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Viscoelastic Properties and Molecular Structure of Amorphous Selenium

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ABSTRACT: The transient and dynamical linear viscoelastic properties of pure amorphous selenium are measured in the temperature range 35–70 °C, and new ideas are proposed to explain them within the framework of the equilibrium polymerization theory. Our experimental results confirm and improve earlier results of Eisenberg and co-workers in establishing more firmly that the viscoelastic response of selenium is similar to that of a narrow molecular weight distribution polymer of low degree of polymerization. The proposed theory shows that a dynamical polymer, as we believe amorphous selenium is, behaves approximately like an ordinary narrow molecular weight distribution polymer. This may solve the problem of reconciling equilibrium polymerization with viscoelastic properties of selenium.

Introduction

The molecular structure of liquid selenium is not completely understood. One generally agrees that it is of a polymeric nature. Recently again, this opinion has been corroborated by careful X-ray[1,2] and neutron[3] diffusion investigations of the structure in the liquid and amorphous states (here, and in what follows, "amorphous state" denotes the state of the liquid after it has been quenched to a temperature higher than, but close to, the glass transition temperature T_g = 30 °C). However, very little is known about the molecular weight distribution of this polymeric liquid.[4] The purpose of this paper is to present the results of an investigation of the linear viscoelastic properties of amorphous selenium and the newly drawn conclusions about the molecular structure of the liquid that can be deduced from the careful discussion of these results.

The viscoelastic properties of amorphous selenium have already been studied in the past by Eisenberg, Tobolsky, and Teter.[5,6] Nevertheless, several reasons incited us to reexamine the subject.

First, progress has obviously been made in the knowledge of viscoelastic properties of polymers since the work of Eisenberg and co-workers. The present situation in this field is very well summed up by the book of Ferry,[7] to which we shall frequently refer. Our main motivation, however, was that the real state of knowledge of liquid selenium has become clearer over the past few years.

In 1959, following precursory papers of Gee[8] and co-workers, Tobolsky and Eisenberg[9] produced a theory of the polymerization of liquid sulfur, called "equilibrium polymerization". This theory succeeded in describing the well-known transition of liquid sulfur near 160 °C, the temperature at which sulfur reversibly transforms from a nonpolymeric liquid, almost exclusively composed of S_8 ring molecules, to a heavily polymerized liquid. The success of this theory has recently been confirmed again by the work of Wheeler, Kennedy, and Pfeuty.[10]

In 1960, another article by Eisenberg and Tobolsky[11] put forward the idea that selenium may obey the same laws of polymerization as sulfur, in spite of the fact that no polymerization transition analogous to that of sulfur is observed in liquid selenium. At that time, these authors had at their disposal experimental results published by Briegleb[12] in 1929 on the selective solubility of selenium in carbon disulfide, according to which Se_8 ring molecules are present in the liquid in proportions that depend on temperature but that are generally greater than 10%. From these results, Eisenberg and Tobolsky predicted that the polymerization transition of selenium should occur near 80 °C. This fact, of course, is not observed, but the authors concluded that the chemical reactions that are responsible for the equilibrium polymerization are critically slowed down when above this temperature.

For a relatively long time, the views of Eisenberg and Tobolsky were considered by many authors as firmly established. But nowadays, one has good reason to think that the experiments of Briegleb were spoiled by serious artifacts.[13] Furthermore, no other experimental method succeeded in proving unambiguously the existence of Se_8 ring molecules in liquid or amorphous selenium. Thus, these molecules, if present in liquid selenium, are in very small concentration. Consequently, the polymerization transition, if it exists, is relegated to a very low temperature and is, in any case, only potential. The essential process of the equilibrium polymerization no longer involves the small ring molecules: it lies in the fact that the chain molecules directly undergo chemical reactions of dissociation or concatenation. The situation is then similar to that described theoretically by Jacobson and Stockmayer[14] for some organic polymers.

In conclusion, the fact that the numerous efforts to prove the existence of Se_8 molecules in liquid selenium have been unsuccessful leads us to reject the quantitative conclusions of the Eisenberg and Tobolsky article published in 1960

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but not the idea that selenium obeys equilibrium polymerization. The foregoing discussion supports the theoretical representation of liquid selenium which follows. First, the mass fraction of the liquid which is in the state of small-ring molecules (the nonpolymeric fraction), if it exists at all, is always low. Second, in the polymeric fraction, chemical bonds are broken or reformed with an average frequency that depends on temperature. One may, in addition, assume that this frequency does not depend on the size of the molecules involved in the reaction. It is then easily demonstrated—as has already been done by Eisenberg and Tobolsky—that the molecular weight distribution of the polymeric fraction follows the "most probable distribution" of Flory,[15] namely

$$W_p = \frac{1}{\bar{P}^2} p \left(1 - \frac{1}{\bar{P}}\right)^{p-1} \tag{1}$$

where W_p is the mass fraction occupied by the molecules of p atoms and $\bar{P}$ the average degree of polymerization of the polymeric fraction. Furthermore, for obvious reasons, $\bar{P}$ and the ring molecules mass fraction must decrease as temperature increases.[16]

Finally, it is necessary to point out the essential significance of the kinetic aspects of equilibrium polymerization. As already mentioned, the measurements to be described further on concern the amorphous state. In the course of their elaboration, the samples are heated to a temperature T_L higher than the crystal melting point ($T_m \simeq 221$ °C) and then quenched to room temperature and reheated to a temperature ranging from 35 to 85 °C. The question thus arises whether the molecular structure during the test is at equilibrium at the temperature of the test, or at T_L, the molecular structure having been frozen-in by quenching. The latter of these two assumptions was made by Eisenberg and Tobolsky[5] in their already quoted work on the viscoelastic properties of amorphous selenium. As a result, they predicted that the preliminary choice of T_L must have an influence on the viscoelastic properties in the amorphous state and tried to measure this effect. They concluded that the influence exists, but is weak—this weakness being indeed difficult to reconcile with their own conception of selenium. As our results will prove, we here state that the influence in question is not significant. We therefore shall be led to consider the opposite assumption, namely that liquid selenium is a "dynamical" or "equilibrium" polymer (i.e., a polymer undergoing equilibrium polymerization), even when approaching the glass transition. It is interesting to note that we agree on this point with the recent conclusions of Stephens,[17] according to whom the structural relaxation of selenium is rather swift near T_g.

