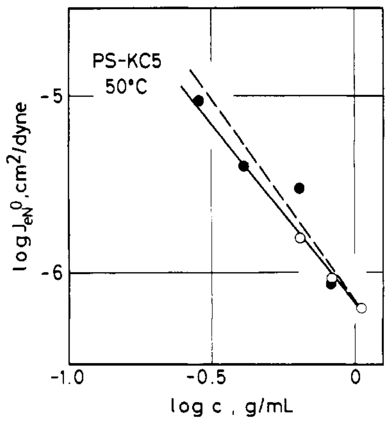

Figure 3. Concentration dependence of rubbery plateau compliance $J_{eN}°$ for solutions of six-branched polystyrene (LS1; open circles) and linear polystyrene (L50; closed circles) at 50 °C. The broken line indicates the de Gennes prediction.[18]

state. This behavior of $J_e°$ for the six-branched polystyrene is very similar to that reported for three- and four-branched star polybutadienes[6] but differs from those obtained by Graessley et al.[9] for solutions of four- and six-branched polyisoprenes as well as those by Kajiura et al.[10] for three-branched poly(α-methylstyrenes).

Recent experimental investigations[3,4,6,9] have shown that the molecular weight dependence of $J_e°$ for star polymers having P up to 4 can well be represented by the Rouse–Ham equation[15,16]

$$J_e° = 0.4(g_2M/cRT) \tag{3}$$

where

$$g_2 = (15P - 14)/(3P - 2)^2 \tag{4}$$

Equation 3 is plotted by a thin line (R-H) in Figure 2, which can represent well the concentration dependence of $J_e°$ of the six-branched star polystyrene. A similar dependence of $J_e°$ on M for star polymers has been reported by a theoretical consideration on a reptation of polymer chain.[17]

Rubbery Plateau Compliance. One of important parameters for characterizing the rubbery region is the rubbery plateau compliance $J_{eN}° = 1/G_{eN}°$, where $G_{eN}°$ is the rubbery plateau modulus. The concentration dependence of $J_{eN}°$ for the solutions at 50 °C is shown in Figure 3. As can be seen from this figure, $J_{eN}°$ for the linear (closed circles) and star (open circles) polystyrenes is proportional to c^{-2}. There is no difference in the concentration dependence of $J_{eN}°$ between the linear and branched polymers, in marked contrast to the case of $J_e°$.

de Gennes evaluated the molecular weight and concentration dependences of rheological parameters for moderately concentrated polymer solutions in a good solvent[18] by using a scaling concept.[19] This theory predicts that both of $J_e°$ and $J_{eN}°$ are proportional to $c^{-2.25}$. This prediction is shown by the dotted lines in Figures 2 and 3. The c^{-2} dependence appears better than $c^{-2.25}$, as can be seen from these figures.

References and Notes

(1) Masuda, T.; Ohta, Y.; Onogi, S. *Macromolecules* **1971**, *4*, 763.
(2) Utracki, L. A.; Roovers, J. E. L. *Macromolecules* **1973**, *6*, 366, 373.
(3) Graessley, W. W.; Roovers, J. E. L. *Macromolecules* **1979**, *12*, 959.
(4) Isono, Y.; Fujimoto, T.; Inagaki, H.; Shishido, M.; Nagasawa, M. *Polym. J.* **1980**, *12*, 131.
(5) Isono, Y.; Fujimoto, T.; Kajiura, H.; Nagasawa, M. *Polym. J.* **1980**, *12*, 369.
(6) Masuda, T.; Ohta, Y.; Kitamura, M.; Saito, Y.; Kato, K.; Onogi, S. *Macromolecules* **1981**, *14*, 354.
(7) Rochefort, W. E.; Smith, G. G.; Rachapudy, H.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1197.
(8) Marin, G.; Menezes, E.; Raju, V. R.; Graessley, W. W. *Rheol. Acta* **1980**, *19*, 462.
(9) Graessley, W. W.; Masuda, T.; Roovers, J. E. L.; Hadjichristidis, N. *Macromolecules* **1976**, *9*, 127.
(10) Kajiura, H.; Ushiyama, Y.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1978**, *11*, 894.
(11) Onogi, S.; Masuda, T.; Kitagawa, K. *Macromolecules* **1970**, *3*, 109.
(12) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980; Chapters 11 and 13.
(13) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(14) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(15) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272.
(16) Ham, J. S. *J. Chem. Phys.* **1957**, *26*, 625.
(17) Doi, M.; Kuzuu, N. Y. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 775.
(18) de Gennes, P. G. *Macromolecules* **1976**, *9*, 587, 594.
(19) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979; Chapters 3 and 8.

