tween the two sets of results is quite marked, though the uncertainty in the Monte Carlo results is rather large. These results suggest that the extrapolation technique becomes less reliable as the extrapolation range increases. However, the difference between the results obtained by the Monte Carlo and extrapolation techniques is small compared to the inaccuracies in the available experimental methods.

For an infinite polymer, the form of the distribution is a δ function at 34.7%B and both sets of results show signs of the emergence of a peak in this region.

The primary advantage of the Monte Carlo approach over exact enumeration is its ability to provide approximate data on longer polymers. A second advantage is its versatility, in that the method could be applied to nonrandom degradation with little increase in complexity.

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The Viscosity of Liquid Sulfur. A Mechanistic Reinterpretation

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ABSTRACT: The viscosity of liquid sulfur above 160° is calculated assuming that molecular flow is the only flow mechanism. The calculation is based on the values of the degree of polymerization and the monomer concentration as applied to the recent theory of Fox and Allen. It is shown that the calculated viscosity is *ca.* 10^4 times greater than the experimental viscosity. The possibility of bond interchange and of chain-end interchange is introduced, but these mechanisms lead to an underestimated value of the viscosity. In spite of the current inability to calculate the viscosity of sulfur precisely on the basis of chemical reactions, it seems highly probable that the viscosity of liquid sulfur is most probably governed by some type of chemical interchange rather than molecular flow.

The sudden reversible increase in the viscosity of liquid sulfur above 160° has been ascribed to an equibrilium polymerization reaction[1-3] and, by implication, the magnitude of the viscosity was assumed to be in some way proportional to the length of the polymer chains. Two attempts were made to correlate the viscosity with the chain length. In the first of these, Gee[1] was able to compute the molecular weight from the viscosity curve to within a factor of 3 of the currently accepted value by deriving an equation based on the then current theories of polymer viscosity and on the equilibrium theory, and by treating three parameters as adjustable (one of them only within rather narrow limits). Touro and Wiewiorowski,[4] utilizing dilute solution theories with some simplifying assumptions and allowing two parameters to be completely adjustable, correlated the viscosity and molecular weight quite precisely. This work will be discussed more fully below.

In spite of its apparent success, it will be shown here that the assumption that the viscosity of high-polymer sulfur is due to a simple chain slippage (as would be encountered in a polystyrene solution, for example) may be seriously in error. Two lines of evidence will be cited to support this contention, both of them indicating that the viscosity of polymeric sulfur should be very much higher if present estimates of the chain length are to be believed. Furthermore, it will be indicated that two mechanisms other than simple chain slippage may exist, either one of which is more than enough to bring the viscosity way below the value found experimentally. From our present knowledge alone, it is unfortunately impossible to determine whether either or both of these two mechanisms are operative or whether still other possibilities must be considered.

Semlyen[5] has recently shown that there exists a large barrier to internal rotation about the sulfur–sulfur bond. Thus it is not unreasonable that in response to stress a sulfur chain may find it energetically more favorable to relax by some chemical means involving chain scission rather than by a molecular flow mechanism which is based on bond rotation.

The "Theoretical" Viscosity of Sulfur. A. General. Fox and Allen[6] extended the viscosity theory of Bueche[7] to include a wide range of variables, *i.e.*, high molecular

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(2) F. Fairbrother, G. Gee, and G. T. Merrall, *J. Polym. Sci.*, **16**, 459 (1955).

(3) A. V. Tobolsky and A. Eisenberg, *J. Amer. Chem. Soc.*, **81**, 780 (1959).

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(7) F. Bueche, *ibid.*, **20**, 1959 (1952).

weights, branching, and diluent concentration. Their results may be summarized by eq 1 with $\alpha = 3.4$ for

$$\eta = \frac{N}{6} X_c \left(\frac{X}{X_c}\right)^{\alpha} \zeta \tag{1}$$

$X \geqslant X_c$ and $\alpha = 1$ for $X \leqslant X_c$. In this equation η is the viscosity, N is Avogadro's number, and

$$X = \frac{\overline{S_0^2}}{M} \frac{Z_w}{\bar{V}_1} \phi_1 \tag{2}$$

for a polymer–diluent system, where $\overline{S_0^2}$ is the unperturbed mean square radius of gyration of the macromolecule of molecular weight M, Z_w is the weight-average chain length, $\bar{V}_1$ is the partial specific volume of the polymer, and ϕ_1 is the volume fraction of polymer. Furthermore

