pronounced shear histories in the capillary instruments and it is possible that the η_0 estimates in the two cases are derived by extrapolation from behavior of polymers in different rheological states.

Cantow[45] studied bulk polymerized polystyrenes at 217° with a Haake consistometer. The η_0 values were obtained by plotting log η *vs.* $\dot{\gamma}^{1/3}$. Examination of the data given shows that η_0 varies with $\bar{M}_w$, as in our study and others quoted, but the agreement is not close compared to that found with fractions and blends of fractions.

Schreiber, Bagley, and West[21] compared extrapolated η_0 values and experimental Newtonian viscosities of fractionated linear polyethylenes. Their conclusion that the two parameters agreed well coincides with results of previous work from this laboratory,[15] in which it was reported that the encouraging behavior of polyethylene data did not extend to whole polystyrene polymers. There is thus no disagreement between the present conclusions and those of the cited authors.[21]

Schreiber and coworkers found a 4.22 slope in log $\bar{M}_w$ − log η_0 plots for polyethylenes. Mendelson and coworkers[46] report a 3.52 slope at 150° for a set of polyethylene whole polymers. As mentioned above, Saeda and coworkers find yet different relations for fractionated and whole polyethylenes.

Results of the studies mentioned and the present work point to the conclusion that η_0 is not necessarily a unique function of $\bar{M}_w$ for all molecular weight distributions. A correlation can certainly be established with $\bar{M}_w$ (or any other average molecular weight) over a series of polymers with similar distributions. Such a relation is illustrated in the present article. It is tempting to conclude that $\bar{M}_w$ is definitive in determining η_0 because the log η_0 − log M slope tends to be generally closer to the 3.4 value characteristic of fractions with $\bar{M}_w$ than any other average. In many cases, however, it seems that normalization on an average reflecting higher moments of the distribution of whole polymers may account for the experimental data much better than $\bar{M}_w$, even though the resulting slope deviates from the expected 3.4 value. We suggest that it is most reasonable to expect that no single average molecular weight can determine η_0 of all distributions. The question is certainly not resolved, but the weight of evidence cited tends to support this view.

Acknowledgment. This work was supported by the National Research Council of Canada.

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(46) R. A. Mendelson, W. A. Bowles, and F. C. Finger, *J. Polym. Sci., Part A-2*, 8, 127 (1970).

Consequences of the Excluded Volume Effect on the Rate of Reactions Involving Two Randomly Coiled Polymer Chains. I. Theoretical Study[1]

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ABSTRACT: Two theoretical models were explored to assess the effect of the attachment of two chemically interacting groups to the backbone of polymer chains on the rate constant characterizing their reaction. In the first, the polymers were represented by two spherical clouds with a uniform chain segment density. In the second, the number of nonintersecting configurations of the reagent chains and of the transition state in which they are linked by a bridge were estimated by Monte Carlo calculations and the resistance to coil interpenetration was estimated from the decrease in the number of these configurations accompanying the formation of the transition state. This approach demonstrates that the rate constant depends on the location along the polymer chain at which the reactive group is attached, but the results of the computation are not easily compared with experimental data.

The very large second virial coefficient A_2 characterizing flexible chain polymers in good solvent media bears evidence to the difficulty for any mutual interpenetration of the randomly coiled chains. It should be noted, however, that the single parameter A_2 cannot describe $\Delta G(r)$, the dependence of the change in free energy on the separation between the centers of gravity of two molecular coils. In particular, the vanishing A_2 in Θ solvents which requires $\int\{1 - \exp[-\Delta G(r)/kT]\}4\pi r^2 \mathrm{d}r = 0$ does not necessarily mean that $\Delta G(r) = 0$ for all values or r. It is quite possible that the mutually excluded volume between two chain molecules vanishes in Θ media because $\Delta G(r)$ changes sign in a manner such that positive and negative contributions to the cluster integral compensate each other and computer simulation studies seem to indicate that this is, indeed, the case.[3a]

It is, therefore, desirable to search for alternative methods which could characterize the mutual interpenetration of molecular coils. Some years ago, Morawetz and Song[3b] suggested that one could use for this purpose studies of reaction rates involving dilute solutions containing two similar copolymers carrying a small number of reactive and catalytic chain substituents, respectively. If the coils have difficulty penetrating one another, a fraction of the interacting groups will be shielded in the interior of the coils at any given time. The reaction of the two polymers was, therefore, expected to be characterized by a second-

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(2) (a) From the Polytechnic Institute of Brooklyn, N. Y. (b) From New York University, New York, N. Y.

