

If the stiffness of chains has an importance, the results obtained here indicate that small cycle structures are irrelevant quantities for the variation of the mechanical properties near the gel point. Actually the  $S$  and  $T$  exponent values are independent of the weight fraction of solvent.

**Acknowledgment.** We thank J. P. Carton, G. Forgacs, P. G. de Gennes, H. J. Herrmann, and D. Stauffer who have given most welcome help and advice.

**Registry No.** (HMDDI)-(LHT 240) (copolymer), 53479-43-9; (HMDDI)-(UGIPOL 3170) (copolymer), 57596-47-1; (HMDDI)-(LG 56) (copolymer), 58450-56-9; (HMDDI)-(LG 56)-(PPG 4000) (copolymer), 98527-37-8.

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## Small-Angle X-ray Scattering from Semidilute Polymer Solutions. 1. Polystyrene in Toluene

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Received April 4, 1985

**ABSTRACT:** Small-angle X-ray scattering has been measured on solutions of polystyrene in toluene at various concentrations covering from the dilute to semidilute regions. The correlation length  $\xi$  for the monomer-density distribution and the number of monomeric units  $g_m$  involved within this range have been determined as a function of the concentration and the molecular weight of the polymer. The results of  $\xi$  and  $g_m$  agree with the scaling predictions for the semidilute-good region and with the blob hypothesis when the molecular weight is higher than  $1.1 \times 10^5$  and  $\xi$  is not very small ( $\gtrsim 20$  Å). On the other hand, for lower molecular weights and smaller values of  $\xi$ , the results are in agreement with Moore's mean-field theory proposed for poor solvents. The value of the binary cluster integral  $B_1$  has been estimated by Moore's theory and is in good agreement with those estimated at infinite dilution.

## Introduction

Since a scaling theory for polymer solutions was first proposed by de Gennes,<sup>1</sup> various studies have been performed on the properties of semidilute polymer solutions.<sup>2-6</sup> In particular small-angle neutron scattering<sup>2,3</sup> has provided experimental evidence for the theory, and the features of the semidilute region distinguishable from the dilute and concentrated regions have been established.

The semidilute region is defined as a concentration range in which the number density of polymer chains is large

enough to enable individual chains to overlap, while still ensuring diluteness of the local number density of the segments. The mass concentration  $c^*$  at the overlap threshold between the dilute and semidilute regions is usually given by

$$c^* = M/N_A \langle S^2 \rangle^{3/2} \quad (1)$$

where  $M$  is the molecular weight of the polymer,  $N_A$  is Avogadro's number, and  $\langle S^2 \rangle$  is the mean square radius of gyration of a single chain.

The semidilute region is divided into two subregions depending on the strength of the excluded volume interaction between segments, i.e., the semidilute good-solvent region and the semidilute poor-solvent region.<sup>7</sup> The former corresponds to the region II and the latter to the region III in the temperature-concentration diagram for polymer solutions proposed by Daoud and Jannink.<sup>8</sup> Recently, Schaefer et al.<sup>9</sup> have pointed out that a marginal region can appear between regions II and III when the polymer chain has local stiffness.

In this study we have measured small-angle X-ray scattering (SAXS) from polystyrene in toluene and determined the correlation length or the screening length for the segment-density distribution and the number of monomers involved within this range. The concentration and molecular-weight dependence of these quantities are discussed in connection with the scaling theory,<sup>1</sup> the blob hypothesis,<sup>1</sup> and Moore's mean-field theory.<sup>7</sup>

### Theory

In the semidilute regions the correlation function  $G(r)$  of polymer segments is expected to follow an Ornstein-Zernike form in the intermediate range of  $r$  as<sup>1,3</sup>

$$G(r) \propto (1/r) \exp(-r/\xi) \quad (l < r < \langle S^2 \rangle^{1/2}) \quad (2)$$

where  $\xi$  is the correlation length or the screening length first introduced by Edwards<sup>10</sup> in the description of semidilute polymer solutions and  $l$  is the segment length. The scattering law  $S_m(h)$  per monomeric unit of Lorentzian type is obtained by the Fourier transform of  $G(r)$  as

$$S_m(h) = g_m / (1 + \xi^2 h^2) \quad (\langle S^2 \rangle^{-1/2} < h < l^{-1}) \quad (3)$$

where  $h$  is the magnitude of the scattering vector defined by  $h = (4\pi/\lambda) \sin \theta$ , with the wavelength  $\lambda$  and half the scattering angle  $\theta$ . The proportionality constant  $g_m$  in eq 3 can be regarded as the number of monomeric units included within a domain of size  $\xi$ . In terms of the blob concept proposed for the semidilute good-solvent region, the correlation length  $\xi$  is regarded as the size of a blob or the distance between interchain contact points, and  $g_m$  as the number of monomers involved in the corresponding part of the chain.<sup>1</sup>