$$X_c = \frac{\overline{S_0^2}}{M} \frac{Z_c}{\bar{V}_1} \phi_1 \tag{3}$$

where Z_c is the "critical entanglement" chain length, *i.e.*, that chain length at which molecular entanglements begin and the 3.4 power law becomes operative. Finally, ζ is the monomeric friction factor, given by a modified Williams–Landel–Ferry[8] (WLF) expression

$$\log \zeta = \log \zeta_0 + \frac{E}{2.3RT} - \frac{B}{2.3 f_g} \left[\frac{\Delta\alpha_f(T - T_g)}{f_g + \Delta\alpha_f(T - T_g)}\right] \tag{4}$$

where E and ζ_0 are characteristic parameters, R is the gas constant, T is the temperature, f_g the fractional free volume at the glass transition temperature, and $\Delta\alpha_f$ the expansion coefficient of this fractional free volume.

By applying these equations to a wide range of polymers, "universal" values for several of the constants were found.[6] These are

$$\eta = 4.8 \times 10^8 \left(\frac{X}{4.7 \times 10^{-15}}\right)^{\alpha} \zeta \tag{5}$$

and

$$\log \zeta = -1.2 + \frac{E}{2.3RT} - 11.4\left[\frac{\Delta\alpha_f(T - T_g)}{0.024 + \Delta\alpha_f(T - T_g)}\right] \tag{6}$$

From a knowledge of the chain length and polymer concentration in liquid sulfur, the viscosity can now be calculated if Z_c is known, and this value, in turn, can be calculated from the rubber elasticity of quenched plastic sulfur after making the appropriate corrections. Thus one can use eq 1 and 2 to calculate the "temperature independent" part of the viscosity and eq 6 to calculate the "temperature dependent" part of the viscosity in preference to eq 4, since ζ_0 and E are not individually accessible.

B. Calculation of Z_c. It should be stressed that in this as well as in all subsequent calculations, we will be concerned only with "order-of-magnitude" values rather than highly precise data. The effects to be presented will extend over more than seven orders of magnitude, so that errors in the viscosity by as much as a factor of 2 will be of relatively little importance.

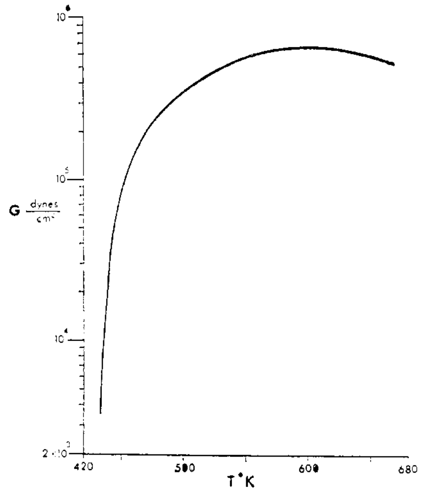

Figure 1. The shear modulus of sulfur *vs.* temperature.

Several methods exist for computing the entanglement coupling spacing in linear polymers.[9] Here, as mentioned before, it will be calculated from the pseudo-equilibrium modulus by eq 7, where M_c is the molecular

$$M_c = \frac{\rho RT}{G_e}\left(1 - \frac{2M_c}{M}\right)\phi^{1/3} \tag{7}$$

weight between entanglements, G_e the "equilibrium" rubbery shear modulus and ρ the density of the sample. The factor $(1 - 2M_c/M)$ corrects for loose chain ends,[10] while $\phi^{1/3}$ (where ϕ is the volume fraction of polymer) corrects for the presence of diluent.[11] While no data for G_e at high temperatures are available, Young's modulus of a sample quenched from 300° has recently been determined by stress relaxation techniques[12] at room temperature and found to be $E = 1.0 \times 10^6$ dyn/cm^2. Since in rubbery sulfur Poisson's ratio is probably very close to 0.5, we obtain $G_e = E/3 = 3.3 \times 10^5$ dyn/cm^2 at room temperature ($\approx$300°K). Assuming that very little reorganization between rings and chains has occurred in the quenching process, and taking the values of M and ϕ from ref 3 (which are in excellent agreement with the results of Gardner and Fraenkel[13] and subsequent studies by Poulis, *et al.*,[14]) we can calculate M_c to be 9.4×10^4 at 300° ($\approx$575°K). Thus from the relations

$$\phi M_c = \text{constant}^6 \tag{8}$$

and eq 7, and from the values of M and ϕ from ref 3, we can calculate not only M_c as a function of temperature, but also G_e, which is shown in Figure 1 and will

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(9) H. Markovitz, T. G Fox, and J. D. Ferry, *J. Phys. Chem.*, **66**, 1567 (1962).

