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Polydispersity and Conformation of Diluted Branched Molecules Prepared by Cross-Linking of Polystyrene Solutions

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ABSTRACT: Polystyrene chains in semidilute solutions have been cross-linked through the action of ^{60}C γ-rays. The reaction has been stopped at different stages before the gel point, and the sol phase has been diluted in a good solvent. Light scattering measurements have been analyzed in terms of theories of sol–gel transition and conformation of randomly branched molecules. The measured dependence of the average molecular weight and the average radius of gyration on the irradiation time suggests that the critical exponent τ characterizing the polydispersity of the pregel phase is smaller than the mean field prediction $\tau = {}^5/_2$.

I. Introduction

The gelation of polymer melts through the action of cross-linking agents (vulcanization) or of high-energy radiation is of substantial industrial importance and has been studied experimentally for many years. A statistical theory of such a gelation process was proposed by Flory[1] and Stockmayer[2] some 40 years ago. de Gennes[3] has shown recently that despite the fact that the Flory–Stockmayer theory neglects the effects of cyclizations and steric hindrances it should give an adequate description of a vulcanization process in a melt of long polymer chains. Hence, the theory is able to predict the distribution of the molecular weight of chains in a sol phase, its evolution as a function of the reaction time, and the gelation threshold.

Less is known about the formation of gels through the cross-linking of precursor polymer chains in a solution. The properties of the gelation transition depend both on the molecular weight of precursor chains and on their concentration. In a relatively dilute solution and/or for short chains cyclizations and steric hindrances should play an important role in the critical region near the gel point.[4] Daoud[4] argues that the gelation transition is then analogous to the connectivity transition in the percolation model and is described by the percolation critical exponents. Such an asymptotic behavior in the vicinity of the gelation threshold would be very different from that predicted by the Flory–Stockmayer theory.[5]

The irradiation with γ-rays offers a particularly convenient method of cross-linking the polymer chains in a solution. The cross-linking action of high-energy radiation has been demonstrated for a large number of polymers (e.g., poly(vinyl alcohol)[6], polystyrene[7], and poly(vinyl chloride)[8]) and solvents.[9] In this paper we present new experimental results concerning the gelation of polystyrene solutions in cyclopentane induced by ^{60}Co γ-rays.[10] We study the solutions with concentration close to the overlap concentration c^* for which it may be expected that the critical region is fairly large and that it is possible to make a distinction between the classical and the percolation-type behavior.

The sol–gel transition can be studied by in situ or dilution experiments. In an in situ experiment one studies one particular sample during the gelation process without affecting the reaction bath. Typical examples are the measurements of the viscoelastic properties of the sol or gel phase with the use of a magnetic sphere rheometer[11,12] or of the quasi-elastic light scattering.[13] The principal obstacle in using in situ observation lies in a difficulty of characterizing the polymer molecules in a concentrated solution by standard physicochemical methods. This difficulty does not exist in dilution experiments in which the reaction is stopped at some stage and the system is then diluted. However, the dilution experiments have one major drawback; they require a preparation of many absolutely identical samples in which reaction proceeds under strictly identical conditions. In usual chemical systems this is not really possible and for instance, the fluctuations of a few percent in the gel point for identically prepared samples are not unusual. Such fluctuations do not allow one to determine precisely the distance from the gel point for each particular sample, and it is difficult to determine the critical exponents near the gelation threshold. This problem may be overcome by measuring simultaneously two different types of averages (moments) of the distribution of the molecular weight of polymer molecules in the sol phase. It is possible then to test the validity of different theories without knowing exactly the advancement of the reaction with respect to the gel point for each particular sample.[14]

In the present work we have characterized the diluted sol phase by elastic light scattering. We measured the weight-average molecular weight $M_w(t)$ and the z-average radius of gyration $\langle R_g^2(t)\rangle_z$ of polymer molecules as a function of the irradiation time t for two different molecular weights of precursor chains. An analysis of the variation of the radius of gyration as a function of the average molecular weight gives information about the distribution of the molecular weight of molecules in a pregel phase and the validity of different theories of the gelation process.

II. Experimental Section

We used two different anionically prepared polystyrenes as linear precursors: one of molecular weight 55 000 and polydispersity 1.2 and the other with $M_w = 205\,000$ and $M_w/M_n = 1.07$.