A scaling theory predicts the concentration dependence of  $\xi$  in the semidilute regions in the power form of<sup>1,3</sup>

$$\xi \propto c^{-\nu/(3\nu-1)} \quad (4)$$

where  $c$  is the mass concentration of the polymer and  $\nu$  is the excluded volume exponent defined by the molecular-weight dependence of the radius of gyration  $\langle S^2 \rangle^{1/2}$  of a single chain at infinite dilution; i.e.

$$\langle S^2 \rangle^{1/2} \propto M^\nu \quad (5)$$

In a good solvent,  $\nu$  is known to converge to a value in the vicinity of 0.6 in the limit of  $M \rightarrow \infty$ ; e.g., the Flory theory gives  $\nu = 0.6$  exactly,<sup>11</sup> while the recent  $n$ -vector model with  $n = 0$  suggests  $\nu = 0.588$ .<sup>12</sup> In a  $\Theta$ -solvent it reduces to 0.5. According to the concentration blob model<sup>1</sup>  $g_m$  is related to  $\xi$  by the following equation, which is similar to eq 5:

$$\xi \propto g_m^\nu \quad (6)$$

The concentration dependence of  $g_m$  in the semidilute regions, therefore, has the form

$$g_m \propto c^{-1/(3\nu-1)} \quad (7)$$

which corresponds to the des Cloizeaux law<sup>1,13</sup> for the osmotic pressure.

Another important feature of the scaling theory is that it predicts a universal relationship between the reduced

Table I  
Characteristics of Polystyrenes

$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2, a}$ Å	$c^*, b$ g/cm <sup>3</sup>
1.75	47	0.28
3.70	69	0.19
5.00	81	0.15
11.0	124	0.096
90.0	405	0.023
200	649	0.012

<sup>a</sup> Calculated from the data measured by Kirste et al.<sup>20</sup> and Yamamoto et al.<sup>21</sup> <sup>b</sup> Calculated by eq 1.

correlation length  $\xi/\langle S^2 \rangle^{1/2}$  and the reduced concentration  $c/c^*$ ;<sup>1,14</sup> i.e.

$$\xi/\langle S^2 \rangle^{1/2} = f_\xi(c/c^*) \quad (8)$$

where  $f_\xi$  is a universal function of  $c/c^*$  with the same asymptotic form as eq 4 at large  $c/c^*$ .

According to Moore's mean-field theory,<sup>7</sup> the scattering law  $S_m(h)$  is again given by a Lorentzian form as shown in eq 3 with explicit expressions for  $g_m$  and  $\xi$ ; i.e.

$$g_m = 12\xi^2/A^2M_u \quad (9)$$

and

$$\xi^{-2} = \langle S^2 \rangle_0^{-1} + 12N_A B_1 A^{-2} c + 36N_A^2 B_2 A^{-2} c^2 \quad (10)$$

where  $\langle S^2 \rangle_0^{1/2}$  is the unperturbed chain dimension,  $A$  is a short-range interaction parameter defined by  $\langle S^2 \rangle_0 = A^2 M/6$ ,  $M_u$  is the molecular weight of the monomeric unit, and  $B_1$  and  $B_2$  are directly related to the binary and ternary cluster integrals for the polymer segments, respectively.<sup>4,15</sup> In a good solvent, where  $B_1 \gg B_2$ , the quadratic term in  $c$  is negligible, and eq 10 reduces to Edwards' expression<sup>10</sup> and also to the expression for the semidilute-marginal region proposed by Schaefer et al.<sup>9</sup> On the other hand, when applied to the  $\Theta$ -condition ( $B_1 \approx 0$ ), it corresponds to Daoud and Jannink's expression for region III<sup>8</sup> and to the formulation for the semidilute- $\Theta$  region by Schaefer et al.<sup>9</sup> Substituting eq 10 into eq 9, we obtain an explicit formula for the concentration dependence of  $g_m$  as

$$g_m^{-1} = (2N_m)^{-1} + B_1 M_u N_A c + 3B_2 M_u N_A^2 c^2 \quad (11)$$

from which we evaluate  $B_1$  and  $B_2$ .

