

Effect of Long Branches on the Flow Properties of Polymers

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The flow behavior of macromolecular liquids is highly sensitive to large-scale molecular structure.¹ Moreover, such structural effects are remarkably similar among different polymeric species, suggesting an underlying generality of some theoretical interest. Effects of structure are also important from a practical standpoint. The melt-processing properties of commercial polymers, for example, can be adjusted over wide ranges by alterations in the average molecular weight, molecular weight distribution, and frequency of long branches in the molecules. Our purpose here is to review current understanding about the influence of long branches.

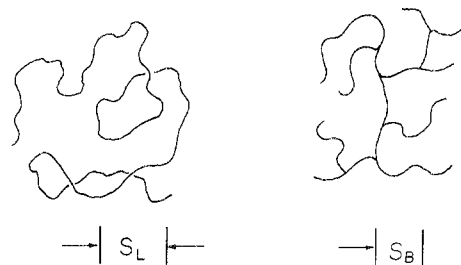
Linear polymers of the same species differ from one another in only one large-scale feature, the chain length or molecular weight. The viscoelastic parameters associated with flow depend systematically on molecular weight. At high concentrations these relationships fit a simple pattern. The viscosity, for example, can be factored into two terms,² one a local friction coefficient which depends only on temperature and the chemical identity and proportions of polymer and solvent, the other a structure factor which depends only on chain length and the volume fraction of polymer in the system. The empirical form of the structure factor is virtually the same for all flexible linear polymers. Molecular theories of flow for random coils and ideas about chain-entanglement interactions play important roles in its interpretation. Thus, the effects of Brownian motion and hydrodynamic forces on flexible chains in a viscous medium are represented by the Rouse model,^{1,3} and additional forces associated with a rope-like coupling between neighboring chains are postulated in concentrated systems where the coils overlap extensively.^{1,2,4} The structure factors of other viscoelastic parameters are interpreted similarly.⁴

When the molecules are branched, the behavior varies with the number, location, and length of the branches. Some quite striking differences from linear polymer behavior are found, especially when entanglement interactions are important. The picture is far from complete, but a partial pattern exists and some tentative theories are beginning to appear. The discussion here will deal only with flexible chains which have long branches but no macrocyclic rings, and with concentrations high enough for the individual molecular domains to overlap extensively. Thus the molecules assume random flight configurations, although possibly perturbed somewhat by crowding near the branch

points. Also, the fraction of mers which serve as branch points is small, so the average neighborhood of the mers, and therefore the local frictional coefficient, should be virtually the same for linear and branched molecules at the same concentration.² We will discuss only systems of narrow molecular weight distribution. The effects of branching reactions during polymerization on molecular weight distribution as well as methods for characterizing branched molecules have been reviewed recently.⁵

Observations on the Flow Behavior of Branched Polymers

Consider the solution viscosities for two polymers of the same species and total molecular weight M , one with long branches and the other linear, at the same concentration c (g/mL). We will designate the viscosity of the branched system $\eta_B(c, M)$ and of the linear system $\eta_L(c, M)$. The branched polymer will have a smaller radius of gyration, S , and a smaller intrinsic viscosity,



$[\eta]$, in the solvent. At low and intermediate concentrations $\eta_B(c, M)$ will be less than $\eta_L(c, M)$. The ratio of viscosities, η_B/η_L , depends primarily on the ratio of radii of gyration, S_B/S_L . Specific details of the branching structure thus affect the viscosity in a simple but rather indirect way, i.e., only through their influence on the mean coil size. The value of η_B can in fact be estimated fairly well from size considerations and data on linear polymers alone. For example, at moderate concentrations $\eta_B(c, M)$ is approximately $\eta_L(c, gM)$,^{2,6} in which

$$g = S_B^2/S_L^2 \quad (1)$$

The parameter g can be either measured by appropriate dilute solution methods^{7,8} or estimated from the structure of the branched molecules by random flight calculations.^{9,10}

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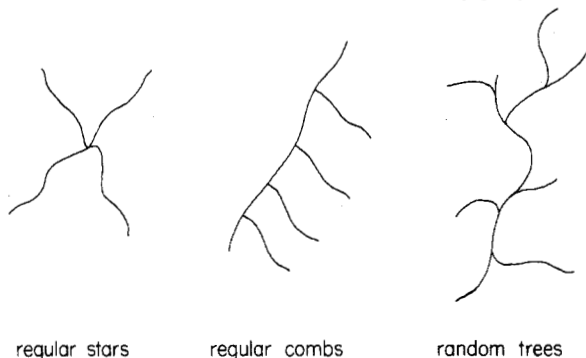
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William W. Graessley was born in Muskegon, Mich., in 1933. He received undergraduate degrees in chemistry and chemical engineering at University of Michigan and, as a NSF graduate fellow, obtained his Ph.D. in chemical engineering from the same institution in 1960. After spending 4 years with Air Reduction Company, he joined the faculty at Northwestern University where he is now Professor in the Chemical Engineering and Materials Science Departments. His research is concentrated in the polymer field and includes work on molecular aspects of rheology, polymerization, molecular characterization, and the structure and properties of rubber networks.

