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Dimensions of Intramolecularly Cross-Linked Polymers. 2. Dilute Solution Thermodynamic Parameters and Photon Correlation Results on the Polystyrene/Cyclopentane System†

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ABSTRACT: In the previous paper a prediction was made for the contraction in dimensions of a homopolymer intramolecularly cross-linked in dilute solution. To test this prediction, Θ dimensions of linear and cross-linked polymers were determined for the polystyrene/cyclopentane system by means of photon correlation spectroscopy. Dilute solution thermodynamic parameters were found from the temperature dependence of the hydrodynamic radius and from viscosity measurements. Good agreement is found between the observed hydrodynamic radii of the cross-linked polymers and theoretical predictions.

Introduction

In a previous paper, a theoretical expression was proposed for the Zimm–Stockmayer[1] contraction factor, g, of a cyclized or intramolecularly cross-linked chain. The prediction is that $g = 1 - 0.7\rho^{1/2}$, where ρ is cross-link density expressed as moles of cross-links per mole of Gaussian statistical segments. It is appropriate to verify this expression experimentally. To do so requires the synthesis of intramolecularly cross-linked polymers and the subsequent determination of their dimensions in the Θ state. By way of definition, a polymer is in the Θ state when the second virial coefficient is zero.

It is of some interest to relate the work that others have done on intramolecularly cross-linked polymers. In 1962 Kuhn and Balmer[2] added terephthalaldehyde (OCH-C_6H_4CHO) to an aqueous solution of poly(vinyl alcohol). They measured the effect of polymer concentration during the cross-linking reaction on the intrinsic viscosity of the cross-linked polymer. It was found that at low reacting solution concentration, the viscosity decreased, indicating intramolecular cross-linking, and that at higher concentrations of polymer, the intrinsic viscosity increased, indicating the usual intermolecular cross-linking. At very high concentrations of polymer, the gel point was reached and the intrinsic viscosity became infinite.

In 1968 Longi, Greco, and Rossi[3] synthesized α-olefin/allylsilane copolymers and treated these with alkali/alcohol mixtures to form quasi-random intramolecular $\equiv$Si–O–Si$\equiv$ bridges. They were unable to observe any change in the intrinsic viscosity of the copolymers after cross-linking. This may be due to the copolymers having a block structure, which makes them prone to formation of relatively small cycles. The cross-links formed in this reaction were found to be very labile.

In 1969 Longi et al.[4] reported the synthesis of styrene/methyl acrylate copolymers, which they cross-linked with 9,10-disodio-9,10-dihydroanthracene in tetrahydrofuran. In this experiment, ca. 10% of the copolymer monomers were of the reactive methyl acrylate type. It was found that the intrinsic viscosity decreased in proportion to the number of intramolecular cross-links per polymer. It was their understanding that this was in agreement with the heuristic theory of Kuhn.[5] In fact, Kuhn's development cannot be applied to the complex statistics of the quasi-randomly cross-linked chain. Any agreement between their experimental results and the theory of Kuhn is fortuitous. To complicate the interpretation of their data further, the intrinsic viscosities they reported were determined in a good solvent. Measurements of the second virial coefficient showed a steady decrease with the extent of cross-linking. In the samples investigated, a twofold variation in the virial coefficient was observed. Modern polymer theories relate a large positive value of the second virial coefficient to a large positive value of the excluded volume parameter, which is indicative of a polymer in a highly expanded state. It is clear, then, that a large portion of the collapse in dimensions observed by Longi et al. was simply due to the approach of the cross-linked polymers to the Θ state.

Allen et al.[6] chloromethylated anionic polystyrene to make a styrene/(chloromethyl)styrene random copolymer. The chloromethyl groups were reacted with n-butylamine, and the resultant secondary amine was cross-linked with diisocyanate in dilute solution. Subsequent measurements of the unperturbed dimensions of these polymers, primarily by intrinsic viscosities, revealed a large contraction relative to the linear polymer, in qualitative agreement

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† This work performed at the University of Washington.

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Table I
Reaction Mixture Compositions

run	$\overline{M}_n$	[$SnCl_4$], M	[DCMB], M	polystyrene wt, mg	DCE, L	reaction time, h
1	498 000	0.0045	0.281	440	0.221	24
2	498 000	0.013	0.171	200	0.10	42
3	498 000	0.085	0.057	200	0.10	72
4	1 800 000	0.085	0.017	200	1.00	70
5	1 800 000	0.071	0.014	200	0.60	42
6	1 800 000	0.171	0.017	250	0.50	70
7	1 800 000	0.171	0.017	400	1.00	64
8	1 800 000	0.086	0.009	200	1.00	100
9	1 800 000	0.085	0.014	400	1.00	42
10	1 800 000	0.085	0.014	400	1.00	60
11	498 000	0.071	0.019	400	1.00	46
12	498 000	0.061	0.016	400	1.00	25
13	498 000	0.061	0.008	400	1.00	46
14	498 000	0.061	0.008	400	1.00	19
15	498 000	0.053	0.007	400	1.00	49
16	498 000	0.043	0.006	300	2.00	71
17	498 000	0.050	0.003	400	1.70	48
18	498 000	0.029	0.004	400	1.50	42

with the theoretical result of Allen et al.[7,8] The results of their work are presented in the Discussion.

Experimental Section

A. Synthesis and Characterization. Paucidisperse polystyrene (ca. 0.40 g), obtained from Pressure Chemical Co., was dissolved in a large quantity of 1,2-dichloroethane (DCE), typically 1–2 L, to make a very dilute solution. (Dichloromethyl)benzene (DCMB) and tin tetrachloride were added to this solution, which was subsequently placed in a reaction vessel in a constant-temperature bath. The mixture was stirred and allowed to react at 35 °C for 20–100 h. During the course of the reaction, dry nitrogen was circulated through the reaction vessel in order to remove the HCl evolved. A sodium hydroxide trap was employed to recover the acid. The dry nitrogen also prevented the seepage of any atmospheric water into the system, which would have had the deleterious effect of hydrolyzing the tin catalyst.