Excluded-Volume Effects in Dilute Polymer Solutions. 12. Remarks on François et al.'s Modified Blob Model

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The blob model[1-3] for a linear flexible polymer in a good solvent involves two assumptions:

(1) The mean-square distance $\langle r^2 \rangle$ between a pair of segments separated by t bonds of unit length depends only on t.

(2) The quantity ν, defined by $\langle r^2 \rangle / N_c = (t/N_c)^\nu$, is given, according to the scaling law, by

$$\begin{aligned} \nu &= 1 \quad \text{for } 0 < t < N_c \\ \nu &= 1.2 \quad \text{for } N_c < t \end{aligned} \tag{1}$$

where N_c defines the size of a blob in which Gaussian chain statistics is obeyed.

It is a very difficult task to remove the first assumption, but we may consider various strategies to improve the second assumption. In this paper, we concern ourselves with making some comments on the latter problem.

Theory of François et al.

Very recently, François et al.[4] approximated ν for $t > N_c$ by a continuous function which increases monotonically from 1 to 1.2 as t is increased. In actuality, they considered two forms for this function:

$$\begin{aligned} \nu &= 1 + 0.2[(t/N_c) - 1]/(k - 1) \quad \text{for } N_c < t < kN_c \\ \nu &= 1.2 \quad \text{for } kN_c < t \end{aligned} \tag{2}$$

and

$$\nu = 1.2 - 0.2 \exp\{-c[(t/N_c) - 1]^2\} \quad \text{for } N_c < t \tag{3}$$

where k and c are adjustable parameters. With these ν functions, they calculated $\langle S^2 \rangle$ (the mean-square radius of gyration of the chain) as a function of N (the total number of bonds in the chain) for $k = 15$ and $c = 0.02$ and found for either function that the slope ν_G of the ln $\langle S^2 \rangle$ vs. ln N curve, i.e., $\nu_G \equiv \mathrm{d} \ln \langle S^2 \rangle / \mathrm{d} \ln N$, is unity for $N < N_c$, increases to a maximum higher than 1.2, and decreases asymptotically to the limiting value 1.2 as N is increased indefinitely. This behavior of $\nu_G(N)$ seems

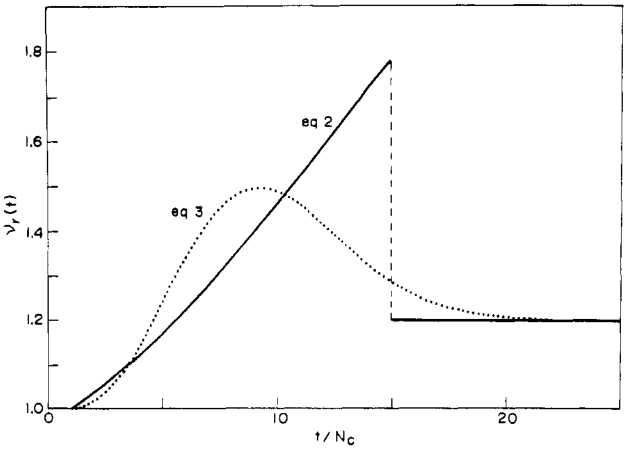

Figure 1. Values of $\nu_r(t)$, i.e., d ln $\langle r^2(t)\rangle$/d ln t, calculated from eq 2 with $k = 15$ (solid line) and those from eq 3 with $c = 0.02$ (dotted line).

anomalous in the sense that it is inconsistent with all the existing theories[5] which predict that ν_G for a linear flexible polymer in a non-Θ solvent varies from 1 to 1.2 in a monotonic fashion with increasing N. The following consideration explains why this "anomaly" occurs in François et al.'s modification of eq 1.