### Experimental Section

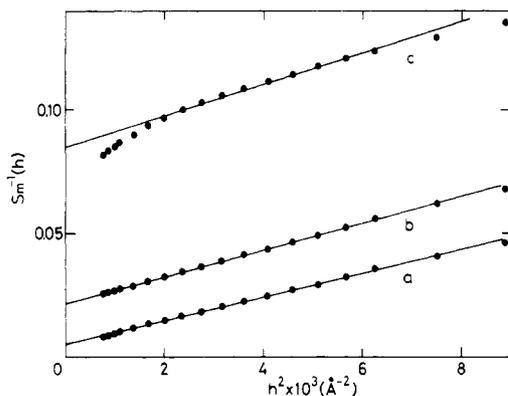
**Materials.** Monodisperse polystyrenes of molecular weights  $M_w = 1.7 \times 10^4$ ,  $3.7 \times 10^4$ ,  $5.0 \times 10^4$ ,  $1.1 \times 10^5$  ( $M_w/M_n < 1.06$ ),  $9.0 \times 10^5$ , and  $2.0 \times 10^6$  ( $M_w/M_n < 1.1$ ) were purchased from Pressure Chemical Co. Their molecular characteristics are listed in Table I. Spectral grade toluene (E. Merck Co.) was dried over calcium hydride and fractionally distilled.

**X-ray Scattering Measurements.** SAXS measurements were made at  $25.0 \pm 0.1$  °C with a Kratky U-slit camera using a broad-focus copper-anode X-ray tube. The scattered intensity was measured with a scintillation counter in connection with a pulse height analyzer focused on the Cu K $\alpha$  line, the Cu K $\beta$  line being eliminated with a 10- $\mu$ m Ni filter. The counter was step-scanned, and at least  $10^5$  pulses were collected at each angle. The collimation error due to the line-shaped cross section of the primary beam was corrected by the iterative method of Glatter.<sup>16</sup> The intensity  $P$  of the primary beam was measured with a secondary standard sample, Lupolen platelet, calibrated by Kratky and co-workers.<sup>17</sup> The scattering law  $S_m(h)$  per monomeric unit was determined by the excess scattered intensity  $I(h)$  of the polymer through the relation

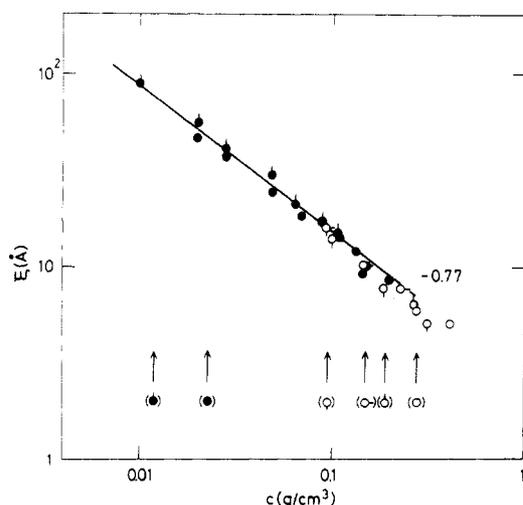
$$S_m(h) = (1/KcM_u)(a^2/Pd)I(h) \quad (12)$$

where  $d$  is the sample thickness and  $a$  is the sample-to-detector distance.<sup>18</sup> The contrast factor  $K$  is given by the equation

$$K = i_e(z - \bar{v}_2 \rho_e)^2 N_A \quad (13)$$



**Figure 1.** Inverse of the scattering law  $S_m(h)$  plotted vs. square of the scattering vector  $h$  for polystyrene of  $M_w = 5.0 \times 10^4$  observed in toluene at 25.0 °C. Measurements were made at concentrations of (a) 0.0105, (b) 0.0953, and (c) 0.229 g/cm<sup>3</sup>, each corresponding to the dilute, crossover, and semidilute region, respectively.



**Figure 2.** Double-logarithmic plots of  $\xi$  vs. concentration  $c$  in semidilute regions for  $M_w = 1.75 \times 10^4$  (O),  $3.7 \times 10^4$  (◊),  $5.0 \times 10^4$  (◻),  $1.1 \times 10^5$  (◻),  $9.0 \times 10^5$  (●), and  $2.0 \times 10^6$  (●). The vertical arrows indicate the overlap concentrations  $c^*$  calculated by eq 1.