After the required reaction time, the solution was quenched with a large amount of distilled water. The acidic aqueous layer was decanted, and the process was repeated several times to ensure quantitative removal of the stannic hydroxide. Often the polymer formed a film at the H_2O–DCE interface, making recovery problematical. It was found that vigorous stirring redissolved the polymer into the organic phase. The purified organic phase was concentrated at room temperature in a rotating vacuum evaporation unit. To this solution of DCMB and polystyrene, now reduced to a volume of ca. 30 mL, was added 200 mL of ether. Ether is a good solvent for DCMB and a nonsolvent for polystyrene. The milky white precipitate thus formed was separated from the solvent by ultracentrifugation at 10 000 rpm for 15 min, whereupon the ether layer was removed. This process was repeated 3–4 times to ensure complete removal of the DCMB. Ultraviolet analysis of the final ether phase showed no trace of residual DCMB. Recovery of the highly purified polymer was quantitative; losses amounted to no more than 10% of the initial polystyrene. Table I lists the reaction conditions for each of the cross-linked samples.

The determination of the cross-link densities of the various polystyrene samples was easily accomplished by ultraviolet absorption spectrophotometry in carbon tetrachloride solvent. Measurements were made with a Varian Superscan UV–visible spectrophotometer.

B. Viscosity Measurements. Viscosity determinations were made with a Cannon-Ubbelohde dilution viscometer. The measurements were made at low shear rates, typical flow times being ca. 400 s. The measurement of the viscosity of the solvent at a variety of temperatures yielded $\eta_{\text{cyclopentane}} = (1.650 \times 10^{-2})e^{959.0/T}$. This relation gives values of the viscosity of cyclopentane that are within 0.1% of the literature values. Values[9] for the density of cyclopentane were satisfactorily interpolated by the polynomial $\rho = 0.7638 - 8.879 \times 10^{-4}T + 9.27 \times 10^{-7}T^2 + 1.55 \times 10^{-9}T^3$, where ρ is the density and here T is the temperature in °C. The density of the polymer solutions was calculated from the specific volume of the polymer, $v = 0.92$ cm^3 g^{-1}.

Thermoregulation was achieved by cooling a 20-gal reservoir with a Lauda circulating refrigeration unit. The cooled water was kept at a constant temperature by a 100-W heater that was connected to a transistorized relay. The relay was controlled by a Philadelphia microset mercury switch sensitive to ±0.002 °C.

C. Correlation Time Measurements. The homodyne photon correlation spectroscopy measurements employed a Spectra-Physics He–Ne laser operating at 632.8 nm. The focused and collimated scattered light was detected by an ITT-FW130 photomultiplier tube. Measurements were confined to the wave vector, q, region $q\langle s^2\rangle < 0.5$ and thus measured center-of-mass diffusion of the polymers. The radius of gyration, $\langle s^2\rangle^{1/2}$, of the polystyrene employed was ca. 20 nm. A 256-channel digital correlator and a PDP 12 computer were used to accumulate and analyze the intensity autocorrelation functions. A single relaxation time, τ, was observed, from which the diffusion constant was obtained as $D = 1/\tau q^2$.

The polystyrene/cyclopentane solutions used in these measurements were very dilute, typically ca. 0.2 mg/mL. This gives $c/c^* \sim 10^{-3}$, where c^* is the concentration marking the onset of the semidilute regime ($c^* \sim 100$ mg/mL). Solutions were rendered dust free by gravity filtration through 0.2-μm Millipore filters. The cylindrical scattering cells were placed in a temperature-controlled water jacket with a stability of ±0.05 °C.

Results

Before giving the experimental results, it is worthwhile to consider some of the limitations of the measurements. This discussion should indicate the motivation for having done the experiment in the manner reported.

The most straightforward method for determination of the radius of gyration of the cross-linked polymer would seem to be static light scattering. Several problems arise, however, in this experiment. First, to obtain even reasonable relative accuracy in the determination of the radius of gyration requires a polymer with $\langle s^2\rangle \gtrsim 40.0$ nm. In the unperturbed state this corresponds to a linear polystyrene sample with a molecular weight of ca. 2×10^6. It is difficult to obtain a monodisperse polystyrene sample of this molecular weight, and once having done so, it is equally difficult to cross-link it intramolecularly. In eq 7 it will be seen that to obtain a given weight of cross-linked polystyrene sustaining a given relative increase in molecular weight due to intermolecular cross-linking requires the reaction solution volume to increase in proportion to the molecular weight. For polystyrene of molecular weight 2×10^6 this would require cross-linking in solutions as dilute as 0.005 g/dL with solvent volumes as large as 8 L. Still another problem arises in the interpretation of the scattering curves obtained for the cross-linked polymers.

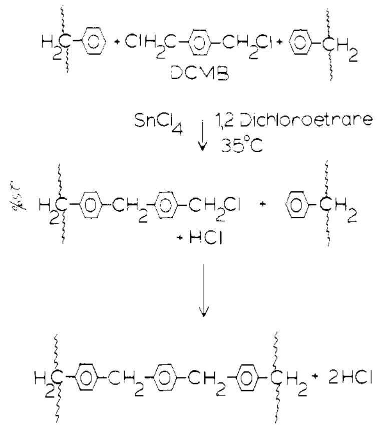

Figure 1. Friedel–Crafts cross-linking reaction.

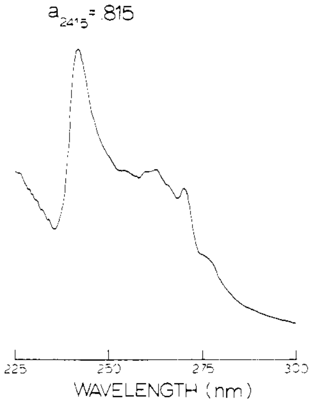

Figure 2. Ultraviolet absorption spectrum of cross-linked polystyrene in CCl_4.

The cross-linking process adds a fair number of para-methylchlorinated xylene structures to the polymer chain. These, along with the cross-links themselves, add to the scattering of the polystyrene. It is proper, then, that the scattering curves be interpreted as the scattering from a copolymer. To do so would require the refractive index increment from essentially three types of scattering centers.[10] Since these quantities are not known, an appreciable ambiguity will arise in the interpretation of the scattering functions. It should be noted that we expect to observe rather small changes in polymer dimensions.

A more feasible experiment would be small-angle X-ray scattering. This allows for the synthesis of polystyrene samples of moderate molecular weight (ca. 5×10^5) and provides for a potentially high-resolution measurement of the radius of gyration. Practical difficulties arise, however, in that an instrument is not conveniently located near us and in the selection of an appropriate polymer–solvent system. The solvent must have a Θ temperature conveniently near room temperature, it must give good polymer–solvent "contrast", and it must be composed of atoms that have a small mass absorption coefficient at $\lambda = 1.542$ Å, the operating wavelength of most instruments. In this connection, we define "contrast" to be the difference in the electron densities of the polymer and the solvent. The only solvent that adequately meets these requirements for polystyrene is cyclopentane. The use of this solvent should give good SAXS results. Nonetheless, the presence of three different scattering centers leads to uncertainties in the analysis of the scattering functions.