If $\langle r^2\rangle$ is assumed to depend only on t (assumption 1), $\langle S^2\rangle$ can be expressed, in the continuum approximation, by

$$\langle S^2\rangle = \int_0^N N^{-2}(N - t)\langle r^2(t)\rangle \, \mathrm{d}t \qquad (4)$$

From this we get

$$\nu_G = \int_0^N (1 - t/N)\langle r^2\rangle\nu_r(t) \, \mathrm{d}t \Big/ \int_0^N (1 - t/N)\langle r^2\rangle \, \mathrm{d}t \qquad (5)$$

where $\nu_r(t)$ is the slope of the ln $\langle r^2(t)\rangle$ vs. ln t curve:

$$\nu_r(t) \equiv \mathrm{d}\ln\langle r^2(t)\rangle/\mathrm{d}\ln t \qquad (6)$$

The following predictions can be made by eq 5:

(a) If $\nu_r(t)$ stays at values between 1 and 1.2, ν_G also stays in the same range. Thus, in this case, no ν_G value exceeding 1.2 appears for any N.

(b) If $\nu_r(t)$ passes through a maximum higher than 1.2 in the course of changing from 1 to 1.2, there appears a region of N in which ν_G exceeds the asymptotic value 1.2 for infinite N, depending on the form of $\nu_r(t)$ and its maximum height.

Figure 1 shows $\nu_r(t)$ evaluated from eq 2 and 3 for $k = 15$ and $c = 0.02$, the cases studied by François et al. The curves exhibit the feature of case b. Thus, François et al.'s finding of ν_G exceeding 1.2 can be attributed to the fact that their ν functions give ν_r functions which exhibit a maximum distinctly higher than 1.2. The question is whether ν_r functions of actual flexible polymers present such behavior. What we can say at present is that, according to the theories[5] available to date for linear flexible chains, $\nu_r(N)$ (=d ln $\langle R^2\rangle$/d ln N) is a monotonically increasing function of N, where $\langle R^2\rangle$ denotes the mean-square end-to-end distance of the entire chain. We believe that this feature holds for $\nu_r(t)$ as well.

Another Modification

On this belief we propose to represent $\nu_r(t)$ by a function which increases monotonically from 1 to 1.2 with increasing t. As an example of such $\nu_r(t)$ we consider

$$\nu_r(t) = \frac{\mathrm{d}\ln\langle r^2\rangle}{\mathrm{d}\ln t} = 1 + \frac{0.2\exp[\sigma\ln(t/N^*)]}{1 + \exp[\sigma\ln(t/N^*)]} \qquad (7)$$

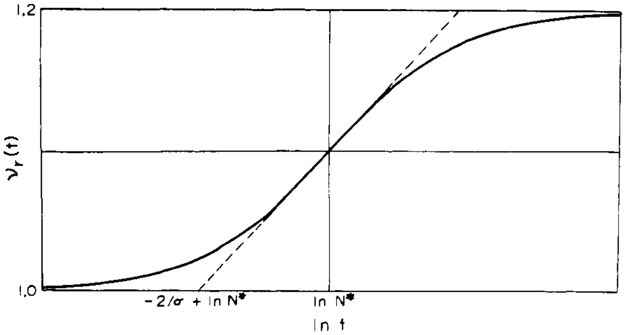

Figure 2. Curve of $\nu_r(t)$ vs. ln t, representing eq 7. The dashed line indicates the tangent of the curve at $t = N^*$.

where σ and N^* are adjustable parameters. As is shown in Figure 2, eq 7 represents a sigmoid curve on the ln t axis. The curve has an inflection point at $t = N^*$ and its slope at this point is proportional to σ. Thus, N^* defines the center of a region of t in which chain statistics changes from the Gaussian to the excluded-volume one and $4\sigma^{-1}$ defines the width of this region. Although the parameter N_c in the simple blob theory[1-3] does not appear here, we may consider N^* to be a quantity corresponding to N_c.