Experimental Methods

Samples. Pyrex tubes of about 1-cm^2 cross-section were filled with pellets of pure selenium and then sealed under vacuum. Selenium from two different sources was used: selenium of 99.99% purity from Kawecki, Inc., and selenium of 99.999% purity from Cerac. Measurements showed no difference in properties according to the source of selenium.

The tubes containing selenium were heated to a temperature T_L, generally 370 °C. To test the possible influence of T_L, temperatures of 250 and 600 °C were also used. After 2 h at T_L, the tubes were quenched in water at room temperature. Pyrex was dissolved in fluorhydric acid. Cylindrical rods of amorphous selenium were obtained. Afterward, they were sectioned and polished on their terminal faces into samples suited to the testing methods we used.

Tests. Transient Measurements. The tensile relaxation modulus $E(t)$, where t is time, was measured with an Instron tester. It is unnecessary here to describe the principle of this well-known method.[7] A reverse compression device was used to allow the sample to be immersed in a water bath of regulated temperature (stability ±0.02 °C).

The linearity of the response was tested by changing the rate of loading before relaxation. Very low rates were used. The maximum shear stress never exceeded 400 Pa. According to Cukierman and Uhlmann,[18] this stress is much lower than the limit above which nonlinear effects appear in selenium. Furthermore, the use of small total strains (of the order of 2%) allowed us to make successive runs at different temperatures on a single sample.

As a general rule, each sample was tested at 40, 45, 50, 55, and 60 °C. Runs at 35 or 65 °C were also performed, but at these temperatures the precision of the measurements becomes questionable, especially at 65 °C where the maximum relaxation time of selenium is hardly longer than the instrumental response time (about 2 s).

The signal delivered by the Instron tester, which is proportional to the force on the sample, was transmitted to a computer programmed for performing the necessary corrections and calculations. Under the assumption that the shear relaxation modulus $G(t)$ simply equals $E(t)/3$, each individual run delivers a recording of the function $G(t)$ for times greater than about 2 s. The sensitivity is limited to about 10^4 Pa.

From $G(t)$, four quantities can be calculated: the steady-state viscosity η, the steady-state compliance J, the terminal time τ_1, and the terminal modulus G_1. These calculations are possible because, as already observed by Eisenberg and Tobolsky, $G(t)$ exhibits a very nearly exponential decrease over 1 decade of time or more until it reaches the sensitivity limit of the apparatus. We interpreted this fact as meaning that the terminal zone is reached and that, therefore, the formulas

$$\eta = \int_0^\infty G(t)\, dt \tag{2}$$

and

$$\eta^2 J = \int_0^\infty tG(t)\, dt \tag{3}$$

can be safely used. To check this, we performed a large number of runs in varying instrumental parameters such as, e.g., the time at which the recording is stopped. The error was apparently random, beeing about 10% for η and 20% for J.

For reasons that will be developed later, we fitted a Rouse function on the terminal part of the $G(t)$ curves. In doing this, we determined for each run the value of the parameters G_1 and τ_1 that appear in the Rouse function. The dispersion on τ_1 was about 20%, whereas it was about 30% on G_1, the large dispersion on G_1 being due to the fact that this quantity appears as a preexponential factor in the Rouse function.

Dynamic Measurements. Dynamic tests were performed on a Metravib tester. This apparatus delivers, at a given temperature, the real and imaginary components of the complex relaxation modulus

$$G^*(\omega) = G'(\omega) + iG''(\omega) \tag{4}$$

for the eight angular frequencies

$$\omega_n = 2\pi(10^3/2^n) \qquad (n = 0, 1, ..., 7)$$

Tests were performed from 40 to 85 °C. However, after runs above 70 °C, we noticed in some cases a slight crystallization at the surface of the sample. This may have provoked a systematic error that we are not able to evaluate. Therefore, the results of runs above 70 °C will not be reproduced. Below this temperature, the reproductibility is about 30%.

Experimental Results

A series of relaxation curves obtained with the Instron tester on a given sample at different temperatures is drawn in Figure 1.

Figures 2–5 show the measured values of the four previously defined quantities η, J, τ_1, and G_1. The experimental points that appear in these figures are seven for

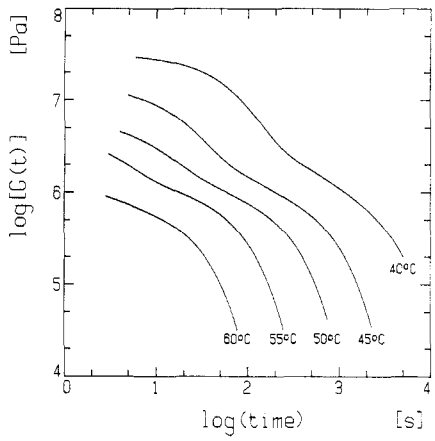

Figure 1. Relaxation modulus of amorphous selenium on a double logarithmic plot. Series of individual runs on a Instron tester at different temperatures for a single sample.

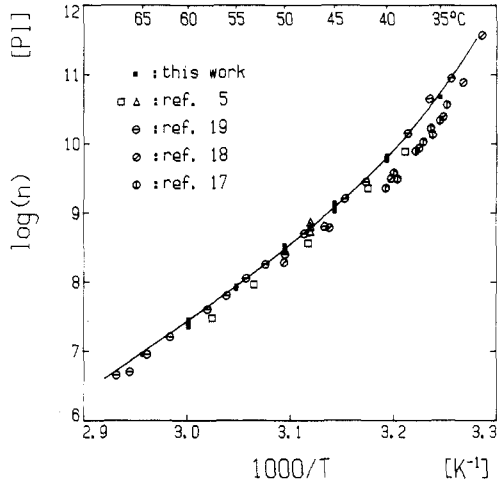

Figure 2. Steady-state viscosity of amorphous selenium on a Arrhenius plot (log η vs. reciprocal temperature). Black squares: measurements from this work, individual runs. Other symbols: measurements from references quoted in the figure. Curve: see text.