Photon correlation spectroscopy was finally chosen as the best method for the determination of the dimensions of the cross-linked polymers. The method yields a very accurate determination of the diffusion coefficient of polymers of even low molecular weight. This allows for the determination of dimensions in the regime where the radius of gyration is much smaller than the reciprocal wave vector. In this regime the specific chemical composition of the polymer is unimportant, so heterogeneity presents no problem in the interpretation of the correlation functions. A minor disadvantage occurs in that the diffusion constant must be related to the radius of gyration via an approximate theory; but at least it is possible to obtain data of high precision. It should also be noted that we are only interested in ratios of radii of gyration and not in absolute values. Therefore, we might expect only small errors in these quantities. We now look at the details of these measurements.

A. Determination of Reaction Conditions and Cross-Link Densities. The Friedel–Crafts reaction employed to cross-link polystyrene was developed by Grassie and Gilks.[11] The cross-linking reaction is depicted stepwise in Figure 1. The reaction is ideally suited to our purpose since the chemical nature of the cross-link is similar to that of the polymer chain itself. This suggests that only small changes in the solution thermodynamic properties of the polymer are to be expected after cross-linking. As we shall see later, even the shift of the Θ temperature of the cross-linked polymers is small.

Grassie and Gilks have shown that no cross-linking is observed in the absence of the DCMB. This result is clearly evidenced by the lack of HCl formation in such mixtures. It had been previously conjectured that a Friedel–Crafts reaction was possible with 1,2-dichloroethane as the cross-linker. The cross-links show negligible lability, as evidenced by the lack of gel formation in concentrated solutions of the pure intramolecularly cross-linked polymer allowed to stand for long periods of time (several months). This stability is certainly to be expected in view of the structure of the cross-link.

Grassie and Gilks also report that the fast step in the cross-linking reaction is the formation of the cross-link itself and not the attachment of the DCMB to the polymer chain. Evidence for this assertion was the absence of chlorine in the elemental analysis of the cross-linked polymers. It was conjectured that the reaction mechanism might even be strongly cooperative (no formation of incomplete cross-links). This proves to be incorrect, as we shall see from analysis of the polymer samples by ultraviolet spectrophotometry. The probable cause for the lack of chlorine in the samples of Grassie and Gilks is the high polymer concentrations with which they chose to work. At the very dilute concentrations in our reaction solutions, we typically found ca. 25% of the DCMB molecules failed to form a complete cross-link.

It is seen from Figure 2 that the ultraviolet absorption spectrum of the cross-linked polymer shows a strong shoulder peak at 276 nm. This shoulder peak is not present in the UV spectrum of the linear polymer as shown in Figure 3. Resolution of this peak was accomplished in the usual way by placing an appropriate concentration of un-cross-linked polymer in the reference cell to obtain the difference spectrum shown in Figure 4. In order to obtain the cross-link concentration in the polymer samples it is necessary to find the molar extinction coefficient of the cross-linked structure. This has been acomplished by Grassie and Gilks.[11] By making a detailed comparison between the quantity of HCl evolved in reactions to the gel point and the UV absorbance of the samples, they found that $\epsilon_{276}{}^{CL} = 1500$ mol^{-1} L cm^{-1}. This value is very reasonable, since *p*-xylene has a peak at 276 nm with a molar extinction coefficient of 500 mol^{-1} L cm^{-1} at that wavelength. It might be expected (Figure 1) that a

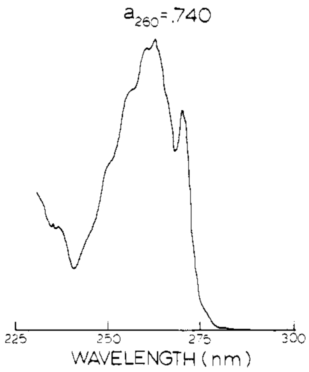

Figure 3. Ultraviolet absorption spectrum of linear polystyrene in CCl_4.

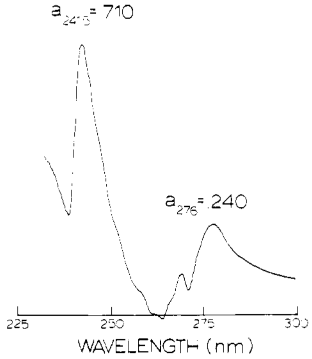

Figure 4. Ultraviolet absorption spectrum of cross-linked polystyrene with linear polystyrene in the reference cell. The absorption peak at 241.5 nm is due to the presence of incomplete cross-links; the peak at 276 nm is attributed to the complete cross-links.

cross-link should have the molar absorbance of three *p*-xylene molecules.

Also present in the difference spectrum of Figure 4 is a large peak at 241.5 nm. This peak is not found in the UV spectrum of *p*-xylene, but it is present in the spectrum of DCMB. The molar extinction coefficient of this peak is very large, being measured as 3720 mol^{-1} L cm^{-1}. It is also apparent that the DCMB spectrum shows an absorbance at 276 nm. Measurements show that $\epsilon_{241.5}{}^{DCMB}/\epsilon_{276}{}^{DCMB} = 12$. Correction must be made for this contribution from DCMB when computing the absorbance at 276 nm due to the cross-links.

A question immediately arises as to the origin of the peak at 241.5 nm. Reprecipitation of the polymer failed to reduce the relative intensity of this peak, and therefore it cannot be ascribed to residual DCMB. It must be attributed to the half-reacted cross-link shown in Figure 1. This conclusion contradicts the conjecture made by Grassie and Gilks regarding the cooperative nature of the reaction. The UV spectrum shown by Grassie and Gilks does not extend into the region below 250 nm.

Since the contribution of the un-cross-linked polymer to the absorbances at 241.5 and 276 nm is small, the reference concentration of polymer is not critical. For the sake of consistency, however, the reference concentration was chosen such that the absorbance in the difference spectrum was zero at 260 nm. The concentration of cross-links, [CL], can be calculated in this way as

$$[\mathrm{CL}] = (\Delta a_{276} - (\epsilon_{276}{}^{\mathrm{DCMB}}/\epsilon_{241.5}{}^{\mathrm{DCMB}})\Delta a_{241.5})/\epsilon_{276}{}^{\mathrm{CL}} = (\Delta a_{276} - \Delta a_{241.5}/12)/1500 \quad (1)$$

The Δ's indicate that these absorbances are to be taken from the difference spectrum. It is expected that cross-link concentrations obtained in this way are fairly accurate.