Integration of eq 7 with respect to t gives

$$\langle r^2(t)\rangle = t[1 + (t/N^*)^\sigma]^{0.2/\sigma} \qquad (8)$$

where the condition that $\langle r^2\rangle \to t$ as $t \to 0$ has been used. Substitution of eq 8 into eq 4 yields

$$\langle S^2\rangle = N\int_0^1 x(1 - x)[1 + (Nx/N^*)^\sigma]^{0.2/\sigma} \, \mathrm{d}x \qquad (9)$$

with

$$x = t/N \qquad (10)$$

If N^* is allowed to increase indefinitely, eq 9 gives $\langle S^2\rangle = N/6$, the Gaussian value of $\langle S^2\rangle$. Thus, the case $N^* = \infty$ corresponds to an unperturbed chain. Division of eq 9 by $N/6$ yields

$$\alpha_s^2 = 6\int_0^1 x(1 - x)[1 + (Nx/N^*)^\sigma]^{0.2/\sigma} \, \mathrm{d}x \qquad (11)$$

where α_s denotes the radius expansion factor.

For small N/N^* we may expand eq 11 to give

$$\alpha_s^2 = 1 + \frac{1.2(N^*)^{-\sigma}}{\sigma(\sigma + 2)(\sigma + 3)}N^\sigma + O(N^{2\sigma}) \qquad (12)$$

We force this expansion to agree with the first-order perturbation theory[6] $\alpha_s^2 = 1 + (134/105)z + ...$ by taking into account the fact that the excluded-volume parameter z is proportional to $N^{1/2}$. We then find that $\sigma = {}^1/_2$ and $(N/N^*)^\sigma = 335z/72$. These values allow eq 11 to be expressed in terms of z only. Performing the integration, we get

$$\begin{aligned}\alpha_s^2 = {}& (75/88)[(a + 1)^{12/5}/a^6] \times \\ & [a^4 - (820/459)a^3 + (1050/459)a^2 - (2500/1071)a + \\ & 3125/3213] + (1875/1309a^6)(a^2 - 125/216) \end{aligned} \qquad (13)$$

with

$$a = (335/72)z \qquad (14)$$

For very large z, eq 13 reduces to

$$\alpha_s^2 = 1.576z^{2/5} \qquad (15)$$

Interestingly, the coefficient 1.576 happens to be close to 1.53 deduced by Domb et al.[7-10] from computer analysis of the average dimensions of various lattice chains and also to 1.55, which was assumed by Domb and Barrett[8] in deriving a semiempirical expression for $\alpha_s^2(z)$. Though not shown here, the α_s^2 vs. z relation given by eq 13 agrees closely with the Domb–Barrett equation[8] over the entire range of positive z, a maximum deviation of about 4% occurring at $z \sim 1$. Thus, eq 13 may be used as a substitute for the Domb–Barrett equation.

Finally, we note that eq 9 gives ν_G which increases monotonically from 1 to 1.2 as N is increased. This can be expected, because $\nu_r(t)$ given by eq 7 is a similar function of t.

References and Notes

(1) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P. G. *J. Phys. (Paris)* **1978**, *39*, 77.
(2) Weil, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(3) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(4) François, J.; Schwartz, T.; Weil, G. *Macromolecules* **1980**, *13*, 564.
(5) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(6) Zimm, B. H.; Stockmayer, W. H.; Fixman, M. *J. Chem. Phys.* **1953**, *21*, 1716.
(7) Domb, C.; Barrett, A. J.; Lax, M. *J. Phys. A: Math., Nucl., Gen.* **1973**, *6*, L82.
(8) Domb, C.; Barrett, A. J. *Polymer* **1976**, *17*, 179. Tanaka, G. *Macromolecules* **1980**, *13*, 1513.
(9) Barrett, A. J. *J. Phys. A: Math., Nucl., Gen.* **1976**, *9*, L33.
(10) Lax, M.; Barrett, A. J.; Domb, C. *J. Phys. A: Math., Nucl., Gen.* **1978**, *11*, 361.