In some cases this simple pattern is maintained at all concentrations, persisting even to the undiluted state. In others, η_B/η_L begins to increase rapidly at high concentrations: η_B may overtake η_L and then exceed it, sometimes by orders of magnitude. The concentration where enhancement begins to appear depends on the structure of the branched polymer, and particularly on the length of the branches. Departures from the pattern of size-dominated viscosity dependence are characterized by a viscosity enhancement factor, Γ_1 , such that²

$$\eta_B(c, M) = \eta_L(c, gM) \Gamma_1 \quad (2)$$

Enhancement has been observed in several families of branch connectivity. Most branching polymeriza-



tions yield a broad distribution of structures,⁵ typically with random tree connectivity. Enhancement has been observed in such polymers.¹¹⁻¹⁴ Fractionation and determination of the fraction structures are required to provide samples for quantitative studies. Quite useful information has been obtained from such fractions,¹⁵⁻¹⁸ but the separation procedures are tedious and difficult, and the resulting samples are small and undoubtedly still contain a range of structures. Alternatively, uniform linear strands can be prepared separately and joined in a controlled manner, yielding relatively large samples of rather uniform structure. Regular stars and combs of several polymers made in this way have been studied.^{6,19-27}

Much of the following discussion will deal with regular stars. They represent the simplest case of branching, a single branch point and only two structural

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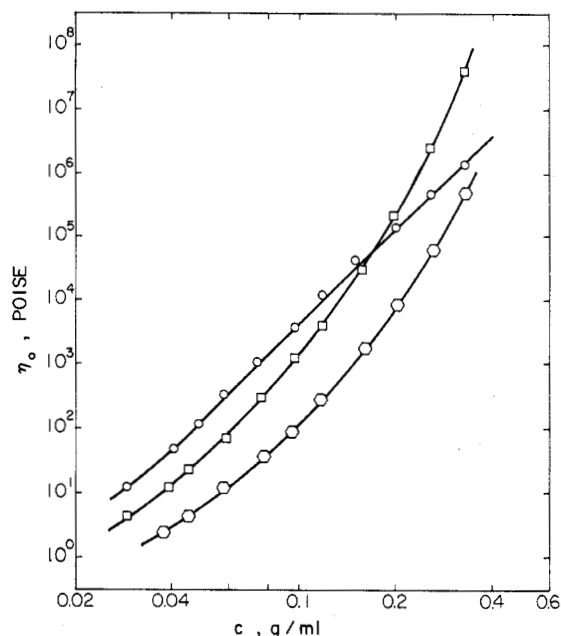


Figure 1. Zero-shear viscosity vs. concentration for linear and star-branched polyisoprenes of similar molecular weight. The linear polymer (O) has a molecular weight (\bar{M}_w) of 1.61×10^6 ; the four-arm star (\square) has $\bar{M}_w = 1.95 \times 10^6$; the six-arm star (hexagon) has $\bar{M}_w = 1.45 \times 10^6$. The diluent is tetradecane; measurements were made at 25 °C.

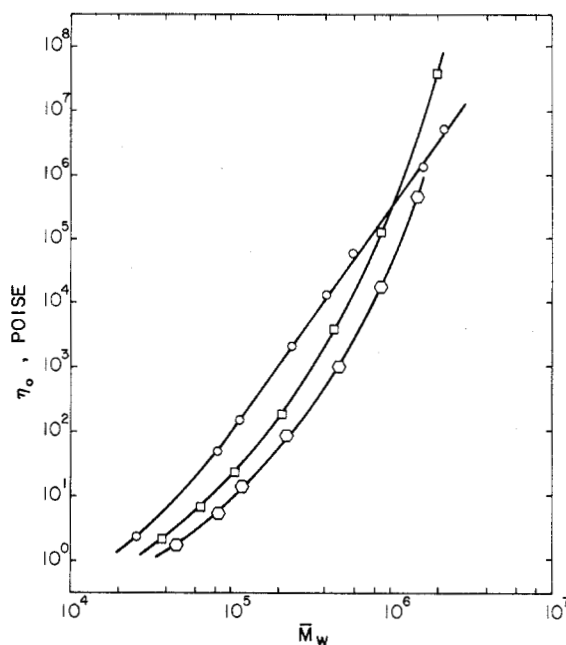


Figure 2. Zero-shear viscosity vs. molecular weight for linear and star-branched polyisoprenes at similar concentrations. The concentrations for all samples are approximately 0.33 g/cm³. Conditions and the designations for linear, four-arm star, and six-arm star polymers are given in the caption of Figure 1.

parameters: the number of arms, f , and the branch molecular weight, $M_b = M/f$. The theoretical expression for g in regular stars is given by eq 3.⁹

$$g = \frac{3f - 2}{f^2} \quad (3)$$

The viscosities of linear, four-star, and six-star polyisoprene solutions in tetradecane at 25 °C are shown in Figure 1 and 2 as functions of concentration and molecular weight.⁶ The weight-average molecular

