of the side chains finds parallel in the stabilization of colloidal particles of carbon black suspended in organic media by adsorption of aromatic compounds bearing long aliphatic side chains.[18] (Aromatic compounds with short side chains are ineffective.) When two particles thus stabilized approach one another, the entropy decrease resulting from "desolvation" (i.e., unmixing) of these pendant chains introduces a repulsion between the particles. This explanation has been developed in detail by Mackor.[19]

The solubility of PBLG and PBLA in a variety of solvents appears to be conditioned by their bulky, flexible side chains. In contrast, other helical polypeptides such as poly-L-alanine, poly-L-phenylalanine, and poly-L-leucine are for the most part insoluble except in those solvents which cause partial or total disruption of the helical structure.[20] Their smaller, less flexible substituents offer little opportunity for side chain, mixing; hence, the repulsions generated by mixing of solvent with long side chains are absent, or much reduced, in these polypeptides. We suggest it is on this account that their tendency to disperse in solvents as intact helices is so limited.

The molecules of poly-L-alanine, etc., having shorter side chains, may be presumed to conform more nearly to the characteristics expected of impervious rod-like particles. The forces operative between two such particles in dense array are inevitably large owing to their size. In the absence of an electric double layer or other source of repulsion, their solubility is consequently very small. The predictions of theory for concentrated solutions of impervious rod-like particles with very small attractive interactions may therefore be beyond reach of experiment.

The previous theory[2,7] of solutions of rod-like particles appears to be in substantial agreement with experiment on PBLG and PBLA polypeptides throughout the low concentration range and including, especially, the region of the tactoidal phase separation. Here the solvent within the domain of the side chains may properly be regarded as a part of the solute particle. Eventual removal of solvent from these domains at high concentrations introduces a feature not accounted for in that theory. Consequently, functions derived previously for the chemical potentials require revision when applied to the helical polypeptides in this range of concentration. In particular, the coexistence of a phase of *high* concentration in equilibrium with a dilute phase, predicted theoretically[7] for a system of coherent, rod-like solute particles in a solvent in which the interaction is unfavorable to mixing (corresponding to a net attraction between solute particles), cannot be expected to occur among solutions of the soluble α-helical polypeptides.

(18) M. van der Waarden, *J. Colloid Sci.*, 5, 317 (1950).
(19) E. L. Mackor, *ibid.*, 6, 492 (1951).
(20) The effects of highly polar substituents involve factors going beyond those considered in the present discussion.

The Viscoelastic Relaxation Mechanism of Inorganic Polymers. Amorphous Selenium[1]

A. Eisenberg and L. Teter

Contribution No. 1766 from the Department of Chemistry, University of California, Los Angeles, California. Received December 4, 1964

Amorphous selenium, a representative inorganic polymer which consists of a mixture of rings and chains, may relax in response to stress in one of several ways, the most probable being bond interchange and molecular slippage. In this work, which was undertaken in an attempt to elucidate the relaxation behavior of this material, the viscoelastic properties of selenium were studied by the technique of stress relaxation. Since the molecular weight dependence of the stress relaxation plots is quite analogous to that observed in the organic polymers relaxing by simple molecular slippage, it is concluded that this is also the mechanism encountered here.

I. Introduction

In a recent publication dealing with the viscoelastic properties of amorphous selenium,[2a] it was found that the material is very strongly reminiscent of the normal organic polymers like polystyrene or poly(methyl methacrylate). Thus, the mechanism of stress relaxation may well be mechanical flow. However, in the melt, selenium is known to reorganize to yield an equilibrium mixture of rings and chains,[2b] indicating that the process of bond interchange is proceeding at an appreciable rate, a process which is exactly analogous to the one occurring in the relaxation of the polysulfide rubbers.[3] In the polysulfide rubbers, flow occurs far

(1) Paper VI in a series dealing with the properties of inorganic polymers; paper V: A. Eisenberg and L. Teter, *Trans. Soc. Rheol.*, in press.