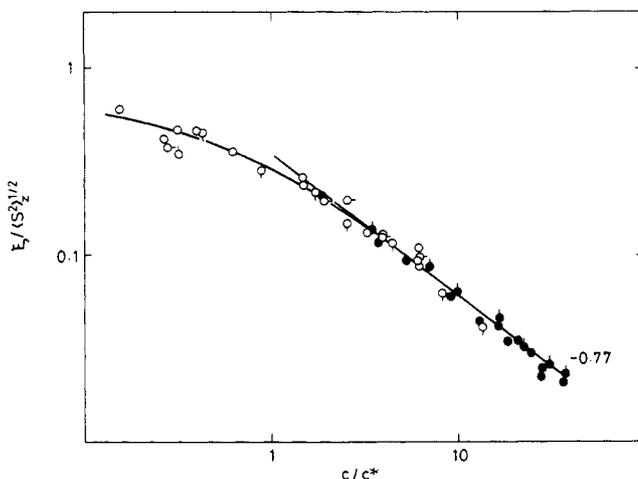
where  $i_e$  is the Thomson constant, i.e., the scattering cross section of a free electron,  $7.94 \times 10^{-26}$  cm<sup>2</sup>,  $z$  is the number of moles of electrons per gram of the solute,  $\bar{v}_2$  is its partial specific volume, and  $\rho_e$  is the mole electron density of the solvent. It should be noted that the value of  $K$  varies with concentration owing to the concentration dependence of  $\bar{v}_2$ . We evaluated  $\bar{v}_2$  at each concentration from the solution density measured by Scholte.<sup>19</sup>

## Results and Discussion

Figure 1 shows typical examples of the plot of the reciprocal of  $S_m(h)$  vs.  $h^2$  for  $M_w = 5.0 \times 10^4$ , each curve corresponding to the dilute, crossover, and semidilute region, respectively, from bottom to top. The linearity observed in the intermediate  $h$  range confirms the Lorentzian scattering law as expected in eq 3. As pointed out by SANS experiments,<sup>3</sup> however, a departure from the Lorentzian scattering behavior, which is due to the single-chain correlation function  $G(r) \propto r^{-4/3}$  leading to  $S_m(h) \propto h^{-5/3}$ , can be observed beyond a characteristic  $h^*$  for dilute solutions ( $c \lesssim c^*$ ). It is also observed that the value of  $h^*$  becomes smaller with decreasing concentration. The fact that the departure cannot be observed in Figure 1 shows that the value of  $h^*$  is beyond the  $h$  range shown in the figure. For these solutions, we determined the values of  $\xi$  and  $g_m$  from the Lorentzian part of  $S_m(h)$ , consisting of

**Table II**  
Data of  $\xi$  and  $g_m$  for Polystyrenes in Toluene at 25 °C

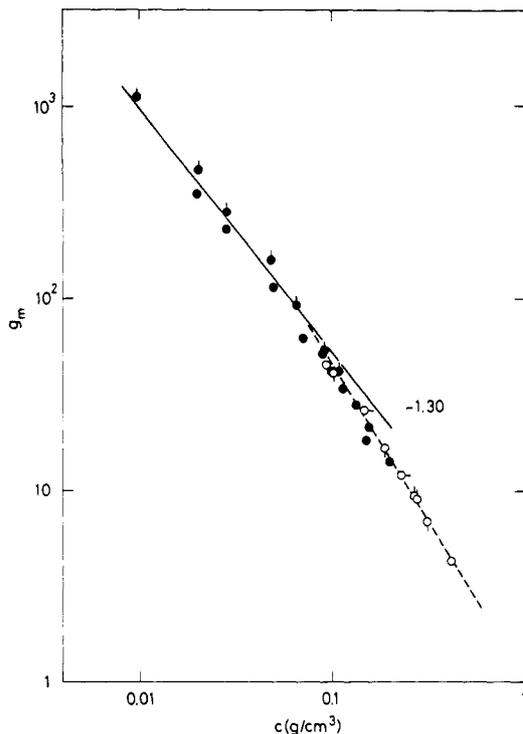
$c \times 10^2$ , g/cm <sup>3</sup>	$\xi$ , Å	$g_m$	$c \times 10^2$ , g/cm <sup>3</sup>	$\xi$ , Å	$g_m$
$M_w = 1.75 \times 10^4$					
5.85	18	76			
1.05	28	165	9.33	16	46
1.81	19	105	10.2	14	41
2.10	22	109	18.8	7.7	17
3.13	19	94	31.3	5.1	6.8
4.22	17	79			
10.1	12	33	$M_w = 9.0 \times 10^5$		
41.3	5.1	4.2	1.01	82	834
			2.01	46	350
$M_w = 3.7 \times 10^4$					
1.43	24	144	2.84	37	228
6.74	16	64	4.94	24	111
14.7	8.9	23	7.01	18	61
26.9	6.4	9.1	8.93	17	51
27.7	5.9	8.9	9.97	14	41
			11.2	14	33
			13.4	12	28
$M_w = 5.0 \times 10^4$					
1.05	31	195	14.9	9.0	18
7.12	16	65	15.4	10	21
9.53	16	48	20.0	8.5	14
14.8	10	26			
22.9	7.7	12	$M_w = 2.0 \times 10^6$		
			1.01	89	1120
			2.04	56	470
$M_w = 1.1 \times 10^5$					
0.987	56	574	2.89	41	282
2.04	35	274	4.88	30	159
4.03	26	155	6.53	21	92
			9.05	17	53
			10.9	15	41