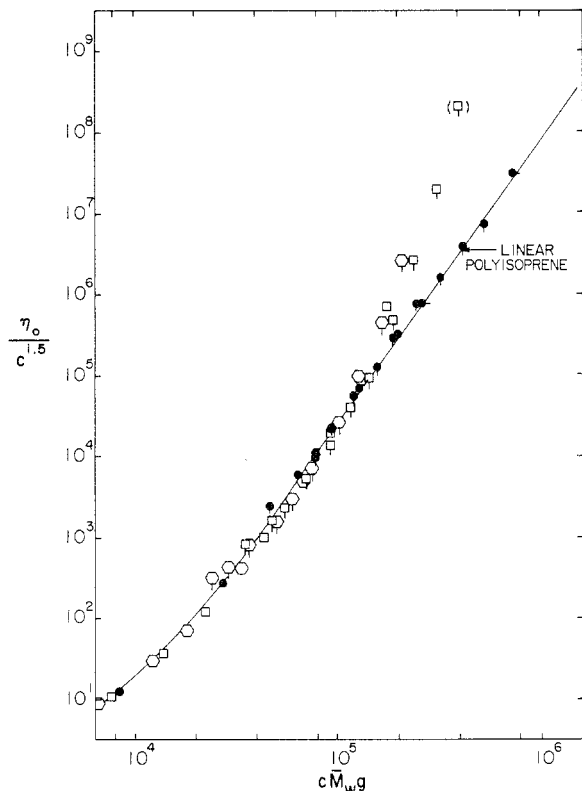


Figure 3. Viscosity data for linear and star-branched polyisoprenes of various molecular weights and concentrations in tetradecane at 25 °C. Behavior of linear polyisoprenes was found to correlate with the form $\eta_0 = Kc^{1.5}(c\bar{M}_w)^a$; \bar{M}_w was replaced by $g\bar{M}_w$ for the branched polymers. Solid circles (●) indicate linear polymers; open symbols indicate star-branched samples.

weight, \bar{M}_w , obtained by light scattering, is used in all the figures. In Figure 3 these data are plotted with $g\bar{M}_w$ in place of \bar{M}_w to adjust for the coil size effect. Values of Γ_1 obtained from the figure range from near unity for small values of $cg\bar{M}_w$ to approximately 100 for the highest.

Other flow properties show parallel effects of branching. Polymer solutions are viscoelastic, and an important parameter governing elastic response is J_e° , the steady-state recoverable shear compliance.¹ Broadly speaking, J_e° characterizes the elastic recoil that occurs when the external forces producing a steady-state flow are suddenly removed. In steady shear flow the shear stress, σ , and the amount of shear recovery, γ_r , are related by $\gamma_r = J_e^\circ \sigma$. One expects to find smaller values of J_e° for branched polymers. For example, the theoretical expression for random flight chains is given by eq 4,²⁸ in which R is the gas constant, T is the absolute

$$J_e^\circ = \frac{2}{5} \frac{g_2 \bar{M}}{cRT} \quad (4)$$

temperature, and g_2 , like g , is unity for linear chains and less than unity for branched chains. For regular stars²⁸

$$g_2 = \frac{15f - 14}{(3f - 2)^2} \quad (5)$$

In dilute solutions J_e° for branched polymers is indeed smaller than for linear polymers of the same molecular weight.²⁹ Figure 4 shows that it also tends to be smaller

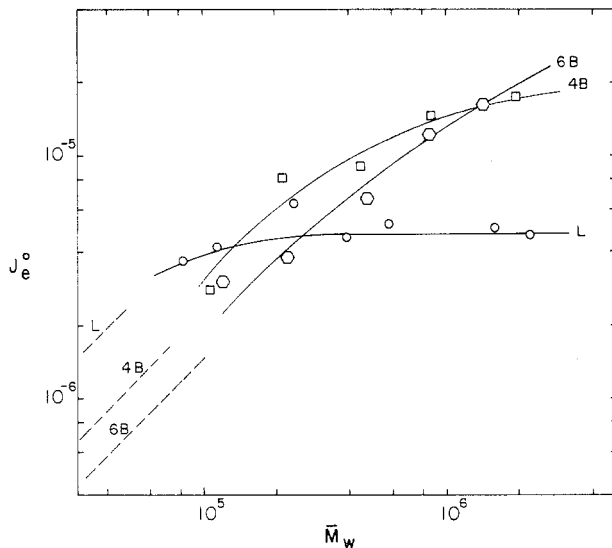


Figure 4. Recoverable compliance vs. molecular weight for linear and star-branched polyisoprenes at a concentration of approximately 0.33 g/cm³ in tetradecane at 25 °C. The symbols are those in Figure 1. The dashed lines indicate the predictions of eq 4 for linear, four-arm star, and six-arm star polymers.

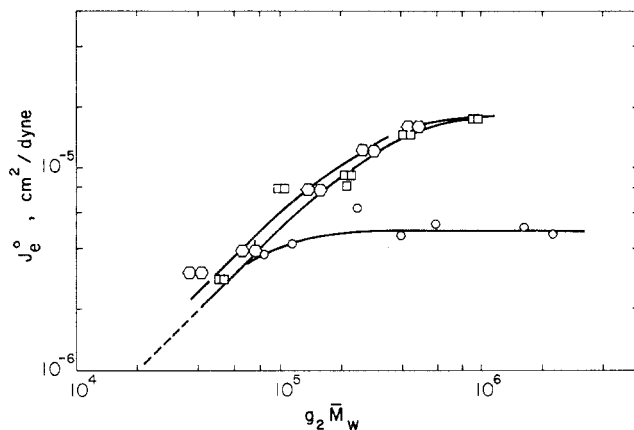


Figure 5. Recoverable compliances from Figure 4 as a function of $g_2\bar{M}_w$. The dashed line is the prediction of eq 4.

for low molecular weight stars even at high concentrations. However, J_e° becomes larger for branched molecules at high molecular weight. Although the data merge satisfactorily for small values of $g_2\bar{M}_w$ in Figure 5, $(J_e^\circ)_B$ is systematically higher for large values. The concentration dependence is more complicated,^{6,30} but, as in the case of viscosity, a pattern of enhancement for polymers with long branches at high concentrations is clearly indicated. An enhancement factor analogous to Γ_1 can be defined for the compliance:

$$[J_e^\circ(c, M)]_B = [J_e^\circ(c, g, M)]_L \Gamma_2 \quad (6)$$

Curiously, compliance enhancement appears at lower concentrations than viscosity enhancement and may already be large even when Γ_1 is still unity.^{6,22,23}