(3) (a) R. Kirste, private communication; (b) H. Morawetz and W. R. Song, *J. Amer. Chem. Soc.*, 88, 5714 (1966).

order rate constant k_2 smaller than the k_2^0 corresponding to an analogous reaction of low molecular weight species. Moreover, since the fraction of the chain near the "surface" of the coil would decrease with increasing chain length, k_2/k_2^0 was expected to decline with increasing length of the polymer chains. Experimental data failed to reveal such a "kinetic excluded volume effect" and no explanation could be suggested to account for this result.

An attempt to characterize the mutual interpenetration of molecular coils by the chemical interaction of groups attached to the polymer was also reported by Vollmert and Stutz.[4] In their system a cross-linked network formed during the reaction but a large fraction of the reactive groups remained unaltered when the reaction had gone to completion. Vollmert and Stutz concluded from this that the interpenetration of the molecular coils is quite small, but their reasoning is faulty since restrictions on the accessibility of reactive groups to each other after the formation of a chain network need not be related to the interpenetration of molecular coils in solution.

On the other hand, a serious discrepancy exists between the results obtained by Morawetz and Song[3] and those reported by Wetmur and Davidson[5] who studied the kinetics of the renaturation of DNA. The rate-determining step in this process is the "nucleation" of the double helix by association of two corresponding nucleotide bases in the two polynucleotide strands. According to Wetmur and Davidson, the rate constant for this nucleation is inversely proportional to the square root of the molecular weight of the DNA. This was interpreted as reflecting the inability of the molecular coils to interpenetrate so that only the portion of the chains close to the "surface" of the molecular coils would be accessible to chemical interactions. The present investigation was undertaken in an attempt to explore theoretical approaches to the "kinetic excluded volume effect."

The two models described below are based on the following assumptions. (a) The solution of the interacting polymers is so dilute that only binary interactions need to be considered in treating the probability of interpenetration of the molecular coils. (b) The rate of conformational transitions is rapid compared to the rate of the chemical reaction under investigation. (This condition would be expected to be amply satisfied for reactions with half-lives of the order of minutes, since hindered rotation around covalent bonds in the backbone of polymer chains seems to take place at rates comparable to those in their low molecular weight analogs[6a-c]). (c) The energy of activation of the reaction under consideration is sufficiently high so that the rate of diffusion of the reagents is not a limiting factor for the reaction rate.[6d]

First Model: Interpenetrating Spherical Clouds of Chain Segments. We consider the interaction of two polymers with the same molecular volume v_2 which are identical except for the attachment of a small number of reactive groups to polymer A and a small number of catalytic groups to polymer B. In view of the similarity of the two polymers, they may be characterized by the same polymer-solvent interaction parameter χ and the polymer-polymer interaction parameter χ_{AB} may be assumed to be zero. The model represents the polymer coils as spheres with a volume $v_e = (4/3)\pi R_e^3$ containing a uniform density of chain segments, and each reactive or catalytic group is given the same probability of being located at any position within the equivalent sphere. The reaction under consideration can take place only on collision of the reactive and catalytic groups requiring an interpenetration of the spheres representing polymers A and B.

If a solution with a volume V contains one polymer chain A and one polymer chain B the probability W_0 that a reactive group is, at any given time, within a volume v_j jointly occupied by the two interpenetrating spheres is

$$W_0 = \frac{1}{v_e} \frac{\int_V v_j(r)\ \exp[-\Delta G(r)/kT]4\pi r^2 \mathrm{d}r}{\int_V \exp[-\Delta G(r)/kT]4\pi r^2 \mathrm{d}r} \qquad (1)$$

where r is the distance between the centers of A and B and $\Delta G(r)$ is the increase in the free energy resulting from the interpenetration of the two spheres. If the system contains N_B chains of type B and if only binary interactions need to be considered, this probability becomes $W = N_B W_0$. Whenever a reactive group finds itself within a volume jointly occupied by a sphere A and B, it is exposed to a local concentration $(C_B)_l$ of catalytic groups which is related to their stoichiometric concentration C_B by $(C_B)_l = C_B(V/N_B v_e)$. The second-order rate constant k_2 involving interacting groups attached to the polymer chains and k_2^0, characterizing the interaction of analogous low molecular weight reagents should then be related by

