BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 135—139 (1968)

Glass Transition Temperature and Isothermal Volume Change of Selenium

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(Received July 14, 1967)

The viscoelastic behavior of selenium and of partially-chlorinated selenium was studied by the dilatometric method. The glass transition temperature, T_g, of selenium was determined to be 32.0°C at a cooling rate of 0.2°C/min. The glass transition temperature decreased linearly with the reciprocal of the average chain length of selenium. The chain length was calculated using the degree of chlorination. An abrupt increase in T_g was observed at a chlorine content of about 0.013%. The volume-time curves obtained by the determination of the volume of selenium in the neighborhood of T_g were superposed on each other by sliding them along the abscissa. The values of the shift factor and of T_g fit well in Williams, Landel and Ferry's equation. The parameters in the WLF equation, $C_1{}^g$ and $C_2{}^g$, of selenium were calculated to be 6.86 and 28.6 respectively. Both the parameters increased with an increase in the chlorine content up to 0.0125%, and reached the values of usual polymers above 0.0125%. The WLF f_g value of selenium was calculated to be 6.33×10^{-2}. This value decreased with an increase in the chlorine content, and reached the universal value of usual polymers (2.5×10^{-2}) when the chlorine content was more than 0.0125%. The chlorine content corresponds to 0.0125% when all the radicals at both ends of the linear chain molecules of selenium have been used in forming bonds with chlorine atoms. Therefore, it may be concluded that the existence of radicals at the molecular ends of selenium chains brings about an augmentation of the fraction of the free volume at T_g.

Amorphous selenium is considered to be a mixture of Se_8 ring molecules and long chains.[1] The properties of amorphous selenium should be governed by those of the long-chain molecules, since the content of the ring molecules in amorphous selenium has been estimated to be only 0.22 wt% at 230°C.[2] The number of selenium atoms in a chain of average length was calculated to be 7200 at 230°C by the thermodynamic theory developed by Eisenberg and Tobolsky.[1] This result agreed with that obtained by Shirai and Hamada by means of measurements of the viscosity of molten selenium.[3] The linear chains may be considered to be diradical molecules with an unpaired electron at each end of the chains. The presence of radicals in amorphous selenium was reported by Abdullaev *et al.*[4] and by Sampath *et al.*[5] on the basis of their ESR studies. Sampath[6] reported that the results obtained by Eisenberg and Tobolsky, and by Shirai and Hamada were supported by the value of the spin concentration in amorphous selenium.

In our work, the viscoelastic behavior of amorphous selenium was investigated by the method of isothermal volume contraction, similar to Kovacs' measurments of organic polymers.[7] Moreover,

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[1] A. Eisenberg and A. V. Tobolsky, *J. Polymer Sci.*, **46**, 19 (1960).
[2] G. Briegleb, *Z. Phys. Chem.*, **A144**, 321 (1929).
[3] T. Shirai and S. Hamada, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 968 (1963).
[4] G. Abdullaev, W. I. Ibragimov, Sh. V. Mamedov, T. Ch. Dzhuvarly and G. H. Aliev, *Dokl. Akad. Nauk Azerb. SSR*, **20**, 13 (1964).
[5] P. I. Sampath and R. C. Keezer, *Bull. Am. Phys. Soc.*, **10**, 613 (1965).
[6] P. I. Sampath, *J. Chem. Phys.*, **45**, 3519 (1966).
[7] A. J. Kovacs, *J. Polymer Sci.*, **30**, 131 (1958).

the effect of radicals on the viscoelastic behavior of amorphous selenium was studied.

Experimental

Materials. The selenium was obtained from the Yokozawa Chemical Company; the guaranteed purity was more than 99.999%. The sample of amorphous selenium was prepared by quenching the molten selenium; the selenium was heated in an electric furnace at 230°C for 1 hr, then dropped in cold water and dried in a cooled vacuum dessicator. Chlorinated selenium was prepared by the method described in a previous paper.[8] The sample of chlorinated selenium was prepared by the same method which was used in preparing the amorphous selenium. The chlorine content in the chlorinated selenium was determined by the colorimetric method described in the previous paper.

Procedure. The glass transition temperatures, T_g, of the selenium and of the chlorinated selenium were estimated by the dilatometric method. A specimen of about 7 g of the amorphous selenium was sealed in a dilatometer containing about 62 g of mercury. The capillary was 0.726 mm in diameter and about 250 mm long. The height of the meniscus of mercury in the capillary was measured, using a measuring microscope, to the accuracy of 1/100 mm. The dilatometer was kept at 50°C for 30 min to establish the thermal equilibrium; then it was allowed to cool slowly at a cooling rate of 0.2°C/min. The glass transition temperature of the amorphous selenium was estimated graphically from the specific volume-temperature relationship.

The isothermal volume contraction phenomena of the amorphous selenium were also studied by the dilatometric method. The dilatometer was first kept at 50°C for 30 min; then it was quickly immersed into a water bath kept at a specified temperature in the neighborhood of T_g. The accuracy of the temperature was about ±0.1°C. The change in the height of the mercury column in the capillary was followed against the time in which the dilatometer had been immersed in the water bath.

Results

The Glass Transition Temperature of the Selenium. Figure 1 shows the specific volume-temperature relationship of the selenium when the specimen was cooled at a rate of 0.2°C/min. This relation was similar to those of usual organic polymers. The glass transition temperature of the selenium was estimated graphically to be 32.0°C at the cooling rate studied. This value was nearly equal to that obtained by Tammann and Kohlhaas (31°C).[9] The value of T_g was reproducible. It is well known that T_g depends on the rate of cooling. The glass transition temperature of selenium was also governed by the time scale of the measurement.[10,11] In the present work, therefore, the cooling rate of the specimen was kept at 0.2°C/min.