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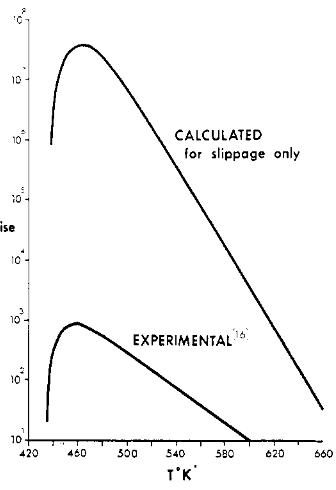


Figure 2. The viscosity of sulfur *vs.* temperature, experimental and calculated for molecular flow only.

be used later. In the case of sulfur, it should be recalled that $M_c = Z_c \times 32$.

C. Calculations of X_c and X. Since we intend to use eq 1 and 2, we calculate X_c as a first step. $\overline{S_0^2}$ can be calculated from the relation

$$\overline{S_0^2} = \overline{r_0^2}/6 \tag{9}$$

$$\overline{r_0^2} = nl^2(1 - \cos\theta)/(1 + \cos\theta) \tag{10}$$

where n is the number of bonds of a polymer chain of molecular weight M ($n = Z = M/32$), l is the bond length, and θ the bond angle. Taking the values for the S_8 molecule given in Wells,[15] *i.e.*, $l = 2.08$ Å and $\theta = 107.8°$, which are very close to those used by Semlyen[5] (except for differences in defining θ), we get

$$\overline{S_0^2}/M = 4.3 \times 10^{-18} \tag{11}$$

and can thus calculate X_c as a function of temperature from eq 3, and X from eq 2. Taking the data from ref 2, we get $X_c = 12.6 \times 10^{-15}$ which falls within a factor of 3 of the "universal" value of Fox and Allen.[6]

D. Calculation of ζ. In the absence of more precise data, we resort to the "universal" eq 6 for the calculation of ζ. Taking E to be 3 kcal (a reasonable value by comparison to other polymers,[6] particularly in view of the complete absence of side groups, even hydrogen), $\Delta\alpha_f$ to be 5×10^{-4}[8] (again a "universal" value for most rubbers), and $T_g = -30°$,[16] we can calculate ζ as a function of temperature. It should be pointed out that plastic sulfur at low temperature has been shown to obey the WLF relation with universal constants,[12] and thus $\Delta\alpha_f$ seems very reasonable.

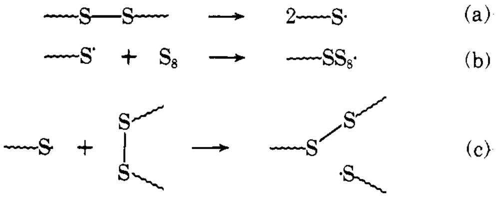
Finally, inserting the results of all these calculations into eq 1, we obtain the viscosity temperature plot shown as the upper curve in Figure 2. The maximum is seen to be almost four orders of magnitude higher than the experimental values,[17] and the temperature dependence is seen to be very much greater.

Unless the equations of Fox and Allen, which are valid for a wide range of polymers, are for some reason not applicable to polymeric sulfur (in spite of the relatively close agreement of the X values), we must conclude from the above considerations that some mechanism or mechanisms, other than simple molecular flow, are operative and lower the viscosity to the observed value.

E. Other Supporting Evidence. Another line of reasoning can be adopted to arrive at the conclusion that the viscosity of sulfur should be much higher than observed experimentally. Bacon and Fanelli[17] recalculated the data of Rotinjanz,[18] who measured the viscosity of sulfur containing 0.02% iodine; the viscosity of that sample was found to be 50 P at 240°. By assuming that all the iodine atoms terminate chains, one can calculate the chain length at that temperature as 8600 S atoms. Without iodine the chain length is 220,000.[3] If we now assume that the viscosity of the iodine containing sample is due to pure chain slippage, and that the exponent of 3.4 is applicable, then we calculate the viscosity of pure sulfur as being 3×10^6 P, in agreement with the value calculated before, and *ca.* 10^4 times greater than the observed value.

Along the same line, Touro and Wiewiorowski[4] determined the viscosities of hydrogen-terminated sulfur chains. They found that at 510°K the viscosity was 1.25 P, that the concentration of the polymer was very close to that of pure sulfur (1.69 *vs.* 1.74 mol/kg), and that the chain length was 42.5 S_8 units. This lies in the region in which an exponent of 1 is valid (see eq 1), so utilizing this idea and the fact that above a chain length of 500 S atoms an exponent of 3.4 should be used, we compute graphically the slippage viscosity of pure sulfur as 6×10^6 P, again close to the value calculated in the preceding section.