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They were diluted in cyclopentane (Θ solvent at 20.5 °C) at a concentration $c = 0.1$ g/cm^3. The solutions were put in small tubes, carefully degassed, and sealed under a residual pressure in oxygen of 10^{-5} torr. They were first kept at 70 °C for 2 weeks and then at 22 °C during several weeks. The solutions were irradiated at a temperature of 22 °C by a ^{60}Co source at a dose rate of 10.5 Gy. Gels were formed after 10^5 min for the smallest precursor and after 2.05×10^4 min for the second one. We stopped the irradiation and quenched the reaction at different times before the gel point and we washed the solutions in toluene. The irradiated samples were then lyophilized in benzene and dried under vacuum at 60 °C.

Molecular weights and radii of gyration were measured by elastic light scattering with a Sofica 50 (λ = 436 or 546 nm) or a Sofica 4200 (λ = 632 nm) photogoniometer. The dried samples were diluted in toluene, and five concentrations were prepared from the initial solution. Careful centrifugation allowed the use of scattering angles θ between 15 and 150°. The wavelength λ of the incident beam was progressively increased for more irradiated samples.

Light Scattering Results. A typical Zimm plot is shown in Figure 1. A strong curvature in the Zimm plot is characteristic for all highly irradiated samples. It is essentially due to the polydispersity effects and to the fact that the scattering vector is comparable with the inverse of the radius of gyration.

In such a case one can try a linear extrapolation to zero scattering angle through the smallest values of scattering angles. Here we prefer to use a more general parabolic or cubic expansion of the scattered intensity including higher moments of the monomer spatial distribution. Such a procedure has been already applied to linear polymers[15] and critically branched polycondensates.[16,17]

For very dilute solutions, for which one can neglect intermolecular interaction, the scattered intensity is proportional to

$$I_p(q) \propto \sum_N P(N) N^2 f_N(q) \tag{1}$$

where $P(N)$ is the number of molecules with N monomers and q is the scattering vector $q = 4\pi \sin(\theta/2)/\lambda$. $f_N(q)$ is given by

$$f_N(q) = \left\langle \frac{1}{N^2} \sum_i \sum_j \frac{\sin(q r_{ij})}{q r_{ij}} \right\rangle_T \tag{2}$$

where $\langle\ \rangle_T$ denotes the thermal average over all spatial configurations of an N-mer. Developing $f_N(q)$ up to the fourth order in scattering vector q one gets

$$f_N(q) = 1 - \frac{q^2}{3} R_g^2 + \frac{q^4}{12} \rho^4 \tag{3}$$

where

$$\rho^4 = \left\langle \frac{1}{10N^2} \sum_{ij} r_{ij}^4 \right\rangle_T$$

$$R_g^2 = \left\langle \frac{1}{2N^2} \sum_{ij} r_{ij}^2 \right\rangle_T \tag{4}$$

The total scattered intensity due to polymer is then

$$I_p(q) \propto \sum_N P(N) N \frac{\sum P(N) N^2}{\sum P(N) N} \left[1 - \frac{q^2}{3} \frac{\sum P(N) N^2 R_g^2}{\sum P(N) N^2} + \frac{q^4}{12} \frac{\sum P(N) N^2 \rho^4}{\sum P(N) N^2} \right] \tag{5}$$

$$I_p(q) = KcM_w \left[1 - \frac{q^2}{3} \langle R_g^2 \rangle_z + \frac{q^4}{12} \langle \rho^4 \rangle_z \right] = KcM_w f(q) \tag{6}$$

where $\langle R_g^2 \rangle_z$ and $\langle \rho^4 \rangle_z$ denote the z average of R_g^2 and ρ^4, M_w is the weight-average molecular weight of the branched molecules, c is the concentration in polymer, and K is a constant.