(2) (a) A. Eisenberg and A. V. Tobolsky, *J. Polymer Sci.*, **61**, 483 (1962); (b) *ibid.*, **56**, 19 (1960).
(3) M. Mochulsky and A. V. Tobolsky, *Ind. Eng. Chem.*, **40**, 2155 (1948).

above the glass transition temperature (T_g), and bond interchange can thus be identified by the presence of only one relaxation time (Maxwellian behavior) in the flow region, which is well separated from the transition region. In amorphous selenium, on the other hand, liquid flow occurs very close to the glass transition,[2a] so that the maximum relaxation time, which may well be caused by chemical bond interchange, blends right into the spectrum of relaxation times accompanying the glass transition behavior. Selenium thus belongs to a group of materials in which the relaxation or flow mechanism may, *a priori*, be either bond interchange or molecular flow, but in which, as was pointed out before,[2a] the investigation of only one sample (*i.e.*, of only one molecular weight) cannot resolve the problem. Other examples of these materials are the polyphosphoryldimethylamides,[4] the relaxation mechanism of which was recently shown to be molecular flow[5]; that publication,[5] incidentally, also contains a more extensive description of the bond interchange *vs.* molecular flow argument.

There is some evidence that in the melt bond interchange may be relatively unimportant. This evidence is based on the fact that melt viscosity was used to estimate the equilibrium chain length in liquid selenium,[6] and that changes of viscosity of liquid selenium with pressure can be interpreted in terms of the ring-chain equilibrium theory.[7] However, since both the fluidity of a polymer melt (due purely to molecular flow) as well as the rate of the possible chemical bond interchange reaction decrease drastically between the melting point and the glass transition region, without a detailed knowledge of the activation energies involved it is impossible to state which of these mechanisms is responsible for the low temperature flow behavior.

The viscoelastic behavior of polymers relaxing by the mechanism of molecular flow has been investigated extensively. Of particular interest here is the correlation between the maximum relaxation time in stress relaxation, τ_m, and the chain length in the transition region, as worked out by Tobolsky and Murakami.[8] It was shown that above the critical entanglement molecular weight, the maximum relaxation time is proportional to the 3.4 power of the chain length, the factor dropping to between 1 and 2 below the critical molecular weight, just as in the case of the bulk viscosity.[9] Thus, if one could synthesize a series of selenium polymers of differing molecular weights, one could, from their viscoelastic behavior in the flow region, determine whether the flow mechanism is molecular flow or bond interchange. If it is molecular flow, then the log of the maximum relaxation time should be proportional to the log of the chain length[8]; if, on the other hand, the flow mechanism is bond interchange, then no such dependence should be observed.

Fortunately, it is possible to synthesize selenium samples of various molecular weights by the simple expedient of melting the sample in the presence of iodine. The effect of iodine in depressing the viscosity of selenium melts is well known[10] and can best be explained on the basis of chain termination by iodine atoms. The quantitative aspects of molecular weight depression by the halogens will be discussed in section IV; suffice it to say here that above *ca.* 0.01 g.-atom of iodine per mole of selenium, the equilibrium chain length is highly insensitive to the original molecular weight (about which there is still some controversy), but depends only on the iodine content. Thus, we have a very reliable estimate of the molecular weight of the polymer and can use that for correlations with the viscoelastic properties.

II. Experimental Procedure

A. Preparation of Polymer. For the stress relaxation experiments, the selenium (A. D. McKay, 99.999%) was mixed with iodine (Baker analyzed reagent, used without further purification) and heated in evacuated and sealed glass ampoules for 2 days at 300°. The ampoule was then cooled, the polymer fragmented, and the fragments placed in several small diameter (~3 mm.) Pyrex or Vycor tubes. These tubes were again evacuated and sealed while at low temperatures, then brought back up to 300° for 1–2 days, and rapidly quenched in cold methanol (at ~−100°). This was done to keep re-equilibration (and therewith a change in the Se_8 ring concentration) to a minimum. The quenched samples, still in the glass tubes, were then removed by cracking the glass envelope in a small press at a temperature at or above T_g of that material to prevent breakage of the sample. Once prepared, the polymer was either tested immediately or stored below its glass transition temperature until used. This procedure yielded a series of samples of uniform iodine content and in a state of internal molecular equilibrium corresponding very closely to that at 300°.

In the case of pure selenium or samples of very low iodine content, the rate of crystallization above T_g is sufficiently slow to allow molding the samples. This was done in small rectangular molds (0.2 × 0.9 × 3.6 cm.) at *ca.* $T_g + 15°$. The higher iodine samples were used in the form of cylinders.

B. Glass Transition Determination. The glass transitions were determined either by monitoring the weight of the sample suspended in a liquid of known uniform expansion coefficient[11] or dilatometrically. Both are standard methods and will not be described here further. The results fell on a smooth line shown in Figure 1.