$$k_2/k_2^0 = (C_B)_l W/C_B = (V/v_e) W_0 \qquad (2)$$

The increase in free energy resulting from the interpenetration of the two equivalent spheres with a uniform density of chain segments is $\Delta G(r) = 2kTv_j(r)[½ - \chi](v_2/v_e)^2/v_1$, where v_1 is the molecular volume of the solvent.[7a] Since $\Delta G(r) = 0$ for $r > 2R_e$ and the solution is assumed to be dilute, the denominator in eq 1 may be approximated by V. Introducing $y = r/2R_e$, we have $v_j = v_e(y^3 - 3y + 2)/2$ for $y < 1$ and $v_j = 0$ for $y \geq 1$, so that we obtain from eq 1 and 2

$$k_2/k_2^0 = 12\int_0^1 (y^5 - 3y^3 + 2y^2) \times \exp[-Z(y^3 - 3y + 2)/2]\mathrm{d}y$$

$$Z = (v_2^2/v_1 v_e)(½ - \chi) \qquad (3)$$

For $Z \ll 1$, eq 3 leads to $k_2/k_2^0 = 1 - (68/105)Z + \ldots$. Thus, the model predicts $k_2 = k_2^0$ for Θ solvents. Values for k_2/k_2^0 computed for $Z > 1$ are plotted in Figure 1; for long chains, k_2/k_2^0 becomes proportional to $Z^{-1.37}$. Since v_e is proportional to $v_2^{1.8}$ for long chains in good solvent media,[7b] we have then k_2/k_2^0 inversely proportional to the 0.27 power of the chain length. To relate the parameter Z to experimentally observable quantities, it is convenient to use the relation

$$[\eta] = 0.025 v_e v_{sp}/v_2 \qquad (4)$$

where $[\eta]$ is the intrinsic viscosity in deciliters per gram and v_{sp} is the specific volume of the polymer. We have then for a polymer with a molecular weight M_2 and a solvent with a molar volume V_1

$$Z = (0.025 M_2 v_{sp}^2/V_1[\eta])(1/2 - \chi) \qquad (5)$$

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(5) J. G. Wetmur and N. Davidson, *J. Mol. Biol.*, **31**, 349 (1968).

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(7) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, (a) p 524; (b) p 600.

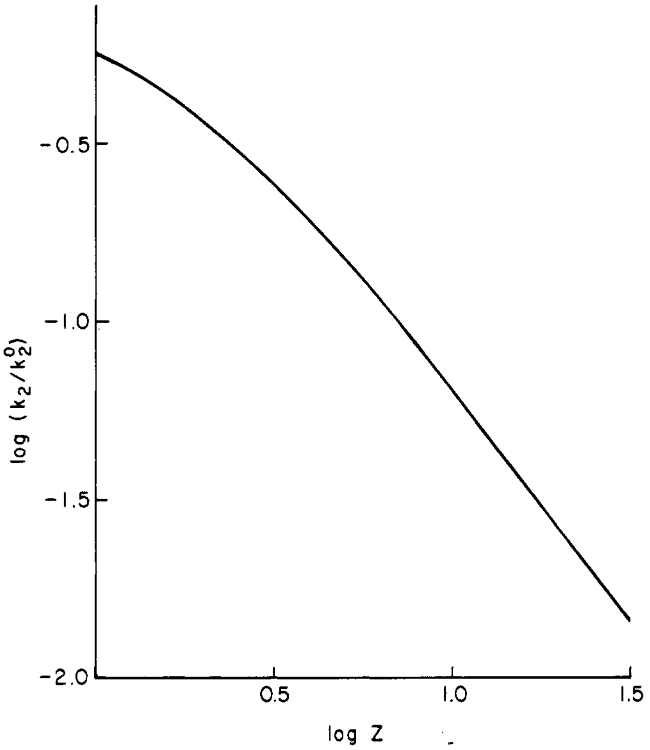

Figure 1. Estimates of k_2/k_2^0 based on the "interpenetrating spherical cloud" model.

Second Model: Monte Carlo Calculation of the Configurational Entropy of Activation. Consider two randomly coiled chain molecules with a reactive and a catalytically active substituent attached to the central segments of the two chains. When these substituents interact to form the transition state complex, the two chains are joined by a link the length of which depends on the spacing of the interacting groups from the chain backbone. The analysis of the "kinetic excluded volume effect" from the point of view of the theory of absolute reaction rates involves then the relations

$$k_2 = \kappa \frac{kT}{h} \frac{Q_{AB}^*}{Q_A Q_B} e^{-\Delta E_0/kT}$$

$$k_2^0 = \kappa \frac{kT}{h} \frac{q_{AB}^*}{q_A q_B} e^{-\Delta E_0'/kT} \tag{6}$$