Chemical Relaxation Mechanisms. In a preceding paper[12] it was pointed out that one or more of reactions a–c might be taking place, some of which would undoubtedly tend to lower the viscosity of sulfur by providing independent flow mechanisms. Reactions a and c would be active in reducing the viscosity, while reaction b would not. Reaction a represents a classical initiation step and its reverse a termination step in the kinetic sense, while reaction c represents a kinetic propagation step. The rate constants for steps b and c are not known, while that for step a can be estimated with some accuracy.



One can, at this point, proceed along one of two independent paths. The first would involve an assumption that only step a and its reverse is important, and that we are thus dealing with a simple bond inter-

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(15) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962.

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change process. The second would be based on the premise that only reaction c is important, which means that a chain-end interchange is involved. Owing to the very high uncertainty in some of the rate constants, it seems unreasonable even to attempt a calculation involving both steps a and c simultaneously.

Since neither the first nor the second possibilities duplicate the viscosity curve well, their application will be discussed only very briefly here. The details of the calculations are presented in a government report[19] and will not be duplicated here.

In both cases, we assume that liquid sulfur would behave as a physically entangled rubber with a very high relaxation time were it not for the chemical reactions which cause it to relax or flow. It has been shown before that chemical reactions of this type do indeed lead to viscous flow or relaxation[20] and correlations have been worked out between rates of chemical reactions and rates of stress relaxation.[21] All that remains then is the correlation between a particular chemical mechanism and its rate constant with the anticipated viscoelastic relaxation time.

A. The Possibility of Chain-End Interchange. Gardener and Fraenkel[13] determined the lifetime of the free radicals in liquid sulfur. They showed that the rate of appearance or disappearance of free radicals is

$$-\frac{d(S\cdot)}{dt} = k(S\cdot)(S) \qquad (12)$$

where (S·) is the free radical concentration and (S) the concentration of sulfur atoms in the melt. k is given by eq 13. We assume that the material is Maxwellian,[19]

$$k = 2.8 \times 10^8 \exp(-3100/RT) \qquad (13)$$

and utilizing the ideas given in ref 21, develop[19] the relation for the relaxation time τ

$$\tau = \frac{0.016M}{k\phi M_c \rho} \qquad (14)$$

where the symbols have been defined before. Equation 14, in conjunction with eq 15, leads to the viscosity

$$\eta = \tau G \qquad (15)$$

curve shown in Figure 3.

B. The Possibility of Bond Interchange. Tobolsky and coworkers[20,22] have found that cross-linked polysulfides relax above *ca.* 70° by a mechanism of bond interchange. A chemical relaxation mechanism was found also in pure sulfur.[12] Furthermore, Kende, Pickering, and Tobolsky[23] found that dimethyl tetrasulfide decomposes in solution with a kinetic chain length close to 1, and with a k value which is close to that given in ref 12. Assuming that the propagation step (reaction c) is kinetically unimportant, taking the k value from ref 12, *i.e.*

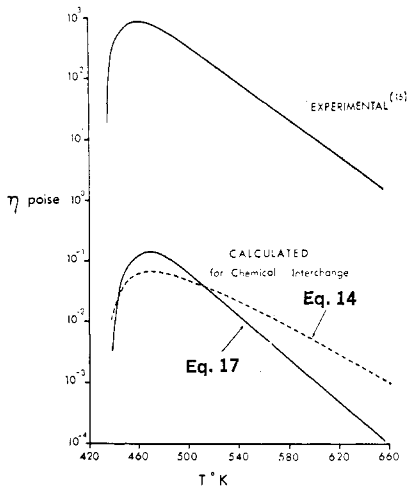

Figure 3. The viscosity of sulfur *vs.* temperature, experimental and calculated for chain-end interchange (- - - - -) and bond interchange (——).

$$k = 1.74 \times 10^{17} \exp(-33{,}400/RT) \qquad (16)$$

and proceeding as before, we obtain

$$\tau = 32\phi/kM_c \qquad (17)$$

from which the viscosity can be calculated. This is also shown in Figure 3.

It is clear that both proposed chemical mechanisms underestimate the viscosity by as much as the assumption of molecular flow overestimates it. They should therefore be taken only as possibilities, not as highly probable mechanisms.