C. Stress Relaxation. The stress relaxation runs were performed in an instrument described briefly elsewhere.[5] In the low modulus region, stress relaxation was performed in tension, whereas bending was employed above $E = 10^9$ dynes/cm.[2]. Pure selenium and the lowest iodine-containing samples were run in the form of rectangular prisms (see above), while the higher iodine-containing samples were run in the form of cylinders.

Iodine is known to accelerate the rate of crystallization of selenium.[12] This manifests itself in an increase of the Young's modulus with storage time at constant

(4) E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **82**, 6009 (1960).
(5) A. Eisenberg and L. Teter, in press.
(6) A. Eisenberg, *J. Polymer Sci.*, **B1**, 33 (1963).
(7) D. E. Harrison, *J. Chem. Phys.*, **41**, 844 (1964).
(8) A. V. Tobolsky and K. Murakami, *J. Polymer Sci.*, **40**, 443 (1959).
(9) T. G Fox, S. Gratch, and S. Loshaek in "Rheology," F. R. Eirich, Ed., Academic Press, New York, N. Y., 1956, Chapter 12; H. Sobue and K. Murakami, *J. Polymer, Sci.*, **A1**, 2039 (1963).

(10) H. Krebs, *Z. anorg. allgem. Chem.*, **263**, 309 (1950).
(11) P. Mondain-Monval, *Ann. Chem.*, [11] **3**, 18 (1935).
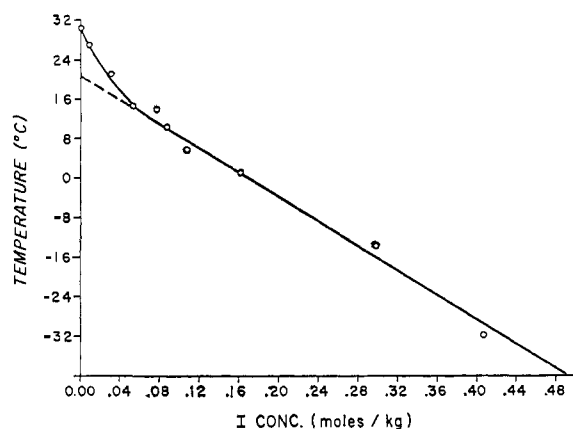(12) L. E. Hedman, *Arkiv Fysik*, **21**, 161 (1962).

Figure 1. Glass transition temperature of selenium *vs.* iodine concentration.
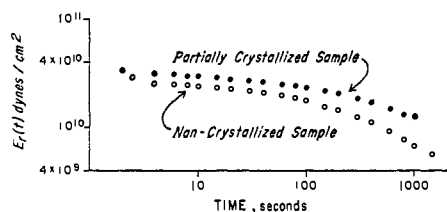

Figure 2. Effect of crystallization on modulus; Young's modulus *vs.* time for material immediately after preparation and after storage.

temperature. Thus, if several stress relaxation runs are performed on one selenium sample, the modulus increases appreciably. This is shown in Figure 2 for [I] = 0.031 mole/kg., run at two different times. Because of this, only one run was made on some samples with a high iodine content, if the temperature was far above T_g. With lower iodine content or near the glass transition, this phenomenon was relatively unimportant.

III. Experimental Results

The original stress relaxation data, plotted as log $E_r(t)$ *vs.* log time (where $E_r(t)$ is the time-dependent relaxation modulus) for pure selenium, are shown in Figure 3. In Figure 4, we reproduce the master curve for that sample, plotted for $t = 30°$, the glass transition temperature of the material. The second approximation to the distribution of relaxation times[13] for that sample is also shown for comparison with the normal organic polymers. The master curve for pure selenium obtained here may be compared with the one determined before[2a] with a much smaller number of runs. The master curves for all the samples are shown in Figure 5 (plotted for the T_g of each sample), which shows very clearly the molecular weight dependence of the flow region. Finally, the applicability of the W.L.F. equation[14] is shown in Figure 6 for pure selenium. The samples of higher iodine content showed a discrepancy from the W.L.F. form, the discrepancy increasing with the iodine content.