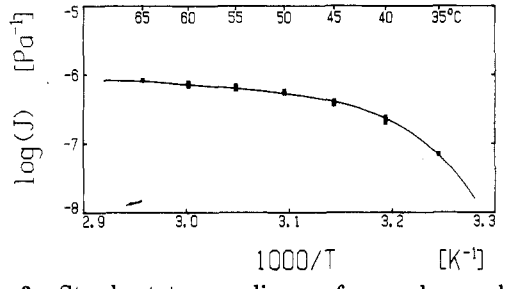

Figure 3. Steady-state compliance of amorphous selenium. Symbols as in Figure 2.

each temperature between 40 and 60 °C. They were obtained on seven different samples, as mentioned before, corresponding to various values of T_L, of the impurity content, and other experimental factors such as the Instron tester loading rate and the shape factor of the sample. Independently, the instrumental uncertainty was evaluated in performing successive runs on a single sample and at a single temperature and is, as already mentioned, about 20%. The dispersion of the results that appears in Figures 2–5 does not exceed the instrumental uncertainty. No significant influence of the mentioned factors was thus observed. Consequently, it did not appear necessary to use different symbols in the figures to represent the results originating from different samples.

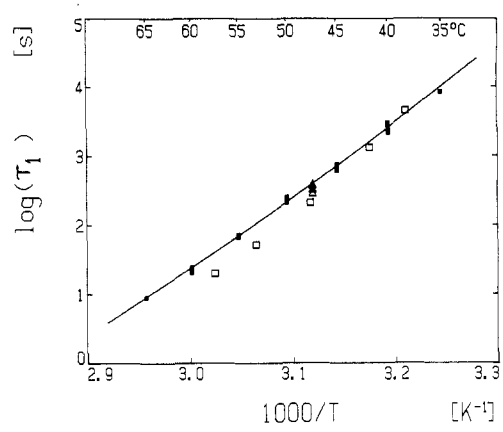

Figure 4. Terminal relaxation time of amorphous selenium. Symbols as in Figure 2.

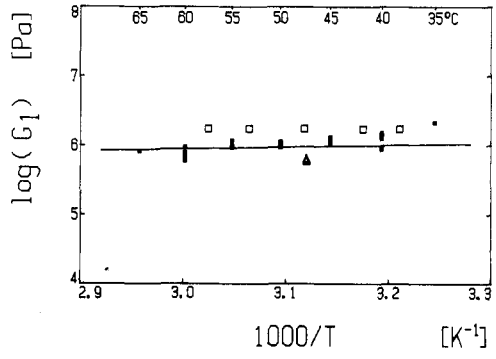

Figure 5. Terminal relaxation modulus of amorphous selenium. Symbols as in Figure 2.

Literature data are shown in the appropriate figures for comparison with ours. Our values of the stationary viscosity are in good agreement with the values given by Ueberreiter and Orthmann.[19] They are in relatively poor agreement with those given by other authors,[5,18,20] if the absolute values of η are examined. The discrepancy, however, is greatly reduced when only the variation of η with temperature is considered. In their attempts to establish the influence of T_L, Eisenberg and Tobolsky performed three measurements at 47.4 °C on three samples of different values of T_L. The corresponding results are represented by specific symbols (open triangles) in Figures 2, 4, and 5. It clearly appears that the order of magnitude of this supposed effect does not exceed that of experimental uncertainty.

One of the newest aspects of our work consisted in measuring the steady-state compliance J. We note that J rapidly decreases as temperature decreases when approaching the glass transition. This very clearly indicates that the time–temperature superposition principle generally verified in organic polymers[7] is not observed, even approximately, in amorphous selenium—at least as far as the long-time relaxation behavior is concerned. This fact was not previously recognized, possibly because it is not easily seen directly from $G(t)$ curves that extend only a few decades of time. We also note that the terminal modulus G_1 exhibits a less pronounced but nevertheless significant tendency to vary with temperature.

A set of values of the components G' and G'' of the complex relaxation modulus obtained with the Metravib tester on a given sample are reported in Figure 6. Again, several samples were tested and gave results that differ only in the amount of the experimental error, which is here of about 30%. It turns out that the time–temperature superposition principle applies to the results of Figure 6, certainly not to perfection but to a significant approxi-

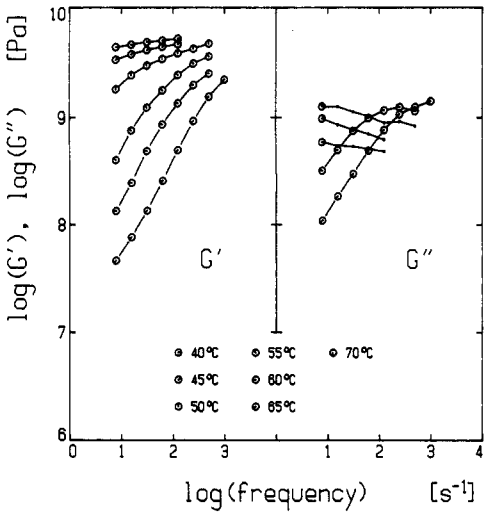

Figure 6. Real (G') and imaginary (G'') components of the complex relaxation modulus of amorphous selenium as functions of temperature and frequency, measured with a Metravib tester on a single sample.

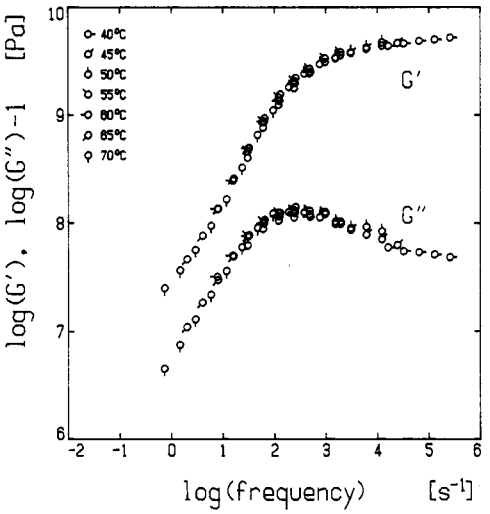

Figure 7. Composite curves for the real and imaginary components of the complex relaxation modulus obtained from the results shown in Figure 6 and reduced to 60 °C.

mation. The composite curves at 60 °C obtained with the help of the method of reduced variables[7] are drawn in Figure 7. In addition, the method delivers values of the ratio a_T of the relaxation times at T to the relaxation times at 60 °C. Following common practice, the WLF or Vogel–Fulcher equation

$$a_T \sim \exp\left(\frac{B}{T - T_0}\right) \tag{5}$$

was fitted to this set of experimental values. The corresponding values of the parameters B and T_0 are given in Table I.