where κ is the transmission coefficient, kT has the usual significance, h is Planck's constant, Q_A, Q_B, and Q_{AB}^* are partition functions of the polymeric reactants and their transition state complex, ΔE_0 is the difference between the zero-point energy of the polymeric reactants and their transition state, while q_A, q_B, q_{AB}^*, and $\Delta E_0'$ are the corresponding quantities for the low molecular weight analogs. It is reasonable to assume $\Delta E_0 = \Delta E_0'$. It is also convenient to represent the partition functions of the polymeric species as a product of two factors, one characterizing the side chain with the reactive or catalytic group (considered identical with the low molecular weight analog) the other the chain molecule to which this side chain is appended. Thus, setting $Q_A = \bar{Q}_A q_A$, $Q_B = \bar{Q}_B q_B$, and $Q_{AB}^* = \bar{Q}_{AB}^* q_{AB}^*$, we obtain

$$k_2/k_2^0 = \bar{Q}_{AB}^*/\bar{Q}_A \bar{Q}_B \tag{7}$$

We may assume that the translational and rotational contributions to $\bar{Q}_{AB}^*/\bar{Q}_A\bar{Q}_B$ are negligible. Similarly, vibrational modes of the two chains should be unaffected by their junction. Thus, if we assume the polymer solution to be thermoneutral and disregard the difference in energy of the various accessible conformations

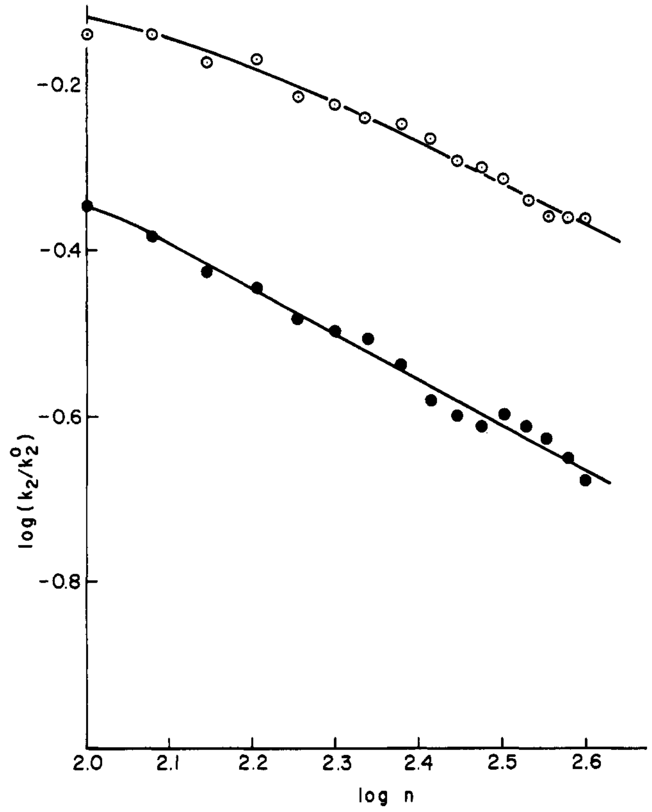

Figure 2. Estimates of k_2/k_2^0 based on Monte Carlo calculations of nonintersecting reagent chains and of their transition state: (○) connecting link of 16 atoms in the transition state; (●) connecting link of 8 atoms in the transition state.

$$Q_{AB}^*/Q_A Q_B = \Omega_{AB}/\Omega_A \Omega_B \tag{8}$$

where the Ω terms stand for the number of conformations of the two linear chains and the species formed when these chains are connected by a bridge. If we place a molecular chain backbone consisting of n C–C covalent bonds in which only staggered conformations are allowed on a diamond lattice, $\Omega(n) = 3^{(n-1)} f(n)$ where $f(n)$ is the fraction of chains which do not lead to multiple occupancy of a lattice point. Thus, if chains A and B with n bonds each, are joined to form an AB structure

$$Q_{AB}^*/Q_A Q_B = f_{AB}(2n)/f_A^2(n) = k_2/k_2^0 \tag{9}$$

To determine the fraction $f_{AB}(2n)$ and $f_A(n)$ of nonintersecting chains, the Monte Carlo method of Wall and Erpenbeck[8] was modified to generate on a diamond lattice two types of chains. The A chains (or B chains) had a side chain of four or eight atoms in the all-trans conformation representing the reactive or catalytic chain substituent, attached to the central segment of the chain. The AB chains, representing the transition state complex, had a bridge of 8 or 16 atoms, in the all-trans conformation, joining the central segments of the two branches. The results of the calculations are shown on Figure 2 as a plot of log (k_2/k_2^0) against log n. For long chains, they are represented by log $(k_2/k_2^0) = 0.79 - 0.56$ log n and by log $(k_2/k_2^0) = 0.84 - 0.48$ log n for bridges of 8 and 16 atoms, respectively.