(13) J. D. Ferry and M. L. Williams, *J. Colloid Sci.*, 7, 347 (1952); M. L. Williams and J. D. Ferry, *J. Polymer Sci.*, 11, 169 (1963).
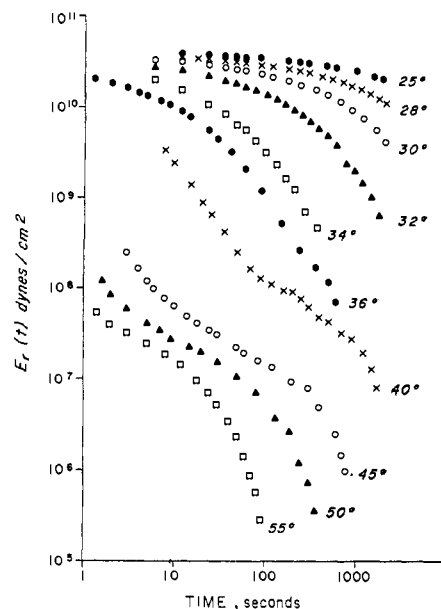(14) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, 77, 3701 (1955).

Figure 3. Stress relaxation data for pure selenium for various temperatures; Young's modulus *vs.* time.
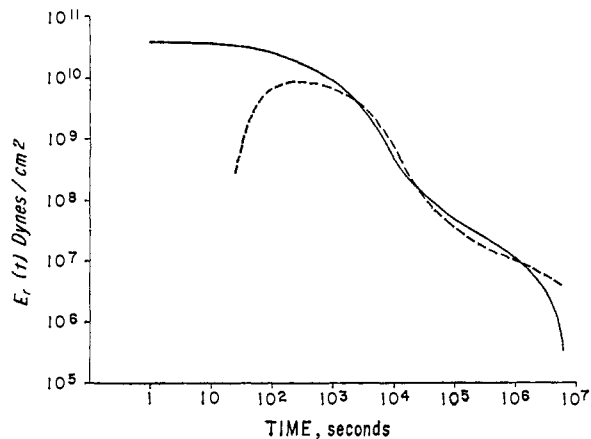

Figure 4. Stress relaxation master curve (solid line) and distribution times (dashed line) for pure selenium; Young's modulus *vs.* time.

IV. Calculation of Molecular Weights

A theoretical discussion of the equilibrium polymerization of selenium was presented before.[2b] In that publication, the selenium ring–chain equilibrium was taken to be analogous to the one occurring in sulfur, the reactions being

$$M \rightleftharpoons M^* \tag{1}$$

(where M is an Se_8 ring and M^* an Se_8 diradical) subject to the equilibrium constant K, and

$$M_n^* + M \rightleftharpoons M_{n+1}^* \tag{2}$$
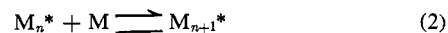
(where n is the number of Se_8 units in the chain) subject to equilibrium constant K_3.

In the presence of initiator, two additional reactions have to be considered. The first of these is chain initiation by an iodine atom

$$X + M \rightleftharpoons XM^{\neq} \tag{3}$$
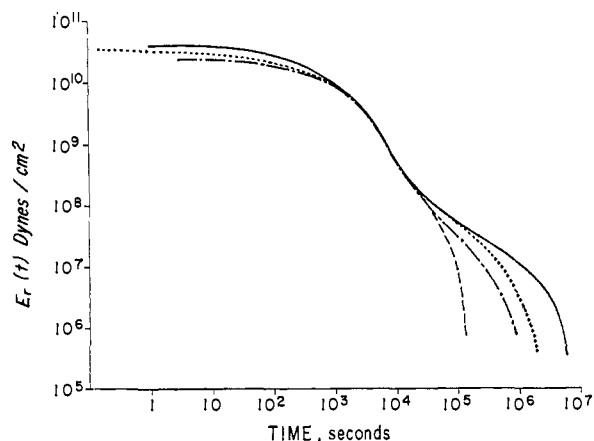
(where $XM^{\neq}$ is an ISe_8 monoradical) in which the reaction

Figure 5. Stress relaxation master curves for all samples; Young's modulus *vs.* time: ————, pure selenium; --------, selenium with 0.00964 mole/kg. of iodine; ———-—, selenium with 0.0312 mole/kg. of iodine; – – – –, selenium with 0.0874 mole/kg. of iodine.