The earlier discussion of viscosity dealt only with the limiting value at low shear rates, η_0 . The viscosity of polymer systems decreases with increasing shear rate $\dot{\gamma}$ beyond a characteristic value $\dot{\gamma}_0$. The values of η_0 , J_e° , and $\dot{\gamma}_0$ for any system are closely related. If $\dot{\gamma}_0$ is defined for convenience as the shear rate at which η has

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fallen to $0.8\eta_0$, then for linear polymers of narrow distribution⁴

$$\eta_0 J_e^\circ \dot{\gamma}_0 = 0.6 \pm 0.2 \quad (7)$$

This simple relationship appears to be unchanged by the presence of branching.⁶ Thus, enhanced values of J_e° produce unusually small values of $\dot{\gamma}_0$ and an early onset of shear rate dependence in the viscosity. As a result, a branched polymer may have both a larger viscosity at low shear rates and a smaller viscosity at high shear rates than a linear polymer of comparable molecular weight.^{6,20}

The enhancement of η_0 and J_e° , although certainly unanticipated, are not necessarily in conflict with ideas about flow behavior which have evolved from the analysis of data on linear polymers. Thus it seems reasonable to regard Γ_1 and Γ_2 simply as modifications of the structure factors for linear polymers whose empirical dependence on concentration and branching structure must be determined and explained. Some progress along these lines for Γ_1 is described below. However, certain other effects have been observed which are more disquieting.

For example, the temperature coefficient of viscosity, normally regarded as a property which is solely determined by local chain structure,¹ appears to be influenced by long branches in some polymers. The flow activation energy, E_a , for branched polyethylene, both unfractionated commercial polymers and their fractions, is about 12–14 kcal, while that for linear polyethylene is much lower, approximately 6.5 kcal.¹⁶ These polymers also differ in local structure, the branched variety containing 10–20 short branches (mostly butyl groups³¹) per 1000 main chain atoms in addition to long branches. However, it does not appear possible to account for the difference in E_a on the basis of the short branches alone.³² This conclusion is supported in recent work by Arnett and Thomas on linear and three-arm hydrogenated polybutadienes.²⁷ Here the polymers have the same local structure, probably rather similar to that of branched polyethylene, and yet E_a for the star is roughly twice that for the linear samples (14 kcal vs. 7 kcal). Substantial departures from time-temperature superposition have also been observed in the linear viscoelastic properties of the star sample.³³ It thus seems inescapable that the temperature coefficient can depend on large-scale structure. On the other hand, the effect has only been observed in one other polymer, poly(vinyl acetate),⁶ and for that case the increase in E_a is rather small (12 kcal increased to 15 kcal). Star polymers of polybutadiene itself appear to have the same temperature coefficient as linear polybutadienes.²⁰

As a second example, in some branched polymers the deformation history has an unusual effect on subsequent flow behavior. Pritchard and Wissbrun¹³ found that flow through a capillary changes the flow properties of branched poly(oxyethylene). The properties change very little with extended rest in the melt state, but they are restored almost completely with dissolution and reprecipitation. Similar effects unrelated to chemical change of structure were noted earlier in

branched polyethylene by Howells and Benbow³⁴ and more recently by Fujiki.³⁵

It is not known how general the temperature coefficient and flow history effects are. Both are observed in crystallizable polymers (aside from the small effect of branching on E_a in poly(vinyl acetate)) with enhanced viscosities. However, the data were gathered well above the melting temperature, so it is difficult to see how crystallizability could be a factor. They could signify some qualitative difference from linear polymers in the molecular mechanism of flow.

All these effects have considerable practical importance. Branching provides a way to achieve flow properties (and therefore commercial processing characteristics) which cannot be obtained with linear chains alone. They are also important theoretically in that they are always found in close association with chain entanglement interactions. Current understanding of entanglement is somewhat limited even in linear polymers, and branching provides an additional structural probe. The following sections review the present status of the theory of entanglements, summarize the progress in relating viscosity enhancement to structure, and note some possible directions for further work.

Chain Entanglement

In undiluted melts of linear polymers the zero shear viscosity and recoverable compliance depend on molecular weight distribution and temperature. For temperatures well above the glass transition and polymers with narrow distributions this behavior can be expressed by eq 8 and 9, in which ρ is the density,

$$\eta_0 = K(T)\rho M \left(\frac{M}{M_c}\right)^a \quad (8)$$

$$a = 0 \text{ for } M < M_c$$

$$a = 2.4\text{--}2.6 \text{ for } M > M_c$$

$$J_e^\circ = \frac{2}{5} \frac{M}{\rho RT} \left(\frac{M}{M_c'}\right)^{a'} \quad (9)$$

$$a' = 0 \text{ for } M < M_c'$$

$$a' = -1 \text{ for } M > M_c'$$

M_c and M_c' are characteristic molecular weights of the species, and $K(T)$ is proportional to the local friction coefficient.

At high molecular weights ($M > M_c$) the mechanical properties for short times after a suddenly imposed deformation resemble those of a rubber network. For simple shear deformation the ratio of shear stress to strain in this region of response is the plateau shear modulus $G_N^\circ(1)$. The plateau modulus is independent of molecular weight. Rubber elasticity theory can be used to calculate an apparent molecular weight of the network strands, M_e , from the measured value of G_N° .

$$G_N^\circ = \left(\frac{\rho}{M_e}\right) RT = \frac{\rho RT}{M} \left(\frac{M}{M_e}\right) \quad (10)$$

Values of M_e , M_c , and M_c' for several common polymers are given in Table I. Their relative magnitudes are indicated in Figure 6.