Table II
Ultraviolet Absorption Data

run	$\Delta a_{241.5}$	a_{260}	Δa_{276}	m	$1/f$	$100(\bar{M}_n - \bar{M}_n{}^0)/\bar{M}_n{}^0$, %
11	0.807	0.550	0.232	340	398	85
12	0.404	0.573	0.100	100	398	25
13	0.150	0.350	0.039	60	398	15
14	0.188	0.700	0.032	18	398	4.5
15	0.116	0.668	0.018	9	398	2.3
16	0.148	0.526	0.040	41	800	5.2

Measurement of the molar extinction coefficient of the un-cross-linked polymer at 260 nm gives the value $\epsilon_{260}{}^{sty} = 223$ mol^{-1} L cm^{-1}, where the "sty" superscript indicates that it is calculated per mole of enchained monomer. Subtracting the contributions to the absorbance at this wavelength from the cross-links and half-cross-links, we obtain

$$[\mathrm{sty}] = (a_{260} - 0.214\Delta a_{241.5} - 0.150\Delta a_{276})/223 \quad (2)$$

and from these two equations and the polymer molecular weight the mean number of cross-links per polymer molecule may easily be found. The results of these measurements and calculations are given in Table II.

B. Relative Occurrence of Intermolecular and Intramolecular Cross-Linking. An important aspect of the cross-linking reaction carried out in this work is the control of the increase of polydispersity due to intermolecular cross-linking.[8] This can be achieved to a lesser or greater extent by the selection of a reaction mixture appropriately dilute in polymer. To this end we seek an expression that relates the polymer concentration to the increase in the average molecular weight after cross-linking.

An approach to this problem may be found by considering the initial stage of the reaction. Suppose that the first molecule of DCMB has become attached to a monomer on the *i*th Guassian subunit of a polystyrene molecule. In a small volume element Δv about this *i*th subunit the total number density of monomers, both inter- and intramolecular, can be calculated. The relative probability of intra- to intermolecular cross-linking will be given by the ratio of the respective monomer number densities. Angular correlations between intramolecular monomers aside, this should give reasonable results in the low cross-link density limit.

In the Gaussian approximation the probability that the *i*th and *j*th subunits are within a small volume Δv is

$$\int_{\Delta v}(3/2\pi|i-j|\langle l^2\rangle)^{3/2}e^{-3r_{ij}^2/2|i-j|\langle l^2\rangle}\,d\mathbf{r}_{ij}{}^3 \cong P(\mathbf{O}_{ij})\Delta v = (3/2\pi\langle l^2\rangle)^{3/2}\Delta v/|i-j|^{3/2} \quad (3)$$

where $\Delta v \ll |i-j|^{3/2}\langle l^2\rangle^{3/2}$ and $\langle l^2\rangle$ is the mean square Gaussian bond length. The number density of intramolecular monomers in this volume element is denoted by [intra] and is given by $[\mathrm{intra}] = \Delta v^{-1}S_m\sum_{i\neq j}\Delta vP(\mathbf{O}_{ij})$, where S_m is the number of monomers per statistical subunit. Averaging this quantity over all initial placements of the cross-linker, the N statistical subunits per polymer, we obtain

$$[\mathrm{intra}] = S_m N^{-1}\sum_{i\neq j}P(\mathbf{O}_{ij}) = 4S_m(3/2\pi\langle l^2\rangle)^{3/2}(1 - 2/N^{1/2}) \quad (4)$$

If one neglects virial interactions, the number density of intermolecular monomers is given by the mean value $cN_A/100M_s$ cm^{-3}. In this expression c is in units of g/dL, $N_A = 6.022 \times 10^{23}$, and M_s is the molecular weight of styrene. From the ratio of these two number densities we

Table III
Comparison with the Data of Grassie and Gilks

[sty]	av exptl *mf*	calcd *mf*	% error
1.442	1.0	1.06	6
0.961	1.55	1.59	3
0.720	1.5	2.13	42
0.481	4.5	3.2	−26

obtain the ratio of the reaction rates of intra- and intermolecular cross-linking:

$$K_{\text{intra}}/K_{\text{inter}} = (100M_s/cN_A)4S_m(3/2\pi\langle l^2\rangle)^{3/2}(1 - 2/N^{1/2}) \quad (5)$$

The appropriate values of S_m and $\langle l^2\rangle$ for polystyrene in a Θ state near room temperature are found from the experimental value of the mean square radius of gyration and the maximum extension of the chain. This gives $S_m = 15$ and $\langle l^2\rangle^{1/2} = 2.67$ nm. Substitution of these values into eq 4 gives, for polystyrene of molecular weight 498000,

$$1/f \equiv K_{\text{intra}}/K_{\text{inter}} = 1.53 \text{ mol L}^{-1}/[\text{sty}] \quad (6)$$

where the styrene concentration, [sty], is in mol L^{-1}. Now, if $f \ll 1$, then the relative increase in molecular weight is given by the assumption that every intermolecular cross-link forms a polymer of twice the initial molecular weight. This yields

$$(\bar{M}_n^{\text{cross}} - \bar{M}_n^0)/\bar{M}_n^0 = mf \quad (7)$$

where m is the mean number of cross-links per polymer molecule and $\bar{M}_n^0$ is the initial number-average molecular weight. A comparison of this relationship to the experimental results of Grassie and Gilks is given in Table III. It is seen that the predictions of this simple relation are quite good.

It might be noticed that the above calculation assumed Θ conditions, whereas difficulties with DCMB solubility forced the use of the good solvent 1,2-dichloroethane. In a good solvent, the polymer becomes more extended so that the intramolecular monomer number density of eq 4 is reduced somewhat. Fortunately, virial interactions in a good solvent tend to keep polymer molecules separated so that a correction of similar magnitude and sign must be made to the local intermolecular monomer number density of eq 5. Note that the potential of mean force between polymer segments does not depend on the location of the pair if they are topologically distant on the chain. This leaves the value of f relatively unaffected.

C. Determination of the Second Virial Coefficient and the Θ Temperature of the Polystyrene/Cyclopentane System. The temperature dependence of the intrinsic viscosity can be related to the temperature dependence of the mean square radius of gyration, which, through the use of polymer solution theory, can provide information concerning the osmotic-pressure second virial coefficient, A_2, the excluded volume parameter, z, the binary segment cluster integral, β, and the solution Θ temperature.