Figure 6. Shift factors for pure selenium *vs.* $T - T_g$; points experimental; curve from W.L.F.[14] expression.

is assumed to be essentially quantitative from bond energy considerations (the strength of the S–S bond is 54 kcal.,[15] that of Br–Br is 46 kcal., while that of S–Br is 58 kcal., or stronger than either of the elements; although data for the Se–I bond strength is not available, if the same trends are followed, the concentration of I_2 in the Se–I mixture should be negligible). For this reason, $XM^{\neq}$ can be taken to be the initiator without loss of generality (if $X << M$), and this is subsequently labeled $Y^{\neq}$; the polymerization reactions involving these species then are

$$Y^{\neq} + M \rightleftharpoons YM^{\neq} \qquad (4)$$

$$YM_n^{\neq} + M \rightleftharpoons YM_{n+1}^{\neq} \qquad (5)$$
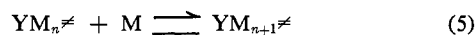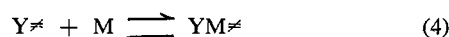
all subject to the equilibrium constant K_3 since $Y^{\neq}$ itself already possesses a long enough segment of selenium atoms. The second new reaction is the recombination of the iodine-containing monoradicals, which can be represented by

$$YM_n^{\neq} + YM_p^{\neq} \rightleftharpoons Y_2M_{n+p} \qquad (6)$$
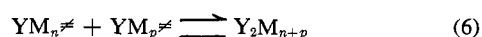
the equilibrium constant for which can easily be shown to be K_3/K.[16] Proceeding exactly as in ref. 2b and the work on sulfur before it, we first sum over all the polymeric species. The concentration of all diradical polymer molecules is (*cf.* ref. 2b)

$$N_1 = KM/(1 - K_3M) \qquad (7)$$

where M is the equilibrium monomer concentration and subsequent italicized letters denote appropriate concentrations. The concentration of all monoradical molecules is

$$N_2 = Y/(1 - K_3M) \qquad (8)$$

and that of all molecules terminated by iodine atoms on each end is

$$N_3 = (Y^2K_3/K)/(1 - K_3M) \qquad (9)$$

The total concentration of polymer molecules of all kinds is then

$$N = (KM + Y + Y^2K_3/K)/(1 - K_3M) \qquad (10)$$

We then sum over all monomer units incorporated in polymer molecules. The concentration of monomer segments incorporated in diradical polymer is

$$W_1 = KM/(1 - K_3M)^2 \qquad (11)$$

just as in ref. 2b. Similarly, the concentrations of monomer segments incorporated in monoradical and completely terminated polymer are, respectively

$$W_2 = Y/(1 - K_3M)^2 \qquad (12)$$

and

$$W_3 = Y^2K_3(2 - K_3M)/K(1 - K_3M)^2 \qquad (13)$$

The total concentration of monomer segments incorporated in all types of polymer is then

$$W = W_1 + W_2 + W_3 = [KM + Y + Y^2K_3(2 - K_3M)/K]/(1 - K_3M)^2 \qquad (14)$$

The number-average degree of polymerization is calculated from

$$P = W/N \qquad (15)$$

Just as in the purely autoinitiated case

$$K_3M \sim 1, \text{ and } 2 - K_3M \sim 1 \qquad (16)$$

Making this approximation, we obtain

$$P \sim 1/(1 - K_3M) \qquad (17)$$

Now, mass-balance equations can be set up. The total monomer concentration must be equal to the equilibrium monomer concentration plus the total concentration of monomer incorporated in the polymer, *i.e.*

$$M_0 = M + W_1 + W_2 + W_3 = M + [KM + Y + Y^2K_3(2 - K_3M)/K]/(1 - K_3M)^2 \qquad (18)$$

Similarly, the total concentration of initiator molecules, Y_0, is equal to the total concentration of monoradical polymer molecules (which contain only one iodine atom) plus twice the concentration of polymer molecules terminated at both sides, *i.e.*

$$Y_0 = N_2 + 2N_3 = Y/(1 - K_3M) + [2Y^2K_3/K]/(1 - K_3M) \qquad (19)$$

We wish to obtain an expression for P in terms of K, K_3, M_0, and Y_0, recalling that for $P >> 1$, $K_3 \sim 1/M$. This can be done by solving eq. 18 for Y in