Previous Correlation of Viscosity and Molecular Weight for Sulfur. In their correlation study, Touro and Wiewiorowski[4] utilized eq 18 and 19, where η_i is the

$$\eta_i = KP^b \qquad (18)$$

$$\eta_i = \frac{\eta_{sp}}{W} - aW \qquad (19)$$

intrinsic viscosity, P the chain length, K the constant in the Mark–Houwink–Sakurada equation, and b is an exponent ranging from 0.5 to 1.0 in that equation. η_{sp} is the specific viscosity defined by $(\eta - \eta_0)/\eta_0$, where η is the viscosity of the solution and η_0 that of the solvent. W is the concentration of polymer in moles per kilogram and a another constant.

Upon rearrangement, after dropping of the aW term, which they consider negligible at high viscosities, and evaluation of K and b (as 1 and 0.9, respectively) from the experimental values of the viscosities and the calculated values of P and W, they obtain

$$P = [(\eta - \eta_0)/\eta_0]^{1.1} \qquad (20)$$

which indeed correlates the values of η and P very well on the basis of simple flow rather than bond interchange.

In evaluating this procedure, we must reexamine eq 19 which, in its original form, is given as[10]

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(23) I. Kende, T. L. Pickering, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **87**, 5582 (1965).

$$\eta_{sp} = \eta_i C + k'\eta_i^2 C^2 \tag{21}$$

where k' ranges from 0.35 to 0.40 for most polymers and C is the concentration, usually in grams per deciliter. Inserting eq 18 for η_i as a function of P, and replacing P by M which changes the numerical value of K, we obtain

$$\eta_{sp} = KCM^b + k'(KCM^b)^2 \tag{22}$$

where the term $k'(KCM^b)^2$ corresponds to the factor aW. It is now crucial to determine whether this term is negligible by comparison to KCM^b.

The ratio of these two terms of η_{sp} is given by eq 23.

$$\text{ratio} = \frac{k'(KCM^b)^2}{KCM^b} = k'KCM^b \tag{23}$$

Typical values of the constants for concentrations in grams per deciliter are $k' = 0.4$ and $K = 10^{-4}$. Taking a value for sulfur of P and W corresponding to 470°K, where $W = 1$ mol per kilogram and $P = 8000$ S_8 units, we get $C \approx 50$ dl/g and $M = 2 \times 10^6$. The constant b 0.9 is quite reasonable for a solvent which resembles the polymer. Thus the ratio is approximately 10^4, showing that the aW term is, under the conditions chosen above, 10,000 times larger than the first term. It is thus not reasonable to drop that term. Even if b were much smaller, say 0.5, which would correspond to θ conditions,[10] the ratio would still be over 100, while an increase in the value of K (Touro and Wiewiorowski found it to be 1.0 using the concentration units of moles per kilogram rather than 10^{-4} as used here) would increase it drastically.

The apparent success of the correlation rests most probably on the coincidence that the product of η_0 WP is, within a factor of 4, equal to the experimental viscosity of sulfur. At low molecular weights (for the hydrogen terminated system) this is reasonable, since the viscosity varies approximately as the first power of the molecular weight. However, for very high molecular weight, this is unreasonable because an exponent of 3.4 has been shown to apply for all other polymers (see the preceding section). It seems that the bond-interchange mechanism proceeds at such a rate that coincidentally the correlation appears to work also at high viscosities.

In the correlation of Gee,[1] the relationship chosen for the calculation of P (eq 26 of ref 1) is such that no account is taken of the rise in the viscosity when entanglements are formed, *i.e.*, the slope of log η *vs.* log P is not taken as 3.4. Thus it is not surprising that a fair correlation is obtained, this time with an exponent for (η/η_0) of 0.75 rather than the 1.1 of Touro and Wiewiorowski. Again, however, the relationship chosen works only because the viscosity is much lower than it should be for a material in the absence of bond interchange.

Summary and Conclusions

It was shown that, if the equations of Fox and Allen are applicable to sulfur, the observed viscosity of the polymer is far too low to be due to simple molecular flow. However, additional mechanisms of viscous flow can be postulated, one a bond interchange (the propagation step being negligible) and the other a chain-end interchange mechanism (the initiation step being unimportant). From available data, the application of which involves many approximations, it is seen that these two mechanisms are indeed capable of reducing the viscosity to well below the value calculated for molecular flow, and to reproduce the shape of the viscosity–temperature curve very well, at least for the case of bond interchange. In view of this, it is very likely that the flow of polymeric sulfur above 160° is not a simple diffusional process but may well involve interchange mechanisms of the type discussed above.

Acknowledgments. The financial assistance of the Office of Naval Research is gratefully acknowledged. Special thanks are due to Professor D. Patterson of this department for a most valuable discussion in connection with theories of polymer solution viscosity.