes, I.; Ojalvo, E. A.; Saiz, E. *Macromolecules* **1979**, *12*, 862.
(23) Kücükyavuz, Z.; Baysal, B. M. *Prep., IUP Symp. Macromolecules, Florence*, Sept 1980, p 466.
(24) Kücükyavuz, Z.; Baysal, B. M., unpublished results.
(25) Chiba, A.; Uzawa, S.-i.; Uda, M.; Doi, S. *Prog. Polym. Phys. Jpn.* **1974**, *17*, 105.
(26) Yamaguchi, N.; Sato, M.; Ogawa, E.; Shima, M. *Polymer* **1981**, *22*, 1464.
(27) Kern, W.; Brawn, D. *Makromol. Chem.* **1958**, *27*, 23. Takashima, K.; Tanaka, G.; Yamakawa, H. *Polym. J. (Tokyo)* **1971**, *2*, 245.
(28) Mohite, R. B.; Fundiah, S.; Kapur, S. L. *Makromol. Chem.* **1968**, *116*, 280.
(29) Mark, J. E. *J. Chem. Phys.* **1972**, *56*, 458.
(30) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J., *Macromolecules* **1975**, *8*, 776.
(31) Yoshihara, M., Work, R. N.; *J. Chem. Phys.* **1982**, *76*, 5174.
(32) Halverstadt, I. F.; Kumler, W. D. *J. Am. Chem. Soc.* **1942**, *64*, 2988.
(33) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

Temperature Dependence of Swelling of Polystyrene Networks

Burak Erman*

School of Engineering, Bogazici University, Bebek, Istanbul, Turkey

Bahattin M. Baysal

Faculty of Sciences, Istanbul Technical University, Maslak, Istanbul, Turkey.

Received December 12, 1984

ABSTRACT: Swelling of polystyrene networks in cyclohexane is measured as a function of temperature in the interval between 16 and 45 °C. The increase of network volume over the stated temperature interval is observed to be three- to fourfold, depending on the degree of cross-linking. Results of swelling in toluene are used to calculate the cross-link density. The expression for the chemical potential of solvent in the network is used to predict the degree of swelling. The interaction parameter required for the formulation is taken from experimental results obtained by previous workers. Satisfactory agreement of experiments with predictions of the theory based on the chemical potential expression confirms the postulate of additivity of the mixing and elastic free energies of swollen networks. Swelling of the networks is also measured in a mixture of toluene and methanol, 75/25 wt %. The experimental technique employed provides a convenient means of comparing the swelling effects of cyclohexane and toluene–methanol, which are both Θ solvents for polystyrene around 35 °C. Results of swelling measurements in the toluene–methanol mixture are used to determine its interaction parameter with polystyrene.

Introduction

The chemical potential of a solvent in a network is expressed as[1]

$$(\mu_1 - \mu_1{}^0)/RT = \ln (1 - v_2) + v_2 + \chi v_2{}^2 + \partial \Delta A_{\mathrm{el}}/\partial n_1 = \ln a_1 \quad (1)$$

where μ_1 and $\mu_1{}^\circ$ are the chemical potentials for the solvent in the presence and absence of the polymer, respectively, v_2 is the volume fraction of polymer in the swollen system, χ is the reduced chemical potential[2] or the so-called χ parameter for the system, and $\partial \Delta A_{\mathrm{el}}/\partial n_1$ represents the elastic contribution obtained as the gradient of the elastic free energy, ΔA_{el}, of the network with respect to the number, n_1, of solvent molecules. a_1 is the solvent activity and R and T are the gas constant and absolute temperature, respectively.

When the network is in thermodynamic equilibrium with the surrounding solvent, the expression given by eq 1 equates to zero. If the elastic contribution and the degree of equilibrium swelling are known, eq 1 may be solved for the χ parameter. Conversely, if the χ parameter and the degree of swelling are known, the elastic contribution may be obtained, from which the degree of cross-linking may be evaluated.

0024-9297/85/2218-1696$01.50/0