(15) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth Scientific Publications, London, 1958.
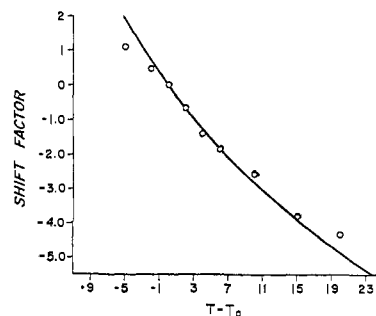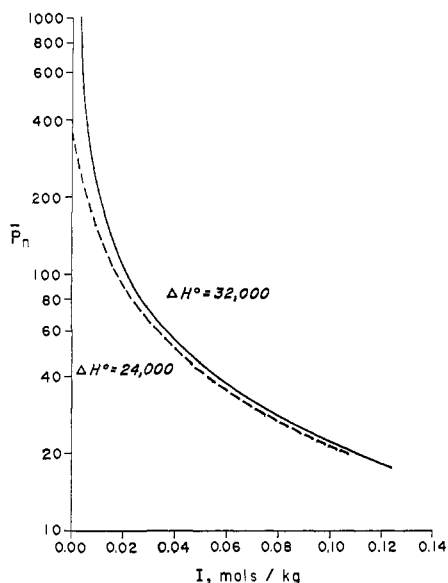(16) A. Eisenberg, Ph.D. Dissertation, Princeton University, 1960.

Figure 7. Calculated degree of polymzerization vs. iodine concentration in selenium for two values of $\Delta H°$.

Figure 8. Young's modulus vs. time (on semilog plot) for pure selenium.

terms of K, K_3, and P [$= 1/(1 - K_3M)$] and inserting the resultant expression into eq. 19. Procedurally it is more convenient to take a value of P, calculate the corresponding value of Y from eq. 18, and then calculate Y_0 from eq. 19. The results of these calculations are shown in Figure 7 for the following values: for curve "A," $T = 300°$ (573°K.), $K_3 = 2.1$ kg./mole, and $K = 1.8 \times 10^{-5}$ (i.e., $\Delta S° = 23$ e.u., $\Delta H° = 24,000$ cal./mole); for curve "B," $T = 300°$ (573°K.), $K_3 = 2.1$ kg./mole, and $K = 7.4 \times 10^{-8}$ ($\Delta S° = 2.30$ e.u., $\Delta H° = 32,000$ cal./mole). The choice of these two constants will be discussed later.

V. Discussion

It is evident from inspection of Figure 5 that the relaxation behavior of selenium as a function of chain length is very similar to that of the normal organic polymers, i.e., those relaxing by molecular flow rather than bond interchange. Since it is extremely unlikely that the relaxation mechanism changes within the narrow temperature range under investigation here, it may be concluded that the same mechanism is operative both in the transition region and in the flow region. This, incidentally, is tacitly assumed when performing the shift of the data from various temperatures (Figure 1) to obtain the master curve (Figures 4 and 5). As is frequently observed[8] the terminal portion of such a master curve, when plotted as log $E_r(t)$ vs. linear time, shows distinct linearity from which the maximum relaxation time can be calculated. A plot of this type for pure selenium is shown in Figure 8, the results for the others being shown in Table I, together with the calculated values of the number-average degree of polymerization. In the absence of an independent method of molecular weight determination, the $\overline{P_n}$ values calculated in Table I can be averaged for the iodine-containing samples where $\Delta H°$ has only a minor influence, and the results plotted against τ_m on a log–log scale (not shown here). The slope of this plot ($\Delta \log \tau_m/\Delta \log \overline{P_n}$) is 1.5, in general agreement with values obtained for polymers below the critical
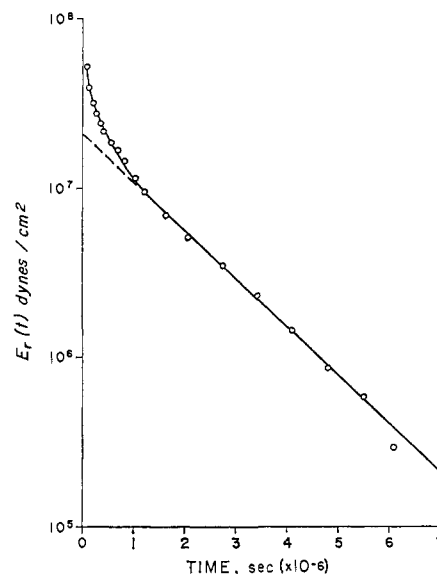
entanglement molecular weight. The τ_m value of pure selenium corresponds on that plot to a chain length of ca. 300 Se_8 units, in good agreement with the original calculation of Eisenberg and Tobolsky[2b] (and the subsequent recalculation of $\Delta H°[6]$) for 300°. This value, however, is lower by a factor of ca. 100 than that obtained by Poulis, et al.,[17] by susceptibility measurements assuming free-radical terminated chains. This latter value of the chain length corresponds to a $\Delta H°$ of slightly over 32,000 and explains the choice of that figure in section IV.