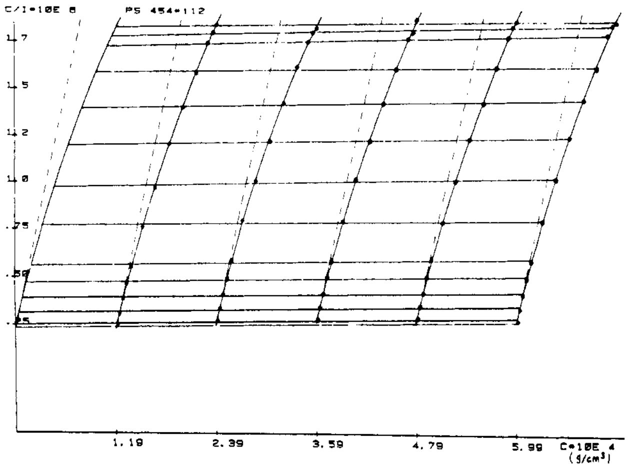

Figure 1. Typical Zimm plot for an irradiated sample. The sample has been irradiated during 17 930 min and then diluted in toluene. The precursor chain molecular weight was $M_w \simeq 2.05 \times 10^5$. Continuous lines are obtained by fitting the data with eq 7. One finds $M_w \simeq 4.9 \times 10^6$, $\langle R_g^2 \rangle_z \simeq 1540$ Å, and $\langle \rho^4 \rangle_z^{1/4} \simeq 1670$ Å. Dashed lines represent linear extrapolation through the smallest values of the scattering angles.

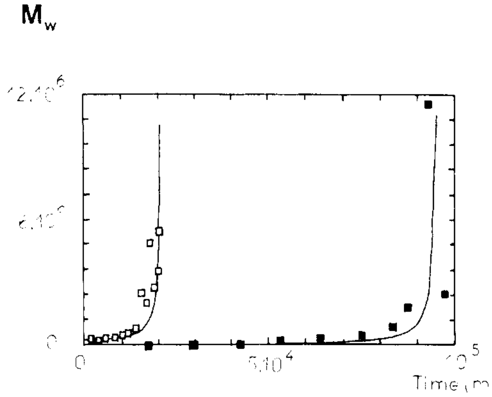

Figure 2. Variation of the average molecular weight $M_w(t)$ as a function of irradiation time t for two different precursor chains: (■) $M_w(0) \simeq 5.5 \times 10^4$; (□) $M_w(0) \simeq 2.05 \times 10^5$. The continuous lines are theoretical variations obtained with the use of the classical kinetic theory (eq 15).

Hence, the quantity $Kc/I(q)$ appearing in the Zimm representation may be approximated by

$$\frac{Kc}{I_p(q)} = \frac{1}{M_w} \left[1 + \frac{q^2}{3} \langle R_g^2 \rangle_z - \frac{q^4}{12} M_4^4 \right] + 2A_2 c \tag{7}$$

with

$$M_4^4 = \langle \rho^4 \rangle_z - \frac{4}{3} \langle R_g^2 \rangle_z^2$$

The last term in (7) proportional to c takes into account small interactions between different molecules and is supposed to be independent of scattering vector, which is a rather good approximation at low concentrations.

For the data plotted in Figure 1, a least-squares analysis with the use of eq 7 gives $M_w \simeq 4.9 \times 10^6$, $\langle R_g^2 \rangle_z^{1/2} \simeq 1540$ Å, and $\langle \rho^4 \rangle_z^{1/4} \simeq 1670$ Å. A linear extrapolation through small-angle values would introduce a nonnegligible error since it gives $M_w \simeq 5.6 \times 10^6$ and $\langle R_g^2 \rangle_z^{1/2} \simeq 1810$ Å.

Moreover, $\langle \rho^4 \rangle_z$, the parameter which characterizes the curvature of Zimm plots, is not just a fitting parameter. It provides information about the structure of irradiated molecules. This point is discussed in the Appendix.

Figure 2 shows the variation of the molecular weight of the irradiated samples as a function of the irradiation time. Figure 3 presents the variation of the z-average radius of gyration.

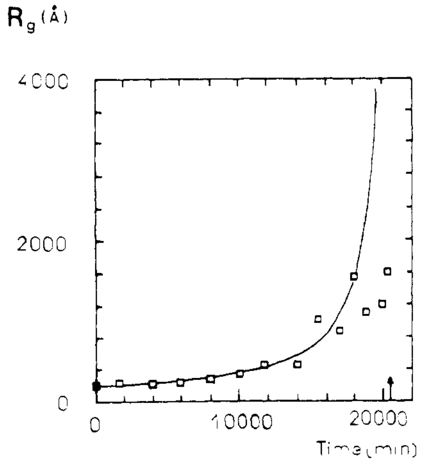

Figure 3. Variation of the average radius of gyration as a function of irradiation time t for the precursor chains of molecular weight $M_w(0) \simeq 2.05 \times 10^5$. The continuous line is a theoretical variation obtained with the use of the classical kinetic theory (eq 19). The arrow indicates the gel point $t_g \simeq 20\,500$ min.