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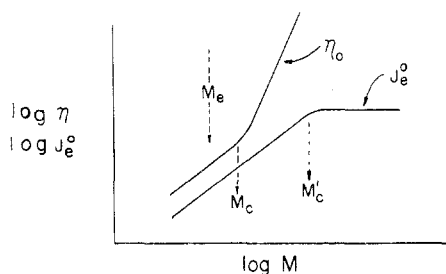


Figure 6.

These properties, primarily the network-like response to sudden deformations for $M > M_c$ and the accompanying increased dependence of viscosity on molecular weight in steady flows, are the basis for the entanglement hypothesis. It is well established that the chains in concentrated solutions and melts assume random coil configurations.³⁶ Consequently the individual molecular domains must overlap extensively, and long molecules, like so many flexible strings, will be looped about neighboring contours in some irregular fashion. It is easy enough to imagine that such a system would behave like a network for small, rapid deformations, the loops serving in some sense as network junctions, and that the viscosity in steady flow would be increased by the extra motions needed for the chains to pass around one another's contours.

The behavior of the characteristic molecular weights also supports the idea of a universal interaction based on large-scale topological factors.⁴ They are insensitive to temperature, and within the same species they lie in approximately the same relationship to one another, $M_e:M_c:M_c' = 1:2:7$. The values for different species correspond roughly to the same contour length, 150–300 main chain atoms in the case of M_e . All three change with dilution in the same manner regardless of the solvent used: $(M_e)_{\text{soln}} = M_e/\varphi$ for example, in which φ is c/ρ , the volume fraction of polymer. Finally, values of M_e which are similar in magnitude to those from G_N^0 have been obtained from the equilibrium modulus of permanent networks containing topologically trapped loops.

Entanglement effects are present in concentrated solutions when the product φM exceeds M_c . Equations 8–10 carry over unchanged except that $K(T)$ now depends on the identity and proportion of the solvent; ρ is replaced by c ; and M_e , M_c , and M_c' are replaced by M_e/φ , M_c/φ , and M_c'/φ . (Entanglement effects become difficult to separate from other influences when the volume fraction becomes less than about 0.1.)

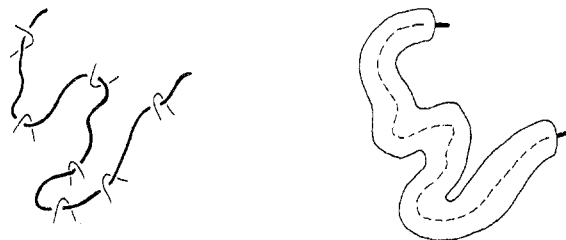
Despite the generality of the experimental relationships and the apparent simplicity of the physical picture, there is still no satisfactory fundamental theory of the entanglement interaction. On the other hand, some simplified views of the problem have been rather useful in suggesting semiquantitative explanations. For example, the diffusion coefficient D and viscosity η are closely related properties of liquids in general. Bueche and co-workers³⁷ derived a relationship appropriate for concentrated macromolecular liquids (eq 11) and demonstrated its validity for a variety of entangled

$$\eta D = \frac{cRTS^2}{6M} \quad (11)$$

linear polymers. To the extent that such a relationship is generally valid, one can discuss the effects of structure on viscosity through the somewhat simple avenue of macromolecular mobility.

Bueche discusses the effects of two kinds of motions for macromolecular diffusion in entangled liquids, a relatively free circulatory motion of each chain along its own contour and motions transverse to the contour, impeded by entanglements with neighboring chains.³⁸ He estimated the contribution of each to chain mobility, arriving finally at $\eta_0 \propto M^{3.5}$ for highly entangled linear chains. Although this and later attempts by other workers employ some questionable approximations in working out results (see ref 4), Bueche's original distinction between free motions along and impeded motions transverse to the chain contour remains a useful and suggestive one.

de Gennes discusses the mobility of flexible linear chains in a network of fixed looplike obstacles.³⁹ At



any time the chain lies within a tunnel among the obstacles, defined by its own contour. The obstacles prevent transverse motions, so the chain must wind its way along its tunnel by small Brownian displacements, continually creating a new tunnel as it moves out among new obstacles. The chain alters its position and configuration only by the sustained action of this stochastic snakelike motion, called reptation. The model was intended to deal with the mobility of unattached molecules in a cross-linked network. It undoubtedly overstates the restrictions on mobility in systems for which the individual obstacles are transitory, as might be expected for the case of entangled liquids.⁴⁰ In Bueche's terminology it ignores transverse motion entirely and deals only with circulation. Nevertheless, it seems reasonable to suppose that reptation contributes a significant component to the mobility of chains in highly entangled liquids.