Table I

Sample no.	I, mole/ kg.	$\overline{P_n}$ $\Delta H = 24,000$	$\Delta H = 32,000$	τ_m at Tg
1	0	357	5600	1.5×10^6
2	0.00964	150	225	4.6×10^5
3	0.0312	63	70	2.3×10^5
4	0.0874	24.5	25.5	2.5×10^4

Although the work performed here does tend to confirm the original chain-length estimates, it should not be taken as the final word on the subject. This study was not performed with a view of settling the question of the chain length of the pure material, but only in an attempt to elucidate the relaxation mechanism. This, we feel, has been shown to be molecular flow rather than bond interchange. The puzzling question in regard to the chain length in pure selenium must await further extensive studies. The conclusions of this study are in no way affected by this uncertainty, since the chain-length values of the iodine-containing samples, on which the conclusions are based, are very insensitive to the $\Delta H°$ value.

Acknowledgments. We thank Professor J. D. McCullough for a most valuable discussion in connection with the quantitative aspects of the reaction of

(17) C. H. Massen, A. G. L. M. Weijts, and J. A. Poulis, *Trans. Faraday Soc.*, 60, 317 (1964).

iodine and selenium. We also thank Mr. D. Venerable for his assistance with some of the glass transition

determinations. The financial assistance of the office of Naval Research is gratefully acknowledged.

Stable Thiotrifluoromethylphosphines[1]

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Thiophosphines can be stable if CF_3 is attached to phosphorus, preventing isomerization to phosphine sulfides in the Arbuzov manner. The new volatile compounds $(CF_3)_2PSP(CF_3)_2$ (m.p. $-33°$; b.p. est. $112°$), HSP-$(CF_3)_2$ (m.p. $-100°$; b.p. est. $55°$), $CH_3SP(CF_3)_2$ (m.p. $-58°$; b.p. est. $92°$), $t\text{-}C_4H_9SP(CF_3)_2$ (m.p. $-18°$; b.p. est. $144°$), and $(CH_3S)_2PCF_3$ (m.p. $-65°$; b.p. est. $168°$) undergo no such conversion, whereas a slow catalytic isomerization of $ROP(CF_3)_2$ is possible. The syntheses were accomplished mostly by $(CH_3)_3N$-assisted thiolyses of $CF_3\text{-}P$ halides, except that HSP-$(CF_3)_2$ came from cleavage of $(CF_3)_2PSP(CF_3)_2$ by H_2S or HCl. The H_2S cleavage is slightly reversible: whereas $(CF_3)_2POH$ is stable, $HSP(CF_3)_2$ forms some H_2S and $(CF_3)_2PSP(CF_3)_2$. The HCl cleavage of $(CF_3)_2$-$PSP(CF_3)_2$ occurs at both P–S bonds, forming more $(CF_3)_2PCl$ than $HSP(CF_3)_2$. Accurate infrared spectra of the five new thiophosphines are compared.

The recent isolation and study of the new oxyphosphines $(CF_3)_2POP(CF_3)_2$,[2] $(CF_3)_2POH$,[2] and the ester types $ROP(CF_3)_2$[2,3] and $(RO)_2PCF_3$[4] led to the question whether the analogous thiophosphines would show any very different chemical behavior. In fact, the new compounds $(CF_3)_2PSP(CF_3)_2$, $HSP(CF_3)_2$, $CH_3SP(CF_3)_2$, $t\text{-}C_4H_9SP(CF_3)_2$, and $(CH_3S)_2PCF_3$ proved to be fairly similar to the corresponding oxyphosphines, but with some significant differences.