Both molecular weight and radius of gyration diverge when the gelation threshold is approached. Beyond the gel point some fraction of the sample is no longer soluble in toluene. The gel point is defined as the highest irradiation time for which all the sample is soluble. The error in determination of the gelation threshold is about 3–5%.

The second virial coeffieint A_2 is of the order of 4.7×10^{-4} mol·mL·g^{-1} for linear polystyrene solutions ($M_w \simeq 200\,000$). This coefficient decreases for irradiated samples and is extremely small ($\sim 3 \times 10^{-5}$ mol·mL·g^{-1}) for samples near the gelation threshold. This effect is due to the increase of the average molecular weight and the branching of the chains. The quantitative analysis of the dependence of A_2 on the irradiation time is much more difficult than that of the average molecular weight or that of the radius of gyration because of the relatively large error (20%) in measuring A_2 by elastic light scattering.

III. Discussion and Conclusions

The simplest interpretation of the variation of the distribution of molecular weight of molecules as a function of the reaction time t is to assume that the probability of cross-linking of two different molecules is proportional to the product of their concentrations. Then the number of N-mers in the sample $P(N,t)$ varies with the time according to a simple Smoluchowski equation:[18]

$$\frac{\partial P(N,t)}{\partial t} = \frac{1}{2} \sum_{\substack{i,j \\ i+j=N}} K_{ij} P(i,t) P(j,t) - P(N,t) \sum_i K_{iN} P(i,t) \quad (8)$$

where K_{ij} controls the rate of cross-linking of species i and j. In a standard mean field approximation, the rate of cross-linking of two species i and j is supposed to be proportional to the product of the number of monomers i and j. In that case, eq 8 may be solved exactly.[19–23] A particularly convenient method of solving (8) is to introduce the generating function[24]

$$\Gamma(z,t) = 1 - \sum_N \phi(N,t) e^{-Nz} \quad (9)$$

where $\phi(N,t)$ denotes the fraction of monomers which belong to an N-mer

$$\phi(N,t) = NP(N,t) / \sum_k kP(k,t) \quad (10)$$

Then eq 8 reduces to

$$\frac{\partial \Gamma(z,\tau)}{\partial \tau} = \Gamma(z,\tau) \frac{\partial \Gamma(z,\tau)}{\partial z} \quad (11)$$

where τ is proportional to the irradiation time t and the proportionality constant ensures that the coefficient in (11) is 1. The solution of (11) reads

$$\Gamma(z,\tau) = u(z + \tau \Gamma(z,\tau)) \quad (12)$$

with $u(\xi)$ being determined by the initial mass distribution of polymers, i.e.

$$u(\xi) = \Gamma(\xi,0) = 1 - \sum_N e^{-N\xi} \phi(N,0) \quad (13)$$

The knowledge of the generating function enables one to calculate all the moments of the distribution function. For instance, the average molecular weight

$$N_w(t) = \sum k \phi(k,t) = \left. \frac{\partial \Gamma(z,t)}{\partial z} \right|_{z=0} \quad (14)$$

is given by

$$N_w(t) = N_w(0) / (1 - t/t_g) \quad (15)$$

where t_g is the gel time, proportional to $\tau_g = 1/N_w(0)$.[1,2,25]

In Figure 2 the experimental data are compared with the theoretical predictions of eq 15. The agreement is quite reasonable for the beginning of the reaction. Unfortunately, it is meaningless to make a comparison near the gelation threshold because of uncertainty in determining the gelation time t_g (cf. section II) and the fluctuations of the gel point from one sample to another (cf. section I). This last effect and not the precision of light scattering is responsible for the scattering of the experimental points near the gelation threshold. Therefore the time dependence of the average molecular weight alone does not allow one to compare the validity of classical and percolation theories.