Kinetics and Thermodynamics of Cationic Polymerization of 3-Methyltetrahydrofuran

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Introduction

The polymerization of tetrahydrofuran (THF) has become the most comprehensively understood cationic polymerization system, and its kinetic and thermodynamic aspects have been thoroughly investigated.[1-5] However, very few studies have dealt with the polymerization of substituted tetrahydrofurans and, in fact, it was thought, from thermodynamic considerations, that these monomers could not polymerize.[6] For example, thermodynamic calculations show that substitution of hydrogen atoms by methyl groups in heterocyclic compounds renders the free energy of polymerization less negative and, hence, polymerization still more difficult. Thus, although Chiang and Rhodes[7] and Stratmann et al.[8] have accomplished the polymerization and copolymerization of 3-methyltetrahydrofuran (MTHF), attempts to polymerize 2-methyltetrahydrofuran have not been successful.[7,9] Moreover, studies reported on the cationic polymerization of MTHF were qualitative and led to the conclusion that, in sharp contrast with what occurs with THF, transfer reactions are present, with the result that the molecular weight of poly(3-methyltetrahydrofuran) (PMTHF) is much lower than that of PTHF.[7]

In order to gain additional insight into the cationic polymerization of heterocycles it is desirable to investigate from a quantitative point of view the kinetic and the thermodynamic aspects of the polymerization of MTHF. These studies may contribute to a better understanding of the influence of the structure on the ring-opening polymerization of heterocycles. Therefore, this investigation focuses on the polymerization of MTHF in the terms expressed above.

Table I
Influence of Temperature on Equilibrium Monomer Concentration and Propagation Rate Constant

T, °C	M_e, mol/L	$10^4 k_p$, L/(mol s)
−12.5	5.5	2.8
−8.0	6.7	4.1
−4.0	7.8	5.8
0.0	8.8	8.2

Experimental Section

Materials. The monomer 3-methyltetrahydrofuran (Fluka) was refluxed successively over potassium hydroxide and over sodium for several hours. It was further distilled in vacuo into a sodium mirror. Acetyl chloride was distilled under a nitrogen atmosphere immediately before use. Silver hexafluoroantimonate was washed in vacuo with SO_2, filtered, and stored under a nitrogen atmosphere in darkness.

Initiator. The initiator (acetyl hexafluoroantimonate) was prepared by reaction of silver hexafluoroantimonate and acetyl chloride at −78 °C in monomer solution. The silver chloride obtained in the reaction was eliminated by filtration. All these operations were carried out under high vacuum.

Polymerization. The polymerization was carried out in bulk at several temperatures in the range 0 to −13 °C. Thermostatic baths were used in which the temperature precision was ±0.05 °C. Conventional dilatometric techniques were used for the polymerization kinetics. The polymerization reaction was terminated with an aqueous solution of sodium carbonate, and the polymers were extracted with benzene and precipitated with methanol. The polymers were then freeze-dried from benzene.

Characterization. The monomer and the polymer were analyzed by ^1H NMR spectroscopy at 60 MHz (Perkin-Elmer R-12). The spectra were analogous to those reported elsewhere.[7] The number-average molecular weight of the polymer was determined with a Knauer vapor pressure osmometer.

Results and Discussion

As stated above, all of the reactions reported here were homogeneous in that the initiator was soluble in MTHF at the given reaction conditions. Assuming that the initiator is quantitatively converted to the growing species, the general kinetic expression of propagation for the system has the form

$$\ln \frac{M_0 - M_e}{M - M_e} = k_p I_0 t \qquad (1)$$

All measurements of equilibrium monomer concentration (M_e) were performed by two different techniques: (a) by gravimetry and (b) by assuming additivity of the specific volumes of the polymer and of the monomer. Both methods gave similar results and the values obtained for M_e are shown in the second column of Table I.

Kinetic results obtained for four temperatures are shown in Figure 1. Analysis of the results clearly indicates that, within experimental error, the polymerization reaction is first order with respect to monomer. The good fit of the experimental data to eq 1 shows that the initiation rate is fast enough to prevent the detection of any induction time. It can be observed that even at the lower temperature, initiation is rapid and quantitative. In this respect, MTHF behaves like THF.

The propagation rate constants were determined from the slopes of the straight lines of Figure 1 and the results obtained are shown in the last column of Table I. The Arrhenius plot gives an activation enthalpy ($\Delta H_p^\ddagger$) of 12 kcal mol^{-1} and an activation entropy ($\Delta S_p^\ddagger$) of −29 cal mol^{-1} K^{-1}, the value of $\Delta H_p^\ddagger$ being similar to that obtained for the bulk polymerization of THF.[4,5,10-12] This similarity, however, may be fortuitous because it has been established[4,12] that $\Delta H_p^\ddagger$ is dependent on the solvating power of the system.

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