The discussion of the linear viscoelastic response is often more straightforward on the basis of the relaxation spectrum $H(\tau)$. The spectrum may easily be calculated from $G'(\omega)$ or from $G(t)$, with the help of approximate formulas given by Ferry and Williams.[21] The result of the computation of $H(\tau)$ from the composite curve for G' of Figure 7 is shown in Figure 8 (curve 1). The computation from the curves of Figure 1 was also performed and led to curves denoted "2" in Figure 8. For the sake of clarity, only the curves calculated from the results at 45 and 60 °C are shown (respectively curves 2a and 2b), and curve 2a is shifted along the time scale by the factor a_T (45 °C).

Table I
Vogel-Fulcher Parameters for Some Quantities[a]

a_t	T_0, K	210
	B, K	3970
	Q, eV	3.0
η^s	T_0, K	239
	B, K	2765
	Q, eV	3.8
ζ_0	T_0, K	170
	B, K	5835
	Q, eV	2.3

[a] Definitions given in the text.

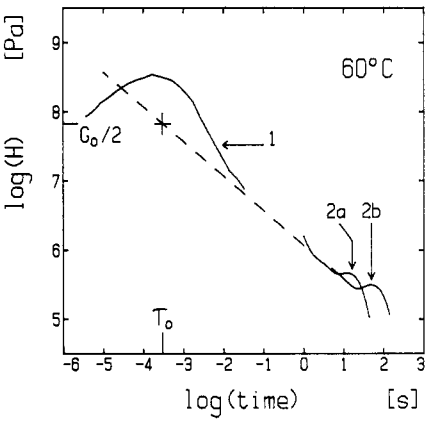

Figure 8. Relaxation spectrum of amorphous selenium at 60 °C calculated from the composite curves of Figure 7 (1) and from $G(t)$ curves (2a, at 45 °C; 2b, at 60 °C). For dashed line of slope −0.5, G_0, and τ_0, see text (eq 6–8).

Regardless of the nature of the spectrum of selenium, Figure 8 gives information on the consistency of the results. The fact that curves 2a and 2b are not superimposed reflects the already mentioned violation of the superposition principle at long times. Leaving this fact aside, i.e., ignoring curve 2a in Figure 8, we note that the continuity between curve 1 and curve 2 is satisfactory within the experimental precision, indicating an overall agreement between transient and dynamical measurements. This agreement is highlighted by the dashed line drawn in Figure 8, the meaning of which will be explained later.

Analysis of the Results

In conclusion of their work on the viscoelastic properties of selenium, Eisenberg and Teter[6] stated that amorphous selenium behaves, on the phenomenological standpoint, as a polymer below the critical entanglement molecular weight. They pointed out that this fact is rather disconcerting in regard to equilibrium polymerization and let the question of its understanding open.

In this and the following section we shall examine in turn both aspects of the problem. We shall begin with the phenomenological analysis of the results. Our conclusions will essentially substantiate that of Eisenberg et al., although they are at variance with it on several points. We therefore shall be led to tackle the problem of reconciling the viscoelastic response of selenium with the equilibrium polymerization theory, and we shall propose a solution for it.

Let us begin the phenomenological discussion with the qualitative inspection of the spectrum in Figure 8. The viscoelastic response of ordinary (i.e., nondynamical) polymers extends on the time scale over many decades. One usually distinguishes between several successive time ranges or zones, which are in ascending values of time: the zone of glasslike consistency, the transition zone, the plateau, and the terminal zone.[7] The most characteristic

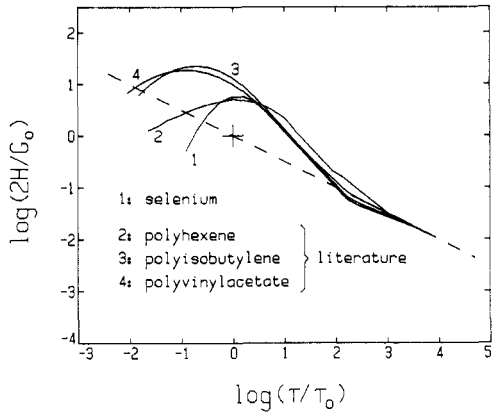

Figure 9. Reduced spectra of amorphous selenium and of the organic polymers shown in the figure (see ref 23). Dashed line: slope −0.5.

is the transition zone, which is shown as a linear region of slope −0.5 in a doubly logarithmic plot of the relaxation modulus or of the relaxation spectrum. For this region, the appropriate theory was given a long time ago by Rouse:[22] the viscoelastic relaxation is controlled by the coordinated motions of the submolecules into which each long-chain molecule may be divided. Furthermore, if the polymer is of low molecular weight, there is no plateau, and the terminal zone cannot be separated from the transition zone: the above mentioned linear region is terminated at long times by an exponential fall, which from the theoretical standpoint corresponds to the uppermost or terminal relaxation time of the Rouse distribution. On the contrary, if the degree of polymerization P is higher than a characteristic value P_e, the molecular entanglements are felt and an inflexion that develops into a plateau if P is very high appears between the transition and the terminal zone. Finally, on the short-time side of the transition zone, the linear region ends with a broad maximum, known as the short-time deviation from the Rouse theory. No quantitative interpretation exists for this deviation, which is thought to originate from the internal motions of the submolecules.[7]