The average radius of gyration provides indirect information about the distribution function $P(N,t)$. However, the interpretation of the results is much more subtle than that of $M_w(t)$. In fact, the observed radius of gyration reflects not only the polydispersity effects but also the swelling effects of the good solvent in which the sol phase is diluted:

$$\langle R_g^2 \rangle_z = \sum P(N) N^2 R_g^2(N) / \sum P(N) N^2 \quad (16)$$

The mean radius $R_g(N)$ of N-mers is a function of the total number of monomers N and also of the molecular architecture of branched molecules, which depends on the conditions under which the gelation reaction occurs (e.g., polymerization index of precursor chains N_0, their concentration, and the quality of the solvent in the reaction bath).

If one supposes that diluted sol molecules behave like randomly branched chains swollen in a good solvent, $R_g^2(N)$ is proportional to the total number of monomers in the molecule.[26] The mean radius of gyration of an N-mer depends also on the average number of monomers between cross-links N_x:

$$R_g^2(N) \sim N N_x^{1/5} \quad (17)$$

Equation 17 may be obtained by the Flory–de Gennes method.[27] It may be interpreted in terms of a blob model in which one treats the molecule as a randomly branched molecule of N/N_x units each of the length $N_x^{\nu_L}$ (with $\nu_L = {}^3/_5$ within the Flory approximation).

In the case of the gelation of chains the average distance between two cross-links N_x should be close to N_0 if the reaction is stopped before the gel point. Then the measured z-average radius of gyration of a diluted sol $\langle R_g^2(t) \rangle_z$ (eq 16) may be approximated by

$$\langle R_g^2(t) \rangle_z \simeq N_x^{1/5} \frac{\sum P(N,t) N^3}{\sum P(N,t) N^2} \tag{18}$$

In writing eq 18 we suppose that all polymer molecules swell in the same manner according to the formula (17) for branched chains. Although an important fraction of linear chains remains in the system even near the gel point, eq 18 is a good approximation since N_0/N_x is small. First, for linear chains, the difference between their actual radius of gyration $R_g \sim N_0^{2\nu_L}$ and the approximate value $N_0 N_x^{1/5}$ is small. Second, small molecules contribute very little to the wave vector dependent part of the scattering intensity since for these molecules $qR_g \ll 1$ (cf. eq 7). Actually the largest contribution to the measured radius of gyration comes from branched chains with high molecular weight.

Within the kinetic theory the variation of the radius of gyration as a function of the irradiation time is readily obtained through eq 18, 12, and 9:

$$\langle R_g^2(t) \rangle_z \simeq \langle R_g^2(0) \rangle_z / (1 - t/t_g)^2 \tag{19}$$

where $\langle R_g^2(0) \rangle_z$ denotes the average radius of gyration of precursor chains swollen in a good solvent. The comparison of the kinetic theory and the experimental results is shown in Figure 3. The discrepancy between the classical theory and our results for the most irradiated samples may suggest that deviations from the classical picture are important. The z-average radius of gyration is determined by higher moments of the molecular weight distribution (cf. eq 18) than those determining the average molecular weight $M_w(t)$. This is the reason why deviations from random intermolecular cross-link are easier to detect when one studies $\langle R_g^2(t) \rangle_z$. However, the precise analysis of the asymptotic behavior of $\langle R_g^2(t) \rangle_z$ in the vicinity of the gelation threshold is hazardous because of the error in determining the gel time t_g and because of the gel point fluctuations.

This essential difficulty in determining exactly the advancement of the reaction in each particular diluted sample may be avoided by considering the variation of the average radius of gyration of diluted sol molecules as a function of their average molecular weight. In fact for a given dilution procedure the relation between the radius of gyration and the molecular weight depends solely on the distribution function of the molecular weight of sol molecules.[14] As pointed out by Daoud et al.[14] this relation should be very different in the vicinity of the gelation threshold for percolation and classical behavior.

In the critical region near the gel point the Flory–Stockmayer theory leads to the following distribution function:

$$P(N) \sim (N/N_0)^{-5/2} \exp\{-A(N/N_0)\epsilon^2\} \tag{20}$$

where $\epsilon = (t_g - t)/t_g$ denotes the relative distance from the gel point and the constant A depends on the length of precursor chains, their concentration in the reaction bath, and the solvent quality. The same distribution function may be obtained from the kinetic model discussed above.