**Figure 3.** Reduced correlation length  $\xi / \langle S^2 \rangle_z^{1/2}$  plotted as a function of the reduced concentration  $c/c^*$ . The values of  $\langle S^2 \rangle_z^{1/2}$  and  $c^*$  are listed in Table I. Symbols are the same as in Figure 2.

enough data to calculate these values. The values of  $\xi$  and  $g_m$  thus obtained are summarized in Table II. In Figure 2 the values of  $\xi$  observed in the semidilute regions are plotted as a function of  $c$  on a double-logarithmic scale. The solid line shows the best fit to the results for the two highest molecular weights plotted by the filled circles. The exponent on  $c$  in eq 4 determined from the slope of the line is  $-0.77 \pm 0.03$ . This value is in good agreement with the theoretical exponent of  $-0.75$  or  $-0.77$  calculated with the values of  $\xi$  in the excluded volume limit, i.e.,  $\nu = 0.6$  or  $0.588$ , respectively. A slight deviation is observed at high concentrations for lower molecular weights ( $M_w \leq 1.1 \times 10^5$ ), probably because the excluded volume effect between monomeric units is small.

The universality represented in eq 8 is examined in Figure 3, in which  $\xi / \langle S^2 \rangle_z^{1/2}$  is plotted as a function of  $c/c^*$  on a double-logarithmic scale. The  $z$ -average radius of gyration  $\langle S^2 \rangle_z^{1/2}$  of a polymer chain at infinite dilution was estimated from the data obtained by SAXS<sup>20</sup> and light

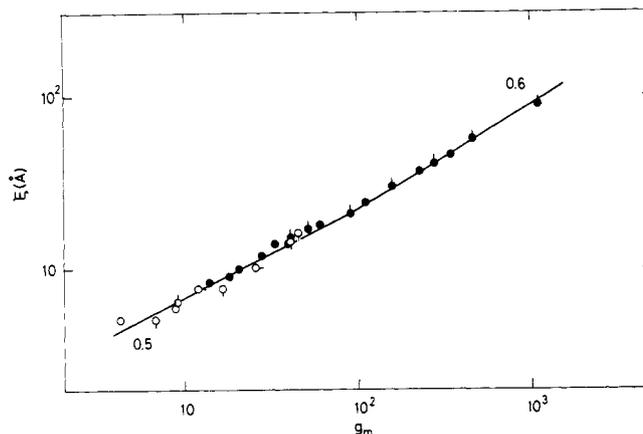


**Figure 4.** Double-logarithmic plots of  $g_m$  vs. concentration  $c$  in the semidilute regions. The numeral on each straight line denotes the value of the slope. Symbols are the same as in Figure 2.