The relaxation spectra of some organic polymers which we took from the compilation done by Ferry[23] are shown in Figure 9, on a reduced scale which will be explained shortly. According to the Rouse theory, the asymptotic behavior at short times of the spectrum $H_R(\tau)$ (the subscript R meaning "Rouselike") is given by

$$H_R(\tau) = \tfrac{1}{2}G_0(\tau_0/\tau)^{-1/2} \tag{6}$$

where G_0 and τ_0 are constants which, at a given temperature, depend only on the material under consideration. The above mentioned reduced variables are therefore H/G_0 and τ/τ_0. The quantities G_0 and τ_0 are given by the formulas

$$G_0 = nRT \tag{7}$$

and

$$\tau_0 = \frac{\sigma^2}{6\pi^2 k_B T}\zeta_0 \tag{8}$$

where R is the gas constant, k_B the Boltzmann constant, n the number of monomers per unit volume, σ the root-mean-square end-to-end distance per monomer (i.e., per Se atom),[24] and ζ_0 the translational friction coefficient per monomer. From the data available in literature, all these quantities, except ζ_0, can easily be calculated for selenium. One finds

$$n \simeq 5.1 \times 10^{-2} \text{ mol cm}^{-3} \qquad \sigma \simeq 3.05 \text{ Å} \qquad G_0 \simeq 1.4 \times 10^8 \text{ Pa (at 60 °C)} \tag{9}$$

For the evaluation of σ, the freely rotating chain model was used.[25] We shall show below that τ_0 can be calculated from the terminal quantitites τ_1 and G_1. We therefore know both G_0 and τ_0 at the reduction temperature (60 °C), and we can draw the spectrum of selenium in the appropriate reduced variables together with those of ordinary polymers chosen as references. This is done in Figure 9. The similarity of the spectrum of selenium to those of ordinary polymers is striking. The broad maximum at short times, which covers the dynamical measurements, belongs to the region of the short-time deviation. The Rouselike linear region can be seen in Figure 8 and more clearly in Figure 1, but it is somewhat obscured by the appearance of two additional features, between which it extends: a small maximum immediately before the terminal fall, visible only in the spectrum, and an inflexion in the short-time direction. Literature data for ordinary low molecular weight polymers apparently give no information on such features. Since the nature of these features may be a cause of controversy, it is worth discussing them in some detail.

The maximum hardly emerges out of experimental uncertainties and has probably no specific signification. While it is not predicted by the formulas given by Rouse, it may appear in other versions of the same theory, for example in the Marvin–Oser version (see below).

As mentioned above, an inflexion in the relaxation curves usually suggests the beginning of an entanglement plateau. On the other hand, the interpretation given above suggests that the inflexion visible in Figure 1 is the onset of the short-time deviation. Close inspection of Figure 1 allows us to conclude in favor of the latter interpretation. First, at 40 °C the inflexion is located at about 2.5×10^6 Pa in the modulus scale. If the first interpretation was correct, this would lead to a value of the number of monomers between entanglements, P_e, of about 60, thus much lower than the values given in the literature for other polymers, which range from 200 to 400. Second, this value would noticeably increase when temperature increases from 40 to 50 °C. This behavior is also in disagreement with the known properties of the entanglement plateau.

To complete the qualitative discussion of the results, let us finally consider the violation of the time–temperature superposition principle observed in the long-time range. This behavior does not belong to the usually listed properties of ordinary polymers. However, deviations from the superposition principle have been clearly observed in some instances, notably by Plazek and O'Rourke[26] in their study of polystyrene samples of narrow molecular weight distribution. These authors observed that when the degree of polymerization is lower than P_e, the steady-state compliance of polystyrene changes with temperature in a way similar to that we observed in selenium. This is illustrated by Figure 10, where our measurements are shown on a reduced scale together with those of Plazek and O'Rourke. Although the reduced scale chosen on the ordinate axis is purely empirical and therefore somewhat arbitrary, it is striking that the $J(T)$ curve for selenium is similar to that for a polystyrene with a degree of polymerization of 158.

Thus, qualitative inspection of the viscoelastic response of amorphous selenium leads us to the conclusion that this response is in all its aspects similar to that of an ordinary polymer of low polymerization degree and of relatively narrow molecular weight distribution. As already mentioned, this was the conclusion of Eisenberg et al. It is not invalidated by the violation of the superposition principle. Before turning to the discussion of this conclusion with

Table II
Viscoelastic Constants of Amorphous Selenium as Functions of Temperature[a]

T, °C	η, P1	J, Pa^{-1}	τ_1, s	G_1, Pa	η^s, P1	log ζ_0, dyn s cm^{-1}	P	Γ, s^{-1}
35	5.5×10^{10}	5.4×10^{-8}	12700	1.0×10^6	3.9×10^{10}	2.86	285	1.7×10^{-7}
40	6.3×10^9	2.3×10^{-7}	3050	0.99×10^6	2.6×10^9	2.33	292	6.9×10^{-7}
45	1.2×10^9	4.3×10^{-7}	800	0.97×10^6	2.5×10^8	1.63	298	2.6×10^{-6}
50	3.0×10^8	5.6×10^{-7}	230	0.95×10^6	3.1×10^7	1.08	303	8.8×10^{-6}
55	8.7×10^7	6.3×10^{-7}	70	0.94×10^6	5.0×10^6	0.55	309	2.9×10^{-5}
60	2.8×10^7	6.7×10^{-7}	23	0.92×10^6	9.7×10^5	0.05	315	8.5×10^{-5}
65	9.6×10^6	7.0×10^{-7}	8	0.89×10^6	2.1×10^5	−0.40	319	2.3×10^{-4}

[a] The far left four columns correspond to the curves drawn in Figures 2–5. The far right four columns relate to models developed in the text.

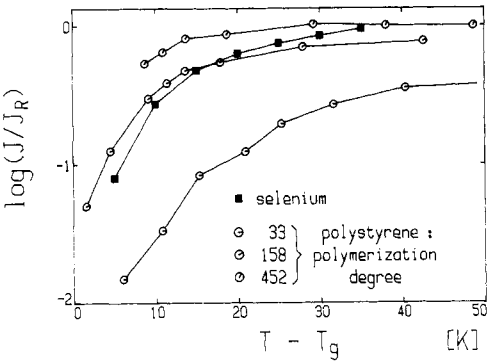

Figure 10. Plot of the reduced steady-state compliance J/J_R vs. the reduced temperature $T - T_g$. J_R is the steady-state compliance according to the Rouse theory. Black squares: selenium. Open circles: polystyrene sample of various polymerization degrees (results of Plazek and O'Rourke).[26]

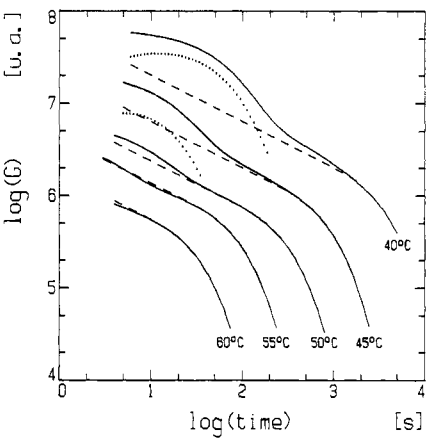

Figure 11. Relaxation modulus of amorphous selenium. Full curves: experimental runs shown in Figure 1. Dashed curves: Marvin–Oser model.[27] Dotted curves: G_s calculated as the difference of the two previous curves.

reference to the equilibrium polymerization theory, we now present the quantitative exploitation of the results.