One difference is the appreciably greater resistance of the $RSP(CF_3)_2$ type to isomerization in the Arbuzov manner: *i.e.*, conversion to the $R(CF_3)_2PS$ type. For example, neither $CH_3SP(CF_3)_2$ nor $t\text{-}C_4H_9SP$-$(CF_3)_2$ could be even slightly converted to the corresponding tertiary phosphine sulfide by the aid of CH_3I during a week at $100°$, whereas $t\text{-}C_4H_9OP(CF_3)_2$ with CH_3I was mostly converted to the phosphine oxide $t\text{-}C_4H_9(CF_3)_2PO$ during 2 hr. below $80°$ and $CH_3OP(CF_3)_2$ could be partially isomerized at higher temperatures and pressures.[2] One reason for the difference might relate to the sometimes observed higher fission-resistance of alkyl–sulfur *vs.* alkyl–oxygen bonding. However, such a kinetic stability of S–C bonding does not prevent the rapid spontaneous isomerization of $RSP(C_6H_5)_2$ compounds.[5]

(1) Supported by Grant No. GP-199 from the National Science Foundation, which contributed also through Grant No. G-14665 toward the purchase of the Beckman IR7 instrument.
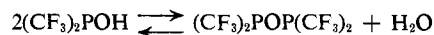(2) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).
(3) H. J. Emeléus and J. D. Smith, *J. Chem. Soc.*, 380 (1959).
(4) A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, **83**, 4333 (1961).
(5) A. E. Arbuzov and K. V. Nikoronov, *Zh. Obshch. Khim.*, **18**, 2008 (1948).

The thiobisphosphine $(CF_3)_2PSP(CF_3)_2$ proved to be almost as stable as the corresponding diphosphoxane, for only 17% decomposed during 6 days at $200°$, forming $(CF_3)_3P$ and other products not identified. Unlike the analogous thiobisarsine, which loses sulfur on contact with mercury at $25°$, producing $(CF_3)_2As$–$As(CF_3)_2$,[6] this P–S–P compound is inert to mercury up to $150°$ (16 hr., slight action). It is not surprising that the P–S–P chain is more stable than As–S–As in the same situation, for phosphorus bonding orbitals are at deeper energy levels than the corresponding arsenic orbitals; also the node in the arsenic $4d_\pi$ orbital would be unfavorable to S_{3p}–As_{4d} π-bonding.

The thiophosphinous acid $HSP(CF_3)_2$ seems to resist a protonic rearrangement quite as well as $(CF_3)_2POH$ does, but is less stable on account of a tendency to undergo condensation, forming $(CF_3)_2PSP(CF_3)_2$ and H_2S. The difference may be explained by assuming that S_{3p}–P_{3d} π-bonding is intrinsically less effective than O_{2p}–P_{3d} π-bonding. Thus if we write

$$2(CF_3)_2POH \rightleftharpoons (CF_3)_2POP(CF_3)_2 + H_2O$$

$$2(CF_3)_2PSH \rightleftharpoons (CF_3)_2PSP(CF_3)_2 + H_2S$$

it can be argued that two molecules of a left-hand component develop more π-bonding energy than is afforded by the corresponding right-hand components; hence the forward reaction would be suppressed more for the system in which the π-bonding is intrinsically stronger. In fact, the forward reaction has not been detected for $(CF_3)_2POH$, whereas for the thio compound it is easily observable. Even so, this condensation is not extensive, for an efficient synthesis of HSP-$(CF_3)_2$ is based upon the reverse process of cleaving $(CF_3)_2PSP(CF_3)_2$ by H_2S.

The same condensation offers one way to account for the unequal cleavage of $(CF_3)_2PSP(CF_3)_2$ by HCl, yielding more than one $(CF_3)_2PCl$ and less than one $HSP(CF_3)_2$. Condensation of the latter would form H_2S and $(CF_3)_2PSP(CF_3)_2$ for further cleavage, thus affording a secondary process equivalent to direct cleavage of $HSP(CF_3)_2$ by HCl. The analogous direct cleavage of $CH_3SP(CF_3)_2$ gave one $(CF_3)_2PCl$ per HCl consumed, but could not be forced to completion: even with HCl at 10 atm. pressure (5.5 days, $100°$) forward progress beyond 15% was not achieved. No such cleavage of $(CF_3)_2POH$ has been noticed: HCl cleaves $(CF_3)_2POP(CF_3)_2$ cleanly, with no secondary effect.[2]

(6) W. R. Cullen, *Can. J. Chem.*, **41**, 2424 (1963).