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(8) F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 634 (1959).

So far, we have only considered the interaction of groups attached to the central segment of two linear chain molecules. If the interacting groups are appended to the ends of two polymer chains, each with n atoms in the chain backbone, then the transition state complex will also be a linear chain and the above approach leads to

$$k_2/k_2^0 = f_A(2n)/f_A^2(n) \qquad (10)$$

According to Fisher and Sykes[9] $f_A(n)$ is of the form

$$f_A(n) = Cn^{\alpha} \exp(-\lambda n) \qquad (11)$$

and using this expression in eq 11 we obtain

$$k_2/k_2^0 = f_A(2n)/f_A^2(n) = (2^{\alpha}/C)n^{-\alpha}$$

With values of C and α obtained by Gans,[10] log $(k_2/k_2^0) = 0.07 - 0.154 \log n$. Thus, the restraint to a reaction involving groups attached to the ends of flexible chains would be expected to be much less severe than for the interaction of groups appended to the central segments of the chains. We also arrive at the conclusion that with chains carrying interacting groups distributed at random along their length, the rate constant should exhibit a dispersion which increases rather rapidly with chain length.

Our computations suggest that $f_{AB}(n)$ is, in analogy to $f_A(n)$, of the form $f_{AB}(n) = C'n^{\alpha'} \exp(-\lambda' n)$, where λ and λ' are indistinguishable from each other. The coefficient of the log n term in $f_{AB}(2n)/f_A^2(n)$ has then the significance of $\alpha' - 2\alpha$. This yields for α' values of -0.25 and -0.17 for AB chains with 8 and 16 atom bridges, in contrast to the positive values of α characterizing linear chains.

Discussion

The first model discussed above contains the implied assumption that the lifetime of states in which two of the equivalent spheres overlap is short compared to the experimental time scale. If for instance, such a state had a duration long compared to $1/k_2^0(C_B)_i$, some of this overlap time would be "wasted" since the catalytic groups would have no reactive groups to attack. Unfortunately, it is difficult to see at this stage how the lifetime of chain entanglements can be assessed and the reliability of the above assumption remains, therefore, uncertain.

The interpenetrating sphere model is similar to that used by Wetmur[11] who assumed a spherically symmetrical Gaussian distribution of chain segment densities. In Wetmur's result k_2/k_2^0 for the interaction of two chain reagents with a contour length L is a function of $Q = 54(\pi/2)^{1/2}L^{1/2}a^2/b^{5/2}$, where b and a are the length and diameter of a cylinder with the physically excluded volume of a chain segment. The parameter Q is analogous to our Z. If we set $\pi a^2L^2/b = (v_2^2/v_1)(\frac{1}{2} - \chi)$ and take as the radius of the equivalent sphere the root-mean-square radius of gyration of the chain, *i.e.*, $v_e = (\frac{4}{3})\pi(Lb/6)^{3/2}$, we obtain $Q \approx 6Z$. Our result leads then to a considerably slower decay of k_2/k_2^0 with an increasing excluded volume than obtained by Wetmur. For instance, he predicted $k_2/k_2^0 = 0.06$ for $Q = 18$, while our computation yields $k_2/k_2^0 = 0.25$ for $Z = 3$. At any rate, the Gaussian distribution of chain segments is inconsistent with the existence of an excluded volume effect. We also feel that it is desirable to specify the parameter governing k_2/k_2^0 in terms of the molecular volume of the solvent, since the excluded volume effect decreases with increasing v_1 and is believed to vanish when v_1 becomes very large.

The formulation of the problem of a bimolecular reaction involving chain molecules in terms of the partition functions of the reagent chains and their transition state complex is much more realistic than any model in which the chains are represented by spherically symmetrical chain segment densities. This approach illustrates the importance of the spacing of the interacting chemical groups from the backbone of the chain and it shows also that the magnitude of the "kinetic excluded volume effect" should depend on the location of the attachment of the reactive group along the length of the chain molecule. Unfortunately, the simple lattice model used for the Monte Carlo calculations is too unrealistic to allow a comparison of calculated results with observations on real chains. In particular: (a) placement of the chains on a diamond lattice with equal probabilities assigned to trans and gauche bonds exaggerates the flexibility of the chain. (b) Since the volume of the side chains and the effect of solvent–solute interaction are not taken into account, the characteristic dependence of the excluded volume effect on the nature of the chain and on the properties of the solvent medium are completely obscured. The usefulness of the model is, therefore, limited at present to the illustration of basic principles.

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