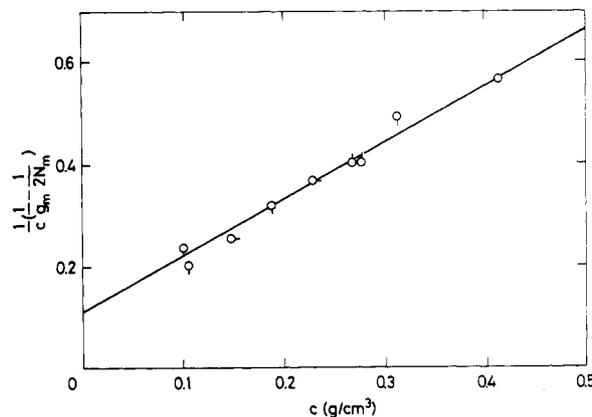
scattering.<sup>21</sup> These values of  $\langle S^2 \rangle_z^{1/2}$ , together with those of  $c^*$  calculated by eq 1, are listed in Table I for respective molecular weights. Over a wide range of concentration, including both dilute and semidilute regions, most of the data fall on a single curve within experimental error, indicating that  $\xi/\langle S^2 \rangle_z^{1/2}$  can be expressed as a function of the reduced concentration  $c/c^*$ , irrespective of the molecular weight of the polymer. The slope of the straight line fitted in the semidilute region ( $c/c^* > 1$ ) is estimated to be  $-0.77$ , which restored the power law of eq 4 in the excluded volume limit.

Figure 4 shows double-logarithmic plots of  $g_m$  vs.  $c$  observed in the semidilute regions. The solid line is fitted to the results for the two highest molecular weights in the concentration range  $0.01 < c < 0.1$  g/cm<sup>3</sup>. The slope of the line is estimated to be  $-1.30 \pm 0.08$ , which is in good accord with the value of  $-1.25$  or  $-1.30$  expected from the power law in eq 7 for the semidilute good-solvent region. However, an apparent deviation is observed as the concentration increases beyond  $c \approx 0.1$  g/cm<sup>3</sup>, irrespective of the molecular weight of the polymer. This deviation may suggest gradual approach to the semidilute poor-solvent region with decreasing  $\xi$  (cf. eq 7 with  $\nu = 0.5$ ). Similar deviation has also been observed in the concentration dependence of the osmotic pressure measured by Noda et al.<sup>22</sup> These authors show that a crossover between the semidilute-good and semidilute-poor regions takes place at a critical concentration  $c^{**}$  (0.15–0.2 g/cm<sup>3</sup>), irrespective of the molecular weight of the polymer.

In Figure 5 we have plotted  $\xi$  as a function of  $g_m$  to examine the relation between  $\xi$  and  $g_m$  observed in the semidilute regions. For large values of  $\xi$  ( $\xi \geq 20$  Å),  $\xi$  is proportional to  $g_m^{0.6}$ , as expected for solutions in the semidilute good-solvent region. Therefore the notion of blob is appropriate for the description of the monomer distribution in this region. However, as  $\xi$  decreases, it varies in proportion to  $g_m^{0.5}$ , implying a mean-field behavior. According to the recent theory of Schaefer et al.<sup>9</sup> a crossover between the semidilute good-solvent and a



**Figure 5.** Double-logarithmic plot of  $\xi$  vs.  $g_m$  in the semidilute regions. The numeral on each straight line denotes the value of the slope. Symbols are the same as in Figure 2.



**Figure 6.** Concentration dependence of  $c^{-1}(g_m^{-1} - (2N_m)^{-1})$  in the semidilute region for solutions of low molecular weights. The straight line indicates a least squares fit to the experiments. Symbols are the same as in Figure 2.

mean-field region is considered to occur when  $\xi$  is commensurate with the size  $\xi_r$  of the thermal blob. Using the semiempirical equations for  $\xi_r$ , proposed by Akcasu and Han,<sup>23</sup> we have estimated the value of  $\xi_r$  to be 26 Å, in good agreement with the threshold value  $\xi \approx 20$  Å found in Figure 5. Details of our estimation of  $\xi_r$  will be published in a subsequent paper.

The deviation observed in Figure 4 and the fact that  $\xi$  is proportional to  $g_m^{0.5}$  for small values of  $\xi$  ( $\xi \leq 20$  Å) seem to suggest the applicability of Moore's mean-field theory predicted for solutions in poor solvents.<sup>7</sup> According to eq 9, the short-range interaction parameter  $A$  can be evaluated from the intercept at  $g_m = 1$  in the double-logarithmic plot of  $\xi$  vs.  $g_m$ . The value determined from Figure 5 is 0.71 Å, in harmony with the results obtained from unperturbed chain dimensions at infinite dilution, which range from 0.68 to 0.77.<sup>15,24,25</sup> Although the values of  $\xi$  are comparable to the segment length  $l$  of the polymer, the good agreement in the value of  $A$  suggests the validity of Moore's mean-field theory and hence suggests that polymer chains of scale  $\xi$  ( $\leq 20$  Å) are virtually unaffected by the excluded volume effect.