We assume that the relaxation modulus $G(t)$ is the sum of two components: first, the Rouselike component $G_R(t)$, which prevails at long times; second, the short-time component $G_s(t)$, which describes the so-called short-time deviation. We thus write

$$G(t) = G_s(t) + G_R(t) \tag{10}$$

Several analytic expressions have been proposed for $G_R(t)$, which are qualitatively equivalent but significantly different on the quantitative standpoint. It turns out that the formulas proposed by Marvin and Oser[27] best fit our results. Figure 11 shows that the fit is good. As stated above, the fit delivers the values of the terminal time and modulus. The polymerization degree P and the time constant τ_0 defined by eq 8 are given by the relationships

$$G_1 = k_1(G_0/P) \tag{11}$$

and

$$\tau_1 = k_2\tau_0 P^2 \tag{12}$$

where $k_1 = 2$ and $k_2 = {}^2/_3$, according to Marvin and Oser. In this way, all the quantities of interest are obtained but some of the experimental results remain to be explained, namely the observed values of η and J.

For each component of eq 10, we may define a (partial) steady-state viscosity and a steady-state compliance, through equations similar to eq 2 and 3. We then obtain the relationships

$$\eta = \eta_R + \eta_s \tag{13}$$

and

$$\eta^2 J = \eta_R{}^2 J_R + \eta_s{}^2 J_s \tag{14}$$

Since the relaxation times characteristic of the short-time component are much smaller than the terminal relaxation time of the Rouselike component (see Figure 11), we may simplify eq 14 and write

$$J \simeq \left(\frac{\eta_R}{\eta_R + \eta_s}\right)^2 J_R \tag{15}$$

Thus, even if J_R does not depend on temperature, J does, provided that η_s is not much smaller than η_R and that these two quantities vary with temperature in different ways. In order that eq 15 reproduces the observed variations of J with temperature, we only have to assume that η_s is of the same order of magnitude as η_R near T_g and decreases more rapidly than η_R as temperature increases. Admittedly, this assumption gives an unusual picture of the temperature range just above the glass transition, since the latter will be positioned mainly by the emergence of the short-time component as the temperature is decreased. However, we shall not enter into the discussion of this problem and we shall restrict ourselves to the phenomenological aspects of the model.

The partial quantities η_R and J_R for the Rouse component are given by

$$\eta_R = k_3 G_1 \tau_1 \tag{16}$$

and

$$J_R = k_4/G_1 \tag{17}$$

where $k_3 = 1.23$ and $k_4 = {}^2/_3$. On the other hand, η and J are measured quantities. Thus, the consistency of the model will be ensured if we can find a function $\eta_s(T)$ that obeys the two independent equations 13 and 15. It turns out that such a function can indeed be found. In fact, due to the experimental uncertainties on the measured quantities, a rather large uncertainty also affects η_s.

The best fit values of η, J, G_1, τ_1, η_s, and ζ_0 (calculated from τ_0) are given in Table II. The corresponding curves

are drawn in Figures 1–5. Furthermore, the WLF law was fitted to the variation with temperature of ζ_0 and η_s. The corresponding values of B and T_0 are given in Table I. Since the shift factor for the dynamical measurements a_T and the partial viscosity η_s relate to the short-time deviation, their variation with temperature should be similar, whereas the variation of ζ_0 should be much less rapid. To make the comparison more meaningful the apparent activation energy Q at some temperature of reference (45 °C) is also given in Table I. The result is reasonable but not very eloquent. On the whole, the proposed model works satisfactorily, but it is nevertheless likely to be a crude simplification of a rather complicated reality.[28]

Discussion

We now have to explain how the viscoelastic properties of a dynamical polymer (as we suppose that amorphous selenium is) may turn out to be similar to those of a narrow molecular weight distribution polymer of low molecular weight. Several authors have, before us, mentioned this problem,[6,29,30] without undertaking to solve it, however. It would probably be a complicated task to elaborate a complete theory of the viscoelastic properties of dynamic polymers, analogous to that of Rouse for ordinary polymers. We shall propose here a very simple argument which, hopefully, will contribute to clarify the problem.

First, we repeat that it is necessary to take into account the fact that the chemical bonds of the chain molecules constantly break and recombine during the viscoelastic relaxation. We may introduce the average frequency Γ of bond breaking at a given temperature. This frequency cannot be much smaller than the reciprocal of the terminal relaxation time τ_1 at the same temperature, otherwise, the viscoelastic response would be that of the very broad molecular weight distribution polymer described by eq 1. This would obviously conflict with our previous conclusions.