Theory of Viscosity Enhancement for Star Molecules

What causes the enhancement of viscosity in branched polymers, and why are branch length and entanglement density so important? A possible answer to both questions is suggested by the reptation model when the molecule contains a long branch.^{6,41} The branched chain is effectively pinned in its tunnel of obstacles at the branch point. Reptation, which allows a linear chain to move freely along its own contour, is

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(41) P. G. de Gennes, *J. Phys. (Paris)*, **36**, 1199 (1975).



largely suppressed. The pin is released only if a free end retraces its tunnel back to the branch point. Displacement can then occur but only until the next pinning obstacle is met, requiring a new unthreading. Mobility is thus controlled by the unthreading rate, which in turn depends on the number of obstacles, or entanglements, along the branch. Accordingly, any branch point should reduce mobility if at least three strands emanating from it are each long enough to participate in several entanglements. For star molecules the number of entanglements along an arm is $\phi M/fM_c$. Thus, from eq 2 and 11:

$$\Gamma_1 = \Gamma_1(\phi M/fM_c) \quad (12)$$

in which for convenience we have replaced M_e by M_c , values of the latter being more generally available.

de Gennes has examined the diffusion of three-arm stars in a regular lattice of obstacles when the lattice spacing is large compared to arm length.⁴¹ He calculated the rate of unthreading and related it to translational mobility. His finding, if we use eq 11 and 12, is equivalent to eq 13. The parameter α depends on

$$\Gamma_1 = \exp\left(\alpha \frac{\phi M}{fM_c}\right) \quad (13)$$

the lattice and may be different for stars with different numbers of arms. Exponential dependence of Γ_1 on arm length is observed experimentally for undiluted stars.² Branch-point functionality is also important; Γ_1 increases with f at constant arm length.^{2,6}

Some polymers, such as polystyrene, appear to be less susceptible to enhancement than others. Also, dilution reduces enhancement more rapidly than would be expected from eq 13.⁶ A tentative explanation for both observations, lattice effects in the de Gennes picture, is suggested by an analogy with ordinary diffusion. The steady-state rate of diffusion through a circular tube of length l and diameter d is proportional to d^2/l ; thus, l^2/d represents a geometrical diffusion impedance. Let l_1 be the average distance between entanglement junctions in the solution and l_2 the average distance between successive junctions along a chain. For the entanglement tunnel of a branch:

$$\frac{l}{d^2} = \frac{l_2(\phi M/fM_c)}{l_1^2} \quad (14)$$

Both l_1 and l_2 have predictable dependences on species and concentration,⁶ resulting in an enhancement variable of the form $Z\phi^{5/6}(\phi M/fM_c)$ in which the species dependence is given by eq 15. Avogadro's number is

$$Z = \frac{\rho^{2/3} N_a^{2/3} (S^2/M)^{1/2} (M_c/M_e)^{7/6}}{M_c^{1/6}} \quad (15)$$

N_a and S^2/M refers to linear molecules of the species. Values of Z calculated for several polymers (with $M_c/M_e = 2$) are given in Table I. The value for polystyrene

Table I

| Polymer | M_e | M_c | M_c' | $Z, \text{\AA}^{-1}$ |
|---------------------|--------|--------|---------|----------------------|
| Polystyrene | 18 100 | 31 200 | 130 000 | 0.078 |
| Poly(vinyl acetate) | 12 000 | 24 500 | 86 000 | 0.079 |
| Polyisoprene | 5 800 | 10 000 | 35 000 | 0.103 |
| Polybutadiene | 1 900 | 5 900 | 13 800 | 0.128 |
| Polyethylene | | 3 800 | 14 400 | 0.143 |

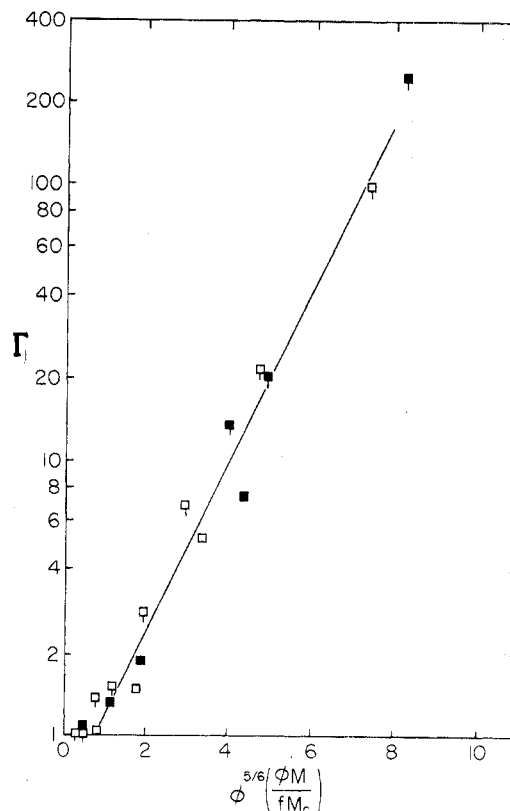


Figure 7. Viscosity enhancement factor for four-arm star polyisoprenes and polybutadienes of various concentrations and molecular weights. The filled symbols indicate polybutadiene, the open symbols polyisoprene. Tick marks indicate the same polymer at different concentrations.

is indeed somewhat smaller than those for other star-branched polymers (polybutadiene and polyisoprene).

Figure 7 shows Γ_1 for four-branch polybutadienes and polyisoprenes^{6,20,42} plotted as a function of $\phi^{5/6}(\phi M/fM_c)$. These polymers have similar values of Z . A smooth increase in Γ_1 with increasing branch point functionality, perhaps approaching a limit for large f , is suggested by data on three-, four-, and six-arm stars in Figure 8. Figure 9 compares these data with enhancements for undiluted polystyrene stars with f ranging from 7 to 13.²⁶ The values of M/fM_c for polystyrene have been multiplied by 0.68, the ratio of Z for polystyrene to the average of Z for polybutadiene and polyisoprene (Table I). Except for the sample with the largest enhancement, the Z adjustment brings the polystyrene data into the expected range. The result for a three-star hydrogenated polybutadiene²⁷ is also shown. In this case Γ_1 varies with temperature because E_a is different for the linear and branched varieties, as discussed earlier. The larger value is Γ_1 at 130 °C; the smaller is Γ_1 at 195 °C. The value of M_c for poly-

(42) G. Kraus and J. T. Gruver, *J. Polym. Sci., Polym. Phys. Ed.*, **8**, 305 (1970).