Figure 6 shows a plot of  $c^{-1}(g_m^{-1} - (2N_m)^{-1})$  against  $c$  according to eq 11. The linearity of the plot validates eq 11, which, in combination with the linear dependence of  $g_m$  on  $\xi^2$ , confirms the concentration dependence of  $\xi$  as expressed in eq 10. From the values of the intercept and the slope of the straight line obtained by the least-squares method in Figure 6, we obtain  $B_1 = 1.8 \times 10^{-27}$  cm<sup>3</sup> and  $B_2 = 9.7 \times 10^{-51}$  cm<sup>6</sup>. A nonzero value of  $B_2$  suggests that

Edwards' mean-field theory<sup>9</sup> is inadequate for this system owing to the lack of the term including  $B_2$ . The value of  $B_1$  can be determined from intrinsic viscosity or light scattering observed in dilute solutions, though some ambiguity remains depending on individual theoretical formulations used for analyzing experimental data. Yamakawa<sup>15</sup> estimated  $B_1 = 2.11 \times 10^{-27} \text{ cm}^3$  from intrinsic viscosity<sup>26</sup> and  $B_1 = 2.19 \times 10^{-27} \text{ cm}^3$  from light scattering<sup>27</sup> measured on dilute solutions of polystyrene in toluene. The result obtained in the present work is in good agreement with these values.

From these results, we conclude that the observed values of  $\xi$  and  $g_m$  are consistent with the scaling predictions and with the concentration blob concept when the molecular weight of the polymer is higher than  $1.1 \times 10^5$  and  $\xi$  is not very small ( $\geq 20 \text{ \AA}$ ). For lower molecular weights and smaller values of  $\xi$ , on the contrary, experimental results deviate from the scaling prediction, and the mean-field theory becomes more appropriate.

**Registry No.** Polystyrene (homopolymer), 9003-53-6; toluene, 108-88-3.

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## Photochemistry of Ketone Polymers. 18. Effects of Solvent, Ketone Content, and Ketone Structure on the Photolysis of Styrene-Vinyl Aromatic Ketone Copolymers

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Received July 2, 1984

**ABSTRACT:** Studies of the kinetics and mechanisms of the type II photoelimination reaction of some styrene-vinyl aromatic ketone copolymers in solution are reported. Effects of solvent, ketone content, and ketone structure on the lifetime of the chromophores and the quantum yield of polymer chain scission were investigated. Solvent polarity has a pronounced effect on the chain scission quantum yield ( $\Phi_s$ ) of poly(styrene-co-phenyl vinyl ketone) (pS-PVK). This solvent effect can be interpreted as a compromise between two opposing effects. In polar solvents H-bond formation enhances the quantum yield of scission, while the polar solvent exerts a polymer coil contracting effect, which leads ultimately to reduction in the rate of polymer chain scission. Dependence of  $\Phi_s$  on PVK content in pS-PVK originates in the large chemical reactivity difference in the two comonomers, which leads to an inhomogeneous distribution of ketone in the copolymer at high conversion.

Study of the kinetics and mechanisms of photochemical reactions of small-molecule carbonyl compounds in the gas phase<sup>1</sup> and in solution<sup>2,3</sup> is highly advanced and extensive. While it is found that the photochemical behavior of the carbonyl chromophore in long-chain polymers often does not deviate much from that in their small-molecule analogues, significant differences sometimes occur.<sup>4</sup> These differences often reflect the characteristic long-chain na-

ture of the polymer and the restriction of the environment on the dynamics of the polymer chains. Thus, studies of photochemistry of ketone polymers have provided a great deal of information for the understanding of polymer structure and the dynamics of polymer reactions.

The major photochemical reactions originating from the carbonyl  $n-\pi^*$  excited state in the photolysis of polymers containing pendant carbonyl chromophores will be the Norrish type I  $\alpha$ -cleavage, giving free radicals, and the type II photoelimination to form an olefin and a lower ketone. The type II reaction leads to polymer main-chain scission

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