Second, we observe that the process of constant breaking and restoration of the bonds is by itself a process of viscoelastic relaxation, since it tends to produce a random distribution of the bond orientations. The problem is to describe how this process combines with the Rouselike relaxation modes. As for the latter, each mode may be characterized by its relaxation time τ and its correlation length (or wavelength) p, measured in monomeric units. With some simplifying assumptions, the relation connecting τ and p is given by eq 12

$$\tau \simeq \tau_0 p^2 \tag{18}$$

It seems likely that a relaxation mode (τ, p) cannot be performed even by the longest molecules if the probability that one out of p bonds breaks during the time τ is near unity. Therefore, we suggest that all the modes such as

$$\tau p \Gamma \geq 1 \tag{19}$$

disappear in the relaxation spectrum. This condition allows us to define a critical time τ_c and a critical molecular length P_c given by

$$\tau_c \simeq \tau_0^{1/3} \Gamma^{-2/3} \tag{20}$$

and

$$P_c \simeq (\Gamma \tau_0)^{-1/3} \tag{21}$$

It is then clear that, provided that the real equilibrium average degree of polymerization $\bar{P}$ is much larger than P_c, the viscoelastic tests on the liquid experience a maximum relaxation time of the order of τ_c and that for times shorter than τ_c the liquid behaves more or less as an ordinary

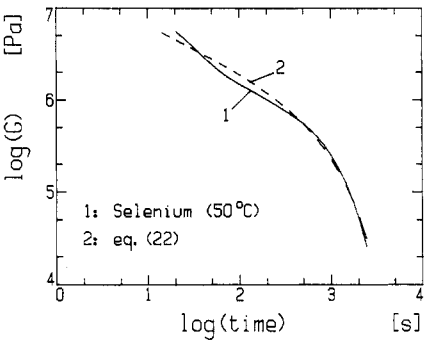

Figure 12. Relaxation modulus vs. time on a double logarithmic plot.

Rouse system. This indeed is the behavior observed in selenium.

These qualitative considerations can be put into a very simple mathematical form,[31] as shown in the Appendix. It turns out that the relaxation modulus of a dynamical polymer with $P_c \ll \bar{P}$ is given by

$$G(t) \simeq (\pi/3)^{1/2} G_0 \left(\frac{\tau_0}{t}\right)^{1/2} \exp\left(-\frac{3}{2^{2/3}} \frac{t}{\tau_c}\right) \tag{22}$$

in all the time range within which the Rouse theory is valid. This function is compared to the experimental relaxation curves in Figure 12. The fit is far from being perfect, but is must be repeated that the assumptions leading to eq 22 are summary. We could determine τ_c and τ_0 (and whence P_c and ζ_0) by fitting eq 22 to experimental curves. However, it is easily seen that the values of P_c and ζ_0 obtained this way would differ from the values listed in Table II only by a temperature-independent factor. Within the precision of the fits, this factor is not meaningful. We shall therefore admit that the previously calculated polymerization degree P is the critical polymerization degree P_c. Consequently, we are in a position to calculate the frequency Γ from eq 21. The corresponding values are listed in Table II.

Γ increases rapidly as temperature increases. An Arrhenius law fits the variation of Γ. The activation energy corresponding to the best fit is about 2 eV, and the preexponential factor is about 10^{20} s. These are very rough estimates, but they are in keeping with the assumption that the bond-breaking reaction is controlled by very local submolecules motions that are insensitive to glass transition. Considering the fact that the energy required to break a bond in the liquid is about 1 eV in sulfur[5] and is probably of the same order of magnitude in selenium, one may conclude that the reaction consists in the simultaneous breaking of two bonds. However, such a conclusion is beyond the reliability of our results. In any case, it is satisfactory that Γ varies with temperature in the way that can be expected for a reaction involving the breaking of the Se–Se bond. This provides a good physical foundation to the interpretation of the effective polymerizaton degree conveyed by our theory.

Conclusion

The models of the molecular structure and of the viscoelastic properties of amorphous selenium presented in this paper are apparently consistent with all the known viscoelastic properties of amorphous selenium. However, the temperature range within which the properties have been measured is relatively narrow. It would be of interest to compare the predictions of the model to other observations. One of the well-known properties of liquid selenium is its viscosity above the crystal melting point.[18,30] It has been noticed that, in the liquid above 221 °C, the rate at which viscosity decreases as temperature increases

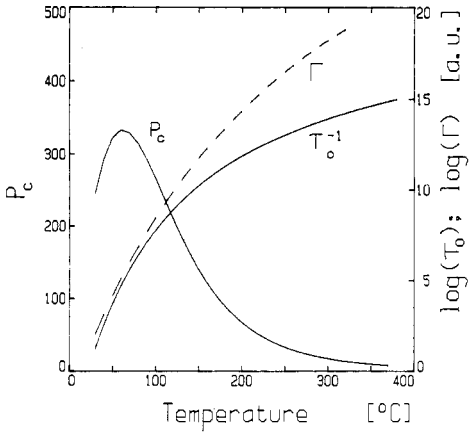

Figure 13. Effective degree of polymerization P_c, time τ_0, and frequency Γ vs. temperature according to the model explained in the text.

is unusually high. Rialland has interpreted this behavior as being due to a decrease of the polymerization degree of the liquid. According to our conceptions, the concerned polymerization degree is the effective polymerization degree P_c of eq 21. In the temperature range of our experiments, P_c increases as temperature increases. However, since τ_0 obeys a WLF law and Γ an Arrhenius law with a relatively high activation energy, there exists a temperature at which the apparent activation energies of Γ and τ_0^{-1} are equal and at which, therefore, P_c passes through a maximum. The variations of τ_0 and Γ at high temepratures which are obtained by extrapolating the low temperature experimental laws are shown in Figure 13. P_c passes through a maximum near 100 °C, and it decreases above this temperature relatively rapidly. Obviously, the curves drawn in Figure 13 are at best qualitatively correct. Nevertheless, they prove that the model is able to give a basis to some of the current views on the high-temperature viscosity of liquid selenium.

Other confirmations of the proposed model could be provided by investigating the viscoelastic properties of amorphous selenium doped with appropriate elements.[4,6,30] Work in this field is presently in progress.

Finally, another characteristic property of polymeric selenium can be deduced from the foregoing discussion. According to our above statements, the viscoelastic behavior of the material, at times markedly shorter than τ_c, is insensitive to the dynamical nature of the polymer. The short-time part of the spectrum may thus be discussed as if amorphous selenium was really an ordinary polymer with a given molecular weight distribution—provided, however, that the influence of the small ring molecules can be ignored. Concerning this part of the spectrum the question that requires discussion is that of the values found for the monomeric friction coefficient ζ_0.