The distribution (20) is a particular example of a more general scaling expression

$$P(N) \sim (N/N_0)^{-\tau} f(\epsilon (N/N_0)^{\sigma}) \tag{21}$$

where $f(\ )$ denotes an analytical function and τ and σ are critical exponents.[5,28] If the sol–gel transition is described by a percolation-type behavior, τ and σ are independent exponents and are equal to 2.2 and 0.46, respectively.[5] A similar scaling form may be also obtained in a modified kinetic model in which the rate constant in Smoluchowski equation (8), K_{ij}, is assumed to be proportional to $(ij)^{\omega}$ (with $1 - 1/d < \omega < 1$) in order to account for the fact that not all molecules are equally reactive. In such a model the exponents τ and σ are not independent: $\tau = \omega + {}^3/_2$ and $\sigma = \omega - {}^1/_2$.[29]

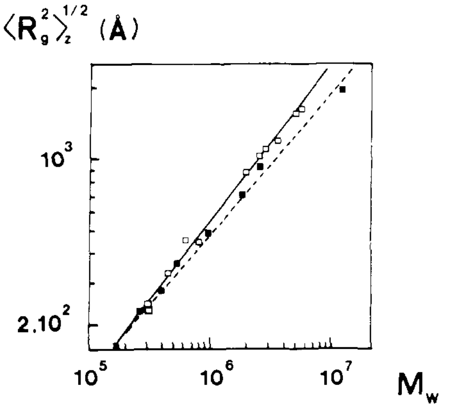

Figure 4. Double-logarithmic plot of the radius of gyration $\langle R_g^2(t) \rangle_z^{1/2}$ vs. the molecular weight $M_w(t)$. Symbols are the same as in Figure 2. Continuous and dotted lines are linear fits through experimental points for longer and shorter precursor chains, respectively.

Exponents τ and σ determine the divergence of different moments of the distribution function at the gel point:[28]

$$\sum_N P(N) N^k \sim N_0^{k+1} \epsilon^{(\tau-1-k)/\sigma} \qquad \text{for } k > 1 \tag{22}$$

Hence, eq 22, 10, 14, and 18 lead to

$$N_w \sim N_0 \epsilon^{(\tau-3)/\sigma} \tag{23}$$

and

$$\langle R_g^2 \rangle_z \sim N_0 N_x^{1/5} \epsilon^{-1/\sigma} \tag{24}$$

for the asymptotic behavior of the average molecular weight and of the average radius of gyration. By eliminating ϵ we obtain

$$\langle R_g^2(t) \rangle_z \sim \langle R_g^2(0) \rangle_z (M_w(t)/M_w(0))^{1/(3-\tau)} \tag{25}$$

where we have approximated $N_0 N_x^{1/5}$ by the radius of gyration of precursor chains $\langle R_g^2(0) \rangle_z \sim N_0^{6/5}$ in a good solvent. Since τ must be greater than 2 but smaller than 3, the apparent swelling exponent

$$\nu_{\text{eff}} = {}^1\!/_2 (3 - \tau)^{-1} \tag{26}$$

is very sensitive to the actual value of τ. The difference between the classical $\nu_{\text{eff}} = 1$ and percolation exponent $\nu_{\text{eff}} \simeq 0.63$ is indeed very important.[14] The very fact that ν_{eff} depends only on the exponent τ does not permit us to distinguish between percolation and modified kinetic theories.

It is to be stressed that the kinetic theory enables one to predict the dependence of $\langle R_g^2(t) \rangle_z$ on $M_w(t)$ not only in the asymptotic region but at any time. In fact, eq 9, 12, 14, and 18 yield (for $K_{ij} \sim ij$)

$$\frac{\langle R_g^2(t) \rangle_z}{\langle R_g^2(0) \rangle_z} = \frac{M_w^2(t)}{M_w^2(0)} \tag{27}$$

which agrees with the classical expression (25) (with $\tau = {}^5/_2$ or $\nu_{\text{eff}} = 1$) in the critical region.

We have plotted in Figure 4 the experimentally measured variation of $\langle R_g^2 \rangle_z$ as a function of M_w. The least-squares analysis of the data for the shorter precursor chains ($M_w(0) \simeq 5.5 \times 10^3$) leads to $\nu_{\text{eff}} \simeq 0.58 \pm 0.06$. A similar analysis gives for the second precursor chains $\nu_{\text{eff}} \simeq 0.64 \pm 0.06$. As shown in Figure 4 the data are in complete