Intrinsic viscosity measurements on a single polymer molecular weight are not sufficient for the determination of the solution thermodynamic parameters. However, use of a range of molecular weights makes possible the determination of the molecular weight dependence of the intrinsic-viscosity excluded volume factor $\alpha_\eta^3 = [\eta]/[\eta]_0$, where the subscript zero denotes the Θ point value. Various theories relate this quantity to those of interest. It is noteworthy that traditional methods for the determination of the temperature dependence of the second virial coefficient, i.e., light scattering and osmometry, rely not on the expansion of polymer dimensions but on intermolecular interactions between polymers. Thus it is the concentration dependence and not the molecular weight dependence that is studied. In this way alternate methods allow the determination of solution thermodynamic properties with a single polymer molecular weight.

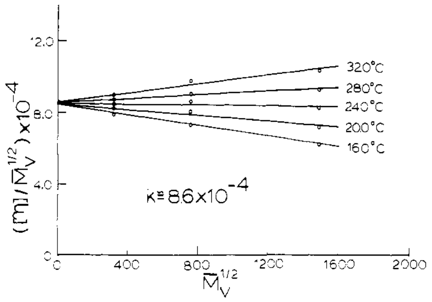

Figure 5. Viscosity plot for the polystyrene/cyclopentane system. From the slopes of these lines the segment binary cluster integral is found as a function of temperature.

Table IV
Thermodynamic Parameters from Viscosity Data

T, °C	$B \times 10^{28}$ (cgs)	*z*
16.00	−1.51	−1.03
20.00	−0.85	−0.057
24.00	−0.12	−0.008
28.00	0.63	0.043
32.00	1.43	0.097

In the Θ regime a useful form for the intrinsic viscosity is[12]

$$[\eta] = KM^{1/2} + \mu\phi_0 BM \quad (8)$$

where $B = \beta/M_s^2$, β is the segment binary cluster integral, and M_s is the segment molecular weight.

The experimental work of many investigators[19] suggests that $\mu = 0.346$ in the region $0 < \alpha^3 < 1.6$. For larger values of $1.6 < \alpha^3 < 2.5$, eq 8 was modified to $[\eta] = 1.05KM^{1/2} - 0.287\ \phi_0 BM$. The early theoretical work of Kurata and Yamakawa[13,14] gave $\mu = 0.51$, but later refinements of Yamakawa and Tanaka[15] modified this to $\mu = 0.349$ in the small-α^3 region. Finally, Shimada and Yamakawa[16] obtained the value $\mu = 0.376$. Tanaka[17] has shown that this value is in substantial agreement with the experimental value, and we will use this value in the calculation of $B(T)$. The constant K is related to the unperturbed mean square dimensions through the Flory–Fox[18] equation

$$K = \phi_0 6^{3/2}(\langle s^2\rangle_0/M)^{3/2} \quad (9)$$

where ϕ_0 is a universal constant whose value is nearly 2.5 × 10^{23} (cgs). Equation 9 and the definition of the excluded volume parameter, $z = (3/2\pi)^{3/2}(M/\langle R^2\rangle_0)^{3/2}(\beta/M_s^2)M^{1/2}$, give

$$z = (3/2\pi)^{3/2}\phi_0 K^{-1}BM^{1/2} \quad (10)$$

Following Flory,[20] we assume $B = B_0(1 - \Theta/T)$, where B_0 is determined by experiment. This treatment of the segment binary cluster integral is based on Flory's formulation of the excess free energy of mixing of a polymer solution; its utility has been demonstrated by experimental investigations.

In Figure 5 the appropriate plot is given for polystyrene of $\bar{M}_n = 97\,200$, $\bar{M}_n = 498\,000$, and $\bar{M}_n = 1\,800\,000$ in cyclopentane. In Table IV are given the values of B and z calculated from eq 8–10. These data indicate a Θ temperature of 24.5 ± 0.5 °C. The value of B_0 is found to be

5.47×10^{-27} (cgs). This result is close to that of Inagaki et al.,[21] who found $B_0 = 6.0 \times 10^{-27}$ (cgs) for the polystyrene/cyclohexane system.

The value of K was found to be 8.6×10^{-2} (cgs). This is slightly larger than the value 8.2×10^{-2} (cgs) found for the polystyrene/cyclohexane system and corresponds to $\langle s^2 \rangle_0^{1/2}/M^{1/2} = 2.86 \times 10^{-9}$ (cgs). This is larger than the corresponding values in most other Θ solvents and substantiates the claim made by Orofino[22] that cyclic hydrocarbons have large specific solvent effects for polystyrene.

D. Determination of the Θ Temperature Shift of the Cross-Linked Polymers. In order to determine the mean square unperturbed dimensions of the cross-linked polymers from the dynamic light scattering data it is necessary to measure the Θ temperature of each cross-linked polymer. In the previous section the Θ temperature of linear polystyrene in cyclopentane has been found by intrinsic viscosity measurements. Clearly, this method is not applicable to the cross-linked polymers, since a range of molecular weights is not available. Instead, the relative precipitation temperatures can be measured and these data can be used to determine the Θ temperatures of the cross-linked polymers relative to the linear polystyrene. As a check on the previous determination of Θ, precipitation data have been taken on a wide variety of polystyrene samples of various molecular weights. These data were then analyzed by Flory[20] theory to give Θ_p, the precipitation temperatures.

Before giving the experimental results, however, it is worthwhile to inquire as to the cause of the Θ temperature shift. According to theories of polymer solutions,[19] the second virial coefficient has the form

$$A_2 = \frac{\beta N_A}{2M_s^2} h_0(z)$$

Theories of $h_0(z)$ can always be expanded for small z to give $h_0(z) = 1 - az + ...$, where the constant a must agree with the first-order perturbation results,[23,24] $a = 2.865$, in order for the expansion to be considered valid for small z. The point is that for all theories of $h(z)$, $\lim_{z \to 0} A_2 = N_A\beta/2M_s^2$. The latter expression is just the virial coefficient expected for a solution of disconnected polymer segments. The limiting value of A_2 is a function of the binary segment cluster integral, which, in turn, depends on the free segment–segment potential of mean force. It is clear that the Θ temperature, being defined through $\lim_{T \to \Theta} = 0$, is therefore independent of molecular topology in the two-parameter polymer theories. Any Θ temperature shift of the cross-linked polymers must be a result of the small chemical modification of the polymer segments due to the presence of reacted DCMB and complete cross-link structures or to high-order corrections in the segment density. In order to minimize this first effect, the cross-linking agent was chosen to be chemically similar to the polystyrene monomer.