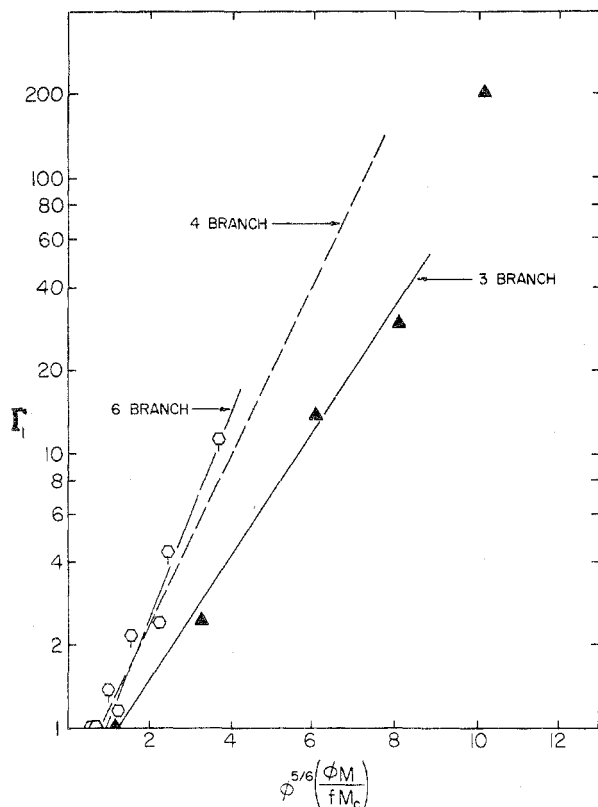


Figure 8. Viscosity enhancement factor for undiluted three-arm star polybutadienes and solutions of six-arm star polyisoprenes. The symbols and the dashed line for four-arm stars are taken from Figure 7.

ethylene was used (Table I), and no Z adjustment was applied.

Thus, the behavior of star molecules, though not simple, is systematic and also consistent with some tentative theoretical considerations.

Speculations and Unresolved Questions

So far we have only discussed regular star polymers, a family with two structural parameters. Regular combs comprise a three-parameter family, the parameters being backbone molecular weight M_{bb} , branch molecular weight M_{br} , and the number of branch points B . The molecular weight is $M_{bb} + BM_{br}$, the branch-point functionality is 3, and the branch-point spacing is random. Random trees, at least those obtained as fractions from branching polymerizations, can perhaps be regarded as a two-parameter *statistical* family, the members being samples in which all structural isomers of the same molecular weight are represented. The structural parameters are the average molecular weight of the chains which are linked to form the tree, \bar{M}_{br} , and the average number of branch points per molecule, \bar{B} . The molecular weight is $(\bar{B} + 1)\bar{M}_{br}$, or approximately $\bar{B}\bar{M}_{br}$ for highly branched fractions, and the branch point functionality is either 3 or 4. Fractions from the same whole polymer have the same value of \bar{M}_{br} .

The question naturally arises: Can the results for stars be used to predict behavior for molecules with several branch points? The simplest assumption is that the effects of widely spaced branch points on the molecular friction coefficient, and thus on the viscosity, are additive:

$$\eta_0 = K(T)(gM)^{3.5} B \Gamma_1(M_{br}/M_c) \quad (16)$$

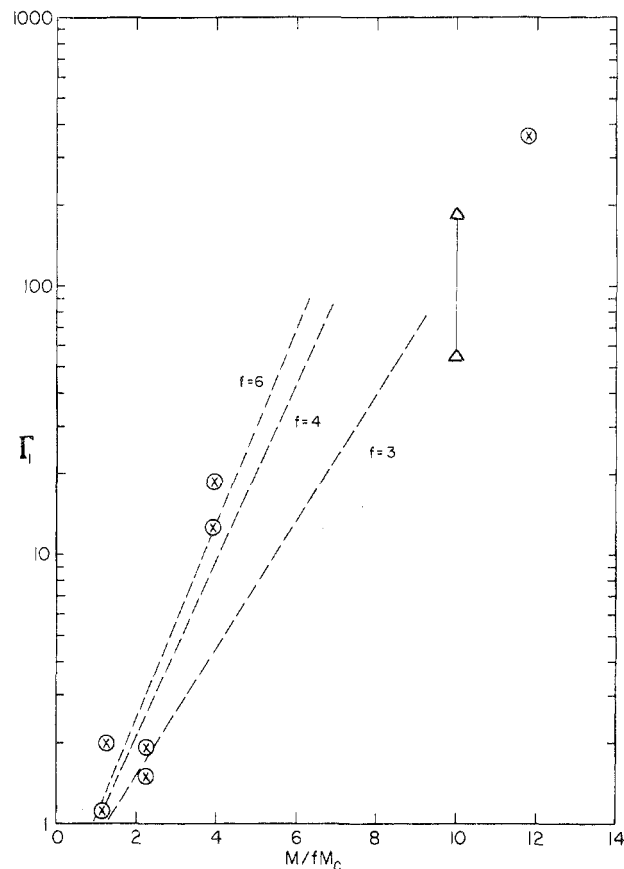


Figure 9. Viscosity enhancement factor for a three-arm star hydrogenated polybutadiene and star polystyrenes with varying large numbers of arms. The circles indicate polystyrene at 200 °C;²⁶ the triangles indicate hydrogenated polybutadiene²⁷ at 130 °C (high value) and 195 °C (low value). The dashed lines are taken from Figure 8.