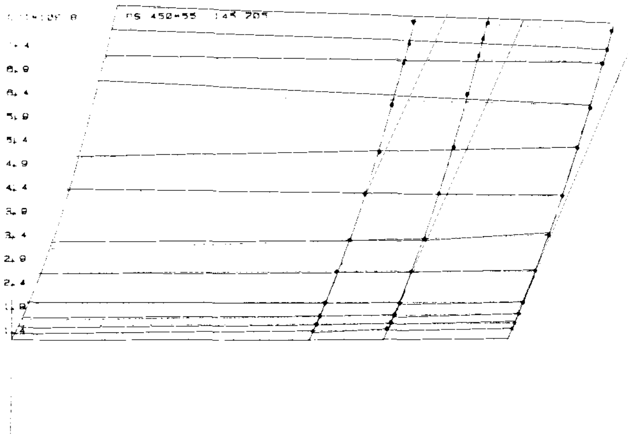

Figure 5. Zimm plot for the high molecular weight fraction of an irradiated sample. It shows an upward curvature characteristic of branched molecules. The Zimm plot for the whole sample would exhibit a downward curvature due to polydispersity. The radius of gyration of the fraction is much smaller than that of a linear chain or that of a whole irradiated sample having the same average molecular weight.

disagreement with the classical kinetic model which leads to eq 27.

Hence, our observations seem to indicate that the exponent $\tau_{\rm exp} \simeq 2.2 \pm 0.2$ is close to the percolation one and is smaller than that predicted by mean field theory, $\tau = {}^5/_2$. It should be stressed however that the relation between the exponent $\nu_{\rm eff}$ and the exponent τ (eq 26) is based on strong assumptions concerning the conformation of branched chains (eq 17 and 18). If the branched molecules were less swollen than implied by eq 17, the conclusions about the actual value of the exponent should be revised.

It is remarkable that the power law (25) is observed for almost all reaction times and not only for samples in which reaction was stopped near the gel point. This is related to the fact that $\langle R_g^2(t)\rangle_z$ depends on a high moment of the distribution function which is influenced essentially by the presence of large molecules. The number of these molecules is governed by the scaling law (21). The same molecules give the largest contribution to the observed scattering intensity.

Values of $\nu_{\rm eff}$ between 0.5 and 0.6 have already been observed for various gelation processes[16,30,31] and are consistent with the theoretical interpretation of Daoud et al.[14]

It is interesting to note that the measured radii of gyration $\langle R_g^2(t)\rangle_z^{1/2}$ of the samples made up from precursor chains of different molecular weight are nearly the same for the same value of $M_w(t)$. This observation is in qualitative agreement with eq 25 and the experimentally observed value of $\nu_{\rm eff}$. The measured radii of gyration are not very different from those of linear chains of the same average molecular weight. This results from the compensation of two effects: each cross-linked N-mer has smaller dimensions than a linear chain made up of N monomers but the sample contains many chains with a mass much greater than the average $M_w(t)$. To illustrate this point we performed light scattering on a high molecular weight fraction of an irradiated sample and compared the result with that obtained for the whole sample. Although the molecular weight of the fraction M_f is much larger than the average molecular weight of the whole sample $M_w(t)$, the radius of gyration of the fraction R_f is smaller than the average radius that would have a more irradiated sample with $M_w(t) = M_f$ or a linear chain of molecular weight M_f. Moreover, the Zimm plot obtained for the fraction (Figure 5) is very different from that of the whole sample. It shows an upward curvature characteristic for branched molecules (cf. Appendix for a more detailed discussion).

To conclude, the simultaneous studies of the average radius of gyration and of the average molecular weight of the diluted sol molecules may provide a useful characterization of the distribution function of the molecular weight. Our experiment on gelation of short precursor chains in a semidilute regime seems to suggest that the exponent τ characterizing the decay of number of molecules with the molecular weight is smaller than that predicted by mean field theories. However, this result is based on the strong assumption that all high molecular weight molecules swell in the same manner like randomly branched chains. The analysis of light scattering experiments shows that the average properties that we measure reflect a complex competition between the effects of polydispersity and the change in molecular architecture of chains during the gelation process. We are performing experiments which should give more direct information about the distribution function and swelling of individual molecules after the dilution in a good solvent.