Of some interest in this connection is the cluster expansion treatment of A_2 for branched and ring polymers. The above form of A_2 is retained, but the constant a is modified. Casassa[25] has evaluated a for star-shaped polymers and has found that a increases monotonically from 3.279 for trifunctional stars to the asymptotic value of $0.2201f^{3/2}$ for very large values of the branch number f. Casassa[26] numerically evaluated a for uniform comb polymers and obtained $a = 3.536$ for a 2-branched comb. This value monotonically increased to 5.293 for the 20-branched comb, which was the most highly branched comb investigated. For the circular chain, Casassa[27] obtained $a = 4.457$. Once again, no change in the Θ temperature of such structures is expected on the basis of chain topology alone.

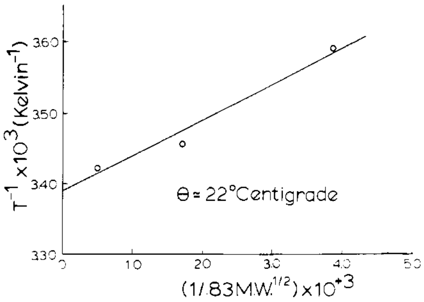

Figure 6. Upper critical solution temperatures of the linear polystyrene samples plotted against $x^{-1/2}$. The precipitation Θ temperature, given by the ordinate intercept, is ca. 22 °C. The Flory excess entropy of mixing parameter, given by the slope, is ca. 6.6×10^{-2}.

The approximate upper critical solution temperatures (UCST) were found for linear polystyrene of molecular weights 97 200, 498 000, and 1 800 000. The data were plotted according to the equation[20]

$$T_c^{-1} = \Theta_p^{-1}[1 + \phi_1^{-1}(x^{-1/2} + 2x^{-1})] \qquad (11)$$

The variable x is proportional to the polymer molecular weight, and in the region of interest $x^{-1/2} \gg 2x^{-1}$. A plot of the UCST's (T_c) vs. $x^{-1/2}$ can be used to obtain the precipitation temperature. This is shown in Figure 6, where the precipitation Θ temperature, Θ_p, is found to be ca. 22 °C. The discrepancy between Θ_p and Θ obtained by viscosity methods is probably due to the lack of precision with which the UCST's could be found. The polymer solutions were sufficiently polydisperse to make an accurate determination of the binodals difficult in the high-concentration region where the UCST is found. At low concentrations, however, the precipitation temperatures were easily and accurately measurable. These values of Θ are higher than that reported by Saeki et al.[28] (20.0 °C from critical point data) and Liu et al.[29] (19.6 °C from $A_2(T)$) but are consistent with the value of 23.0 °C reported by Leger et al.[30] These variations are probably due to the purity of the cyclopentane used.

To determine the Θ-temperature shifts of the cross-linked polymers, dilute solutions (ca. 0.4 g/dL) were made in purified cyclopentane. The precipitation temperatures, T_p, were then measured and compared to the precipitation temperature of the linear polymer of the same molecular weight and concentration. The Θ-temperature shift was taken to be equal to the shift of this precipitation temperature.

The results showed that even for the most heavily cross-linked polymer, with ca. 100 cross-links per polymer, the Θ temperature increased by only 0.7 °C. These Θ temperatures were then used to determine the unperturbed hydrodynamic radius of the cross-linked polystyrene samples.

E. Temperature Dependence of the Hydrodynamic Radius. The diffusion coefficients of the cross-linked and un-cross-linked polystyrene samples ($\bar{M}_n = 498000$, $\bar{M}_w/\bar{M}_n = 1.20$) were determined as functions of temperature. The measurements were made in cyclopentane in the region of the Θ temperature.

The first correction that must be applied to the experimental data accounts for hydrodynamic interactions of the nearly isolated polymers in the scattering medium. At infinite dilution a polymer diffuses through a fluid that is at rest in the laboratory reference frame. At a finite concentration, consideration must be given to nearby polymers that are also undergoing diffusional motions.

Table V
Infinite Dilution Values of the Diffusion Coefficients of the Cross-Linked Polymers

m	T, °C	$D_0 \times 10^7$ (cgs)	a_h, Å
0	12.0	2.79	156.5
	14.6	2.86	158.7
	18.6	2.97	161.7
	21.6	3.07	163.2
	24.8	3.18	165.0
	29.6	3.36	166.5
9	16.6	3.15	148.4
	19.5	3.27	149.9
	24.6	3.40	153.8
	29.4	3.55	157.4
	34.7	3.74	160.3
	40.2	3.94	163.3
18	14.8	3.08	147.6
	18.9	3.22	150.0
	22.7	3.33	152.9
	26.5	3.43	156.7
	30.2	3.58	157.7
	38.5	3.89	161.7
41	19.5	3.29	148.0
	23.1	3.40	150.8
	27.2	3.50	154.7
	31.3	3.67	156.0
	36.1	3.83	159.5
60	15.9	3.19	144.8
	19.2	3.27	148.0
	24.0	3.38	153.3
	29.2	3.56	156.6
	34.2	3.71	160.3
	38.5	3.86	162.9
100	23.4	3.52	146.0
	27.3	3.59	151.0
	29.7	3.67	152.6
	33.9	3.80	156.2
	38.0	3.96	158.1
	44.2	4.21	160.6

They exert a force on the polymer under consideration through a perturbation of the fluid velocity field.

Clearly, such a concentration-dependent effect can be removed by extrapolation to infinite dilution.

Rather than extrapolate to infinite dilution, which is time-consuming, we chose to run the samples at a very dilute concentration, typically ca. 0.2 mg/mL. Only a very small correction need be made to obtain the infinite dilution diffusion coefficient, D_0, for such low concentrations. Yamakawa[31] and Imai[32] have shown that the value of k_D in the expression $D = D_0(1 + k_D c)$ is given by

$$k_D = 0.655A_2M - b(4\pi/3)(N_A a_h^3/M) - \bar{v} \qquad (12)$$

where $\bar{v} = 0.92$ cm^3/g is the specific volume of the bulk polymer and A_2 is the solution second virial coefficient. The second term contains a hydrodynamic radius, a_h, in the form of the specific hydrodynamic volume $4\pi a_h^3/3$. The constant b, which is 1.0 in the theory of Yamakawa, has been experimentally determined by Pritchard and Caroline[33] for polystyrene in cyclopentane. For MW = 37 000 they obtained $b = 1.69 \pm 0.08$, whereas for MW = 180 000, 670 000, and 1 260 000 they obtained the value 1.75 ± 0.05. For high molecular weight samples (MW = 10^6–10^7), Jones and Caroline[34] obtained similar results.