The role of the different pysical factors that determine the value of ζ_0 for a given polymer has not been completely elucidated. The comparison between different polymers is difficult since ζ_0 varies rapidly with temperature in the vicinity of T_g. The choice of the corresponding temperatures at which the values of ζ_0 should be compared is of importance. According to Ferry,[32] one may choose a corresponding temperature of T_g plus a constant. In the case of selenium T_g + 30 °C (60 °C) is a convenient choice. The value of ζ_0 for selenium at this temperature is of about 1 dyn s cm^{-1}. The information given in Ferry's book allows us to calculate the values of ζ_0 at T_g + 30 °C for a number of organic polymers. These values range between 10^{-6} and 10^2 dyn s cm^{-1}. Selenium therefore turns out to have a relatively high but reasonable monomeric friction coefficient. This high value of ζ_0 may be attributed to a high value of the potential barrier for the internal rotation of the individual molecules or to some peculiarity of the local packing geometry. The former argument is supported by the estimates of the internal rotation barrier of sulfur and selenium existing in literature.[33] Therefore, another characteristic property of polymeric selenium, besides its dynamical character, is that its molecules have relatively low flexibility.

Appendix

The Rouselike relaxation modulus of an ordinary polydispersed polymer is given by[7]

$$G(t) = \sum_{p=1}^{\infty} W_p G_p(t) \tag{A1}$$

where

$$G_p(t) = G_0 \frac{1}{p} \sum_{q=1}^{p} \exp\left[-\frac{t}{\tau_0} \left(\frac{q}{p} \right)^2 \right] \tag{A2}$$

is the modulus of a monodispersed polymer of degree of polymerization p.

We assume that the proportion of the (p, q) modes that are still active at time t is

$$\exp\left(-\Gamma \frac{p}{q} t \right) \tag{A3}$$

Therefore, using eq 20 and 21, we write

$$G(t) = \sum_{p=1}^{\infty} W_p G_p'(t) \tag{A4}$$

with

$$G_p'(t) = G_0 \frac{1}{p} \sum_{q=1}^{p} \exp\left\{ -\frac{t}{\tau_c} \left[\frac{p}{qP_c} + \left(\frac{qP_c}{p} \right)^2 \right] \right\} \tag{A5}$$

Equation A5 may be written

$$G_p'(t) = G_0 \frac{1}{p} \sum_{q=1}^{p} \exp\left[-\frac{t}{\tau_c} \left(\frac{1}{x} + x^2 \right) \right] \tag{A6}$$

where $x = qP_c/p$. The function of x in the exponent passes through a relatively sharp minimum for $x_m = 2^{-1/3}$. Therefore, provided that $p > x_m P_c$ and $t > \tau_c$, one may replace the sum in (A6) by a integral over x, to which only the values of x near x_m give a significant contribution. Developing the exponent around x_m, one then obtains

$$G_p'(t) = G_0(\pi/3)^{1/2} \left(\frac{\tau_0}{t} \right)^{1/2} \exp\left(-\frac{3}{2^{2/3}} \frac{t}{\tau_c} \right) \tag{A7}$$

This function does not depend on p. Therefore, eq A7 is also a good approximation for $G(t)$ at long times, if $\bar{P} \gg P_c$. Direct computation of the sums in eq A4 and A5 (using eq 1 in the text) allowed us to establish a convenient numerical formula, valid at short times as well

$$G_p'(t) \simeq G_0 \left(1 - \frac{1 - 3^{1/2}/2}{1 + 3t/\tau_c} \right) \left(\frac{\pi}{3} \right)^{1/2} \left(\frac{\tau_0}{t} \right)^{1/2} \exp\left(-\frac{3}{2^{2/3}} \frac{t}{\tau_c} \right) \tag{A8}$$

Registry No. Se, 7782-49-2.

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Coil Dimensions of Polystyrenes in Isorefractive Viscous Solvents by Small-Angle Neutron Scattering

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ABSTRACT: The radii of gyration of perdeuterated polystyrenes with molecular weights ranging from 10 000 to 104 000 have been determined at infinite dilution in Aroclor 1248 and tricresyl phosphate by small-angle neutron scattering. Measurements were carried out at the National Bureau of Standards, the Oak Ridge National Laboratory, and the University of Missouri. The coherent scattering in all cases is well described by the Debye function. The radii are very close in magnitude to those obtained in cyclohexane at the Θ temperature, although for these solvents all indications are that the solvent quality is intermediate to good. This result is interpreted as another manifestation of the solvent dependence of the unperturbed dimensions of polystyrene. Remarkably, however, literature values of the intrinsic viscosity of polystyrenes in these two solvents are considerably higher than those reported in cyclohexane. Thus, in these particular systems the scattering and viscosity experiments are apparently sensitive to quite different properties of the chain, and extraction of coil dimensions directly from intrinsic viscosity data should be performed with caution.

Experiments designed to probe the dynamics of conformational change in solutions of flexible polymers can serve as a valuable tool in molecular characterization, especially in terms of the so-called "internal motions". When combined with information about the radius of gyration, intrinsic viscosity, translational diffusion coefficient, and second virial coefficient, all of which reflect predominantly the behavior of the polymer as a whole, a more complete understanding of macromolecular physics may be developed. The linear viscoelastic (VE) and oscillatory flow birefringence (OFB) techniques in particular have demonstrated the sensitivity and precision necessary to explore the relaxation behavior of isolated polymer chains via extrapolation to infinite dilution.[1-3] The results of both experiments are interpretable in terms of the bead–spring models, and as these models predict, the information content of the two techniques is essentially identical, at least at low and intermediate frequencies.[4] However, OFB has been shown to exhibit greater sensitivity and precision when infinite dilution properties are of interest.[3] For polymers dissolved in "typical" solvents with viscosities around 1 cP (e.g., toluene, benzene, and THF), the time scales relevant to conformational rearrangement range from nanoseconds to milliseconds, whereas OFB and VE apparatuses generally operate up to at most a few kilohertz. Thus, internal modes would be largely inaccessible via these techniques. This difficulty may be overcome by the use of viscous solvents and the principle of time–temperature superposition; for example, in the polystyrene/Aroclor system, infinite dilution OFB results have been reported up to reduced frequencies corresponding to a time scale of tens of nanoseconds in a low-viscosity solvent.[3] Unfortunately, as well-suited as solvents such as Aroclors and tricresyl phosphate (TCP) are to conformational dynamics experiments, they are essentially isorefractive with polystyrene. As a consequence, it is very difficult to obtain radius of gyration, translational diffusion, and second virial coefficient information by established light scattering methods. Therefore, although the bead–spring model is

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