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Appendix

The curvature of a Zimm plot (cf. Figures 1 and 5) provides additional information about the conformation of molecules since it enables one to measure

$$\langle \rho^4 \rangle_z = \sum P(N) N^2 \rho^4 / \sum P(N) N^2 \qquad \text{(A1)}$$

with ρ^4 being the fourth moment of the average monomer–monomer separation defined by eq 4. The moment $\langle \rho^4(t)\rangle_z$ can be measured with sufficient precision only for the most irradiated samples. A derivation analogous to that of eq 25 yields

$$\langle \rho^4(t) \rangle_z \sim M_w(t)^{4\nu_{\rm eff}} \qquad \text{(A2)}$$

The measurements are consistent with eq A2 and give the value of $\nu_{\rm eff} \simeq 0.6$ but with an error greater than the value determined from the radius of gyration. The coefficient

$$\zeta = \frac{3}{4} \rho^4 / (R_g^2)^2 \qquad \text{(A3)}$$

gives some details about the distribution function of monomers. For instance, in the case of linear Gaussian chains $\zeta = {}^3/_4$ whereas for excluded volume chain $\zeta \simeq 0.69$.[32] We do not know calculations of ζ for randomly branched chains which take excluded volume effects into account.

In experiments one measures a mean value of

$$\bar{\zeta} = \frac{3}{4} \frac{\langle \rho^4 \rangle_z}{\langle R_g^2 \rangle_z^2} \qquad \text{(A4)}$$

which is very strongly affected by polydispersity. In the case of the less irradiated sample for which $\bar{\zeta}$ is still measurable, we find $\bar{\zeta} \simeq 1.3$. For more irradiated samples $\bar{\zeta}$ decreases and tends asymptotically to $\bar{\zeta} \simeq 1$. Such a variation may seem paradoxical at first, since $\bar{\zeta}$ should increase when the polydispersity of the sample increases.[32] However, this is only the case when all molecules have the same spatial monomer distribution characterized by the same value of ζ. In the gelation experiment the number of linear chains and weakly branched molecules decreases in favor of highly branched huge molecules. Thus a decrease in the mean value of $\bar{\zeta}$ means that ζ of individual molecules decreases when the degree of cross-linking increases. This is confirmed by light scattering on the high molecular weight fraction of an irradiated sample shown in Figure 5. For the fraction, Zimm plot curves upward, which means that $\bar{\zeta} < 1$ whereas the nonfractionated sample has $\bar{\zeta} > 1$.

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Conformational Characteristics of Poly(1-alkenes). Flexible Side Groups and the Limits of Simple Rotational Isomeric State Models

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ABSTRACT: Rotational isomeric state models were constructed, based on the model for poly(propylene) with five states per bond, and assuming mutually independent side groups, for poly(1-butene) (P1B), poly(1-pentene) (P1P), poly(4-methyl-1-pentene) (P4MP), and poly[(*S*)-4-methyl-1-hexene] (PS4MH). Values for the unperturbed dimensions were calculated and found to be in good agreement with experiment for P1B and P1P, and poor agreement with experiment for P4MP and PS4MH. The reason for the poor agreement for P4MP and PS4MH was found to lie in the mutual interdependence between side groups. A remedy is offered by direct numerical integration; this approach, however, is limited by the amount of computational effort necessary that increases exponentially with the number of rotational degrees of freedom in the side chains. Conformational statistics for PS4MH, the optically active polymer investigated, were analyzed.

Introduction

The conformation of poly(1-alkenes) with articulated side chains has been the subject of many investigations. Crystal structure analysis of partially crystalline, isotactic samples revealed the helical nature of these chains shortly after the first stereoregular synthesis.[1,2] Since then very detailed crystal structures have been obtained, and polymorphisms have been observed in several cases (see ref 3–9 and references cited therein). Calculations of the intramolecular potential energy of regular conformations of poly(propylene) (PP) as a function of the torsion angles were first performed by Natta, Corradini, and Ganis.[10] Their results were confirmed,[11] and the method was refined and extended to isotactic polymers with longer side chains.[3,12–14] Agreement between experiment and calculations was very good. These experiments and the corresponding computations indicate a strong influence of the side chains on the minimum-energy conformation with regular repetition of torsion angles. Unfortunately, these calculations are not directly applicable to polymers in melt or in solution.

Experimental results on the conformational characteristics of isotactic and atactic poly(1-alkenes) in solution are also numerous. Foremost among them are values for the characteristic ratio of the unperturbed end-to-end distance and its temperature coefficient;[15–26] they comprise

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