At the Θ temperature the value of k_D for polystyrene is calculated to be -37.2 g^{-1} cm^3 for the linear polymer. This gives a value of $100(D - D_0)/D_0 = 0.74\%$ for a solution at the Θ temperature with $c = 2.00 \times 10^{-4}$ g/cm^3. For solutions not at the Θ temperature we must have an estimate of $A_2(T)$ in order to apply this small correction. Using the value of B_0 obtained from viscosity data gives $A_2 = 1.65 \times 10^{-3}(1 - \Theta/T)$. The infinite dilution values of D, corrected in this way, are reported in Table V.

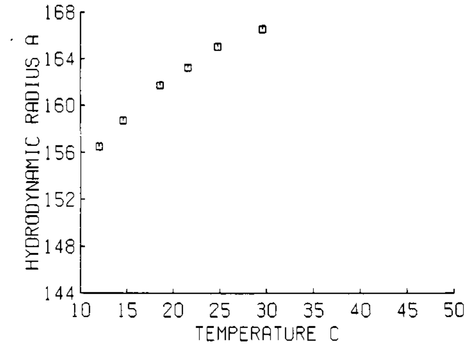

Figure 7. Hydrodynamic radius vs. temperature for linear polystyrene of $\bar{M}_n = 498\,000$ in cyclopentane.

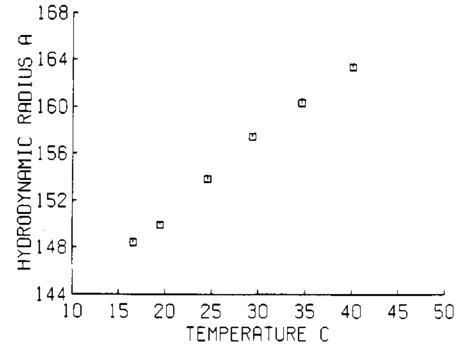

Figure 8. Hydrodynamic radius vs. temperature for cross-linked polystyrene of $\bar{M}_n = 498{,}000$ in cyclopentane. The average number of cross-links per polymer was nine.

The hydrodynamic radii of the polymers were obtained from the Stokes–Einstein equation

$$D_0 = kT/6\pi\eta_0 a_h \qquad (13)$$

In this way the hydrodynamic radius was calculated for the various polystyrene samples. The results are reported in Table V and in Figures 7 and 8.

From these graphs we can obtain some of the dilute solution thermodynamic properties of polystyrene in cyclopentane. Stockmayer and Albrecht[35] used a cluster expansion method to show that

$$\zeta \equiv a_h(T)/a_h(\Theta) = 1 + 0.609z \qquad (14)$$

where again $z = (3/2\pi\langle l^2\rangle_0)^{3/2}N^{1/2}\beta$ is the excluded volume parameter and β is the segment binary cluster integral. Using the expression $\beta = \beta_0(1 - \Theta/T)$, we find

$$(\mathrm{d}\zeta/\mathrm{d}T)|_{T=\Theta} = 0.609(3/2\pi\langle l^2\rangle_0)^{3/2}N^{1/2}\beta_0/\Theta \qquad (15)$$

From the data on polystyrene we obtain a temperature dependence of the expansion factor of the hydrodynamic radius of 4.4×10^{-3} °C^{-1}, which gives a value for the parameter $B_0 = \beta_0/M_s^2 = 2.8 \times 10^{-27}$ (cgs). This value of B_0 is smaller than the value obtained from viscosity data.

Discussion

The relation of the hydrodynamic radius to the radius of gyration forms a key step in the analysis of the experimental data. For randomly coiling polymers of molecular weight greater than ca. 10^4 it has been found that at the Θ condition the nondraining expression for the hydrodynamic radius is valid. This expression, obtained by Kirkwood,[36] is

$$\langle a_h\rangle^{-1} = N^{-2}\sum_{i\neq j}^{N}\sum\langle R_{ij}^{-1}\rangle \qquad (16)$$

where N is the number of beads on the polymer chain and R_{ij} is the distance between the ith and jth beads. Evidence

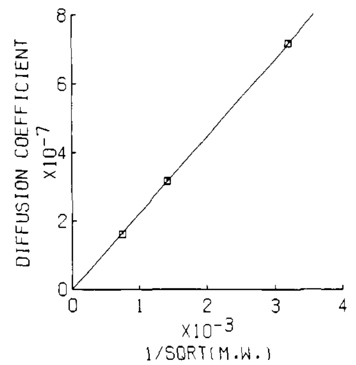

Figure 9. Diffusion coefficient of polystyrene in cyclopentane plotted against $M^{-1/2}$. The data points correspond to samples of $\bar{M}_n$ = 97 200, 498 000, and 1 800 000. This linear dependence of D (cm^2 s^{-1}) on $M^{-1/2}$ indicates that the non-free-draining hydrodynamic radius expression, eq 16, is applicable.

for the nondraining nature of the polystyrene/cyclopentane system is given in Figure 9. As required by eq 20, it is seen that the hydrodynamic radius is proportional to the square root of the molecular weight.

A similar expression for the radius of gyration is

$$\langle s^2\rangle = (2N^2)^{-1}\sum_{i\neq j}^{N}\sum\langle R_{ij}^2\rangle \qquad (17)$$

For the unperturbed linear chain it can be shown that $\langle s^2\rangle_0^{1/2} = 1.50\langle a_h\rangle_0$. Let h denote the relative contraction in the hydrodynamic radius after cross-linking, that is, let $h \equiv \langle a_h\rangle_0^{\text{cross-linked}}/\langle a_h\rangle_0^{\text{linear}}$, and let g, the Zimm–Stockmayer contraction factor, be defined as $\langle s^2\rangle_0^{\text{cross-linked}}/\langle s^2\rangle_0^{\text{linear}}$. Then if it is assumed that the proportionality constant between $\langle a_h\rangle_0$ and $\langle s^2\rangle_0^{1/2}$ is independent of polymer topology, one obtains $g = h^2$.

The calculations of many show that $h/g^{1/2}$ does depend on the polymer topology. For the many branched polymers investigated it has been found that $1 \leq h/g^{1/2} \leq 1.39$. For relatively small changes in the polymer topology the ratio $h/g^{1/2}$ is nearly 1.0 and so it is probably a reasonable, if not entirely satisfactory, assumption to let $g = h^2$. This assumption will certainly underestimate the true contraction in dimensions and may be a principal source of disagreement between the theory of g and the experimental data.