Enhancement in a set of random tree fractions (\bar{M}_{br} constant, $\bar{B} = M/\bar{M}_{br}$) would, from eq 16, increase in direct proportion to M . For fractions from a polymer with trifunctional branching⁹

$$g = \left(\frac{3\pi}{4\bar{B}} \right)^{1/2} \quad (\bar{B} \gg 1) \quad (17)$$

Therefore

$$\bar{B} = \frac{4}{3\pi} \frac{(gM)^2}{\bar{M}_{br}^2} \quad (18)$$

and

$$\eta_0 = K(T) \left[\frac{4\Gamma_1(\bar{M}_{br}/M_c)}{3\pi\bar{M}_{br}^2} \right] (gM)^{5.5} \quad (19)$$

The predicted proportionality of η_0 to a high power of gM is supported by a variety of data on fractions.^{2,15,16,18}

There are other questions which should be explored experimentally. First, can viscosity enhancement be understood simply in terms of reptation suppression, as suggested here, or does it depend on the interactions between branched molecules? Measurements on the composition dependence of viscosity for blends of suitably chosen branched and linear polymers would answer this question. Second, is the increased temperature coefficient of viscosity in branched polyethylene directly related to viscosity enhancement? A knowledge of the concentration dependence of both Γ_1

and E_a in branched polyethylene would be useful.

The enhancement of J_e° remains entirely without explanation. Although Γ_2 , like Γ_1 , correlates satisfactorily with $\varphi^{5/6}(\varphi M/fM_c)$ for polyisoprene stars,⁶ its concentration dependence in general is clearly more complicated.³⁰ The influence of deformation history on the flow properties of certain branched polymers is similarly unexplained. Are such effects associated with crystallizability, or do they reflect an extremely slow relaxation process merely related to viscosity enhancement, perhaps involving only the largest, most structurally complex molecules in a polydisperse system?

A detailed understanding of commercial branched polymers may remain beyond reach for some time. The most highly branched molecules in a polydisperse system appear in the high molecular weight tail of the

distribution and are extremely difficult to detect and characterize by conventional dilute solution methods. Flow properties on the other hand, especially those associated with elastic response,⁴³ are most sensitive to these same molecules. On the other hand, the qualitative features of branched polymer behavior—increased η_0 , increased J_e° , reduced macromolecular mobility, and increased shear rate dependence of viscosity—will probably appear even in the most complex systems.

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Trends in Metalloporphyrin Stereochemistry

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Metalloporphyrins are a class of tetrapyrrolic compounds derived from the nucleus of porphine, 1. Metalloporphyrins are (usually) easily prepared by the substitution of the two central protons of the macrocycle with a metal ion. Various ring substituents of 1 lead to the commonly studied porphyrins: protoporphyrin IX, 2; octaethylporphyrin, 3; and tetraphenylporphyrin, 4. These porphyrins will be abbreviated as H₂Proto IX, H₂OEP, and H₂TPP and their metal derivatives as MProto IX, MOEP, and MTPP.¹

Initial interest in the stereochemistry of metalloporphyrins stems from the occurrence of these species and closely related substances in biological processes. Photosynthetic processes utilize chlorophyll or bacteriochlorophyll which are magnesium porphyrin derivatives related to protoporphyrin IX but which have a fifth isocyclic ring and one or two reduced pyrrole rings. Iron protoporphyrin IX or a closely related derivative serves as the prosthetic group in the several classes of heme proteins, including hemoglobin, myoglobin, catalase, peroxidase, and the cytochromes. The properties of the heme proteins have been studied by the variation of axial ligands (see General Considerations) and by the substitution of other metal ions for iron. Thus the study of metalloporphyrins other than the iron derivatives is of interest for the detailed understanding of the function of the heme proteins.

Moreover, the stereochemistry of metalloporphyrins is interesting in its own right. The principal theme of this Account is a detailing of structural trends observed

by us and others for several groups of metalloporphyrin complexes. These trends are discussed in terms which we believe illuminate the primary structural principles of this interesting class of compounds.

General Considerations

The porphinato ligand, which loses the two pyrrolic protons on complexation of the metal ion, is a dianion. With very few exceptions, the porphinato dianion acts as a tetradentate ligand with metal ions. Thus the usual minimum coordination number of the metal ion in a metalloporphyrin is four. The extensive electronic delocalization which occurs in the porphinato ligand leads to a substantial planarity of the macrocycle and an essentially square-planar environment for the metal ion in the four-coordinate complexes. Coordination numbers greater than four result from the addition of other ligands, either neutral or anionic, and metalloporphyrins in which the metal ion has a coordination number of five, six, seven, or eight have been characterized. The five-coordinate complexes have a square-pyramidal geometry with the single axial ligand occupying the apex of the square pyramid. The two axial ligands of the six-coordinate metalloporphyrins are found on opposite sides of the porphinato plane, yielding complexes with tetragonal geometries. In principle, the two axial donor atoms could be placed on the same side of the porphinato plane, but such complexes have not been characterized.² The seven-

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(1) The general form for the abbreviation of metalloporphyrin derivatives will be the metal symbol, followed by the abbreviation for the porphinato ligand, and then by the symbol(s) for the axial ligand(s). Thus chloro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(III) will be abbreviated as FeTPP(Cl). Ligand abbreviations: Pip, piperidine; 4-MePip, 4-methylpiperidine; Im, imidazole; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; Py, pyridine.