In Figure 10 is a graph of the experimentally measured contraction factor vs. the cross-link number. The two theoretical curves drawn through the data are taken from eq 17 of paper 1, $g = 1 - 0.7\rho$, where $\rho \equiv m/N$ is the cross-link density in terms of the number of cross-links per Gaussian segment. The curve labeled $N = 320$ is the contraction factor anticipated for a polystyrene of molecular weight 5×10^5, providing the number of statistical segments has been fixed in the manner described previously. The curve labeled $N = 1000$ fits the data better and corresponds to a statistical segment containing ca. five styrene monomers. It does not seem unreasonable that a ring of ten styrene monomers could form, but we must be careful not to put too much interpretation into the data until a satisfactory relation can be found between h^2 and g.

Two sources of error could explain deviations of the experimental data from the theoretical prediction. First, the proportionality constant between h^2 and g tends to increase as the chain topology becomes more perturbed. Failure to account for this would give values of g that were higher than the true values. A second source of disagreement arises from cross-linking in a good solvent. As discussed in paper 1, good solvent conditions more strongly favor the formation of small circuits than do Θ conditions. This too would tend to make the data lie above the theoretical curve.

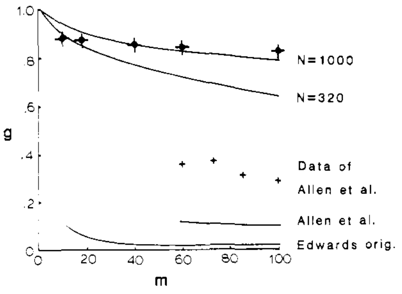

Figure 10. Zimm–Stockmayer contraction factor plotted against the average number of cross-links per polymer molecule. The data for the cyclized chain (top of graph) were taken from diffusion coefficient determinations. The data of Allen et al. were taken primarily from intrinsic viscosity measurements.

As a matter of interest, the data and theory of Allen et al.[7,8] are plotted on the same graph. Since the method of cross-linking employed in their experiment was quasi-random, large contractions in dimensions were observed. It is seen that the excluded-volume-modified theory also achieves qualitative agreement with the experimental data.

The primary reason for including the theory and data of Allen et al. on this graph is to contrast the different results obtained by different methods of cross-linking.

A ring-weighted intramolecularly cross-linked polymer can be prepared by cross-linking a homopolymer in dilute solution. Since every monomer is a potential cross-linking site, the probability of bond formation between monomers i and j depends only on the monomer–monomer contact probability, $P(\mathbf{O}_{ij})$. In paper 1 this was taken to be proportional to $|i - j|^{-3/2}$. In a good solvent a better approximation would be $P(\mathbf{O}_{ij}) \propto |i - j|^{-(3/2+\Delta)}$, where Δ is a monotonic nondecreasing function of $|i - j|$ and tends toward $^7/_{15}$ as $|i - j| \rightarrow \infty$. In either case (but especially so in a good solvent) the tendency is to produce a chain with many small circuits. The final product will not be unlike a random comb polymer with the linear arms replaced by circular chains.

A randomly cross-linked polymer could be synthesized in the following way: chemically convert, in dilute solution, A-type monomers on a homopolymer to B type, while allowing these then to cross-link to each other via a B-type cross-linker. If the cross-linking rate is large compared to the conversion rate, then the cross-linking process will not depend on the monomer–monomer contact probability. Intramolecular fluorescence quenching studies of Winnik et al.[40] on pyrene end-labeled polystyrene chains indicate that a reasonable reaction rate could be achieved for the cross-linking step. Since large circuit formation is very probable in this scheme, the randomly cross-linked structure should be very compact, and it is to this polymer that the theory of Allen et al. should apply.

A quasi-randomly cross-linked polymer can be synthesized from a random copolymer of A- and B-type monomers. In a dilute solution let this copolymer react with reagents that cross-link only the B-type monomers. For a given final cross-link density the polymer structure will depend on the solvent quality and the number fraction, f_n, of B-type monomers. Clearly, as $f_n \rightarrow 1$ the product will be the ring-weighted chain. The randomly cross-linked chain will be produced only in the limit of one pair of B-type monomers per copolymer and one cross-link. In all other cases ring-weighting will play an important role in the final structure. Equation 19 in paper 1 gives the contraction factor for a singly cross-linked copolymer as a function of f_n. It is seen that the statistics of this system are complex, but intuitively an inequality is clear: for a given molecular weight and cross-link number $g_{\text{random}} \le g_{\text{quasi-random}} \le g_{\text{ring weighted}}$.

Finally, the fundamental difference between these types of intramolecular cross-linking is exemplified by the natural variables for each process. The ring-weighted contraction factor is a universal function of the cross-link density, the random contraction factor is a universal function of the cross-link number, and the quasi-random g is a complex function of the cross-link number and the molecular weight. With the effects of excluded volume added, it should be mentioned that contraction in dimensions always depends on both the molecular weight and the cross-link number, regardless of the type of cross-linking employed.

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Registry No. Polystyrene, 9003-53-6; *p*-bis(chloromethyl)benzene, 623-25-6.

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Scaling Picture for Polymer Melt Rheology: A Critique of the Curtiss–Bird Model

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ABSTRACT: The reptation concept of de Gennes has recently been combined with kinetic theory and incorporated into a new model of polymer melt rheology by Curtiss and Bird (CB). We discuss the structure of this model by regarding it as an extension of dilute solution theory to concentrated systems. We examine the linear viscoelastic predictions of the CB model by carrying out detailed calculations of the storage and loss modulus curves and comparing them with experimental data for polystyrene. We discuss in depth the modified form of Stokes' law and introduce a scaling picture of the CB model chain. Using this scaling picture, we argue that the only value of the link tension coefficient ϵ consistent with both the internal subchain structure and the bead–rod configuration of the model chain is $\epsilon = 0$. Our interpretation of kinetic theory in concentrated polymer systems strongly suggests applying the reptational constraint to a scaling picture with Rouse-like chains.

1. Introduction

Viscoelastic properties of high-polymer melts have acquired renewed interest and a very interesting perspective in the recent development by Curtiss and Bird[1] (CB) and by Doi and Edwards[2] (DE) of microscopic theories of rheology which incorporate the reptation idea of de Gennes.[3] Prior to the development of these models, concentrated polymeric systems have resisted theoretical analysis due to the difficult problem of entanglement effects.

The reptation model provides a key to the study of concentrated polymers since it describes these effects in a simple and fundamental way. In essence it uses Edwards'

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