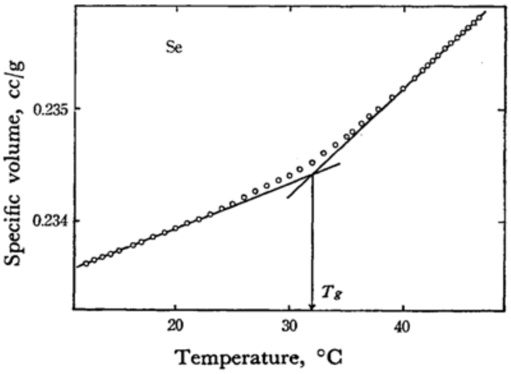

Fig. 1. Plot of specific volume against temperature.

The Glass Transition Temperature of the Chlorinated Selenium. The specific volume-temperature relationships of the chlorinated selenium specimens were similar to that of the selenium. Figure 2 shows the relationship between the T_g of the chlorinated selenium and the chlorine content. The glass transition temperature of selenium decreased as the chlorine content increased up to about 0.013%, while an abrupt increase in T_g was observed at about 0.013%.

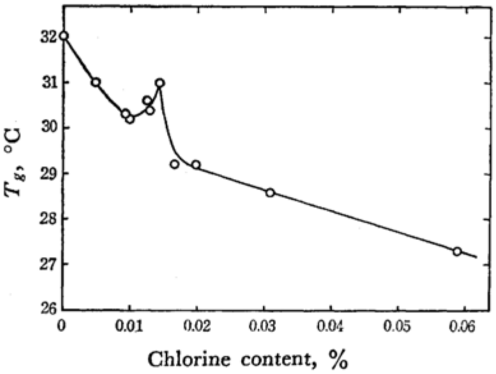

Fig. 2. Plot of T_g against chlorine content.

It is well known that an elevation of the T_g of organic polymer is observed when the polar group is introduced into the chain molecules. The abrupt increase in the T_g of the chlorinated selenium at a chlorine content of about 0.013% probably arose because of the large electronegative character of the introduced chlorine atoms, which terminated the radicals at the chain ends of the selenium molecules. The glass transition temperature of the chlorinated selenium with a chlorine

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[8] S. Hamada, T. Sato and T. Shirai, This Bulletin, **40**, 864 (1967).

[9] G. Tammann and A. Kohlhaas, *Z. anorg. Chem.*, **182**, 49 (1929).

[10] E. Jenckel, *Z. Elektrochem.*, **43**, 796 (1947).

[11] T. Sekiguchi, *Sci. Papers I. P. C. R.*, **54**, 281 (1960).

content above 0.013% decreased linearly with an increase in the chlorine content. Fox and Flory[12] reported that the T_g of polystyrene decreased linearly with the reciprocal of the molecular weight when the molecular weight was not very large. The relation between the number of selnium atoms in an average-length chain of chlorinated selenium, Z_n, and the chlorine content, p, is shown as follows, after the chain ends have been terminated by chlorine atoms:

$$Z_n = 2\times 35.5(100-p)/78.96p$$

If the chlorine content is very small, Z_n is expressed as follows:

$$Z_n = 89.92/p$$

That is, the chlorine content is proportional to the reciprocal of the number of selenium atoms in an average-length chain of chlorinated selenium. The glass transition temperature of the chlorinated selenium decreased linearly with an increase in the chlorine content, as is shown in Fig. 2. This result agrees with that obtained by Fox and Flory.

The Isothermal Volume Change of the Selenium. A retardation of the volume change of the selenium was observed as in the case of organic polymers. Figure 3 shows the relation between the volume change of the selenium and the time, when the specimen kept at 50°C for 30 min was quickly immersed into a water bath kept at a specified temperature in the neighborhood of T_g. The volume changes, which were the differences between the equilibrium volume, $V_{T(\infty)}$, and the volume at the time $(t-a)$, $V_{T(t-a)}$, at several temperatures, are shown as the readings of the mercury meniscus in the capillary. The time which the dilatometer had been immersed in the water bath was expressed as $t-a$. The corrective factor, a, is a half of the time needed to attain the thermal equilibrium from 50°C to a specified temperature. The value of a was estimated to be 25 sec by a measurement made when the dilatometer containing mercury alone was quickly cooled in the same manner.

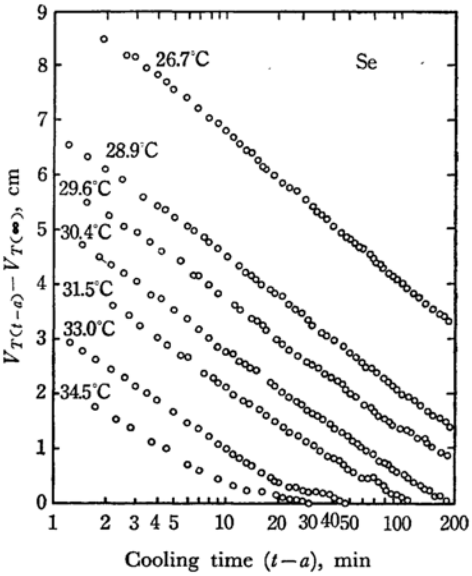

Fig. 3. Relationship between volume change and cooling time.

In order to study the volume relaxation phenomena of the selenium, the time-temperature superposition principle was applied.[7,13] The values of the shift factor, a_T, were estimated, since the volume-time curves could superpose upon each other by sliding along the abscissa. From

TABLE 1. PARAMETERS OF THE WLF EQUATION OF SELENIUM AND OF CHLORINATED SELENIUM

Chlorine content %	T_g °C	C_1^g	C_2^g	f_g (WLF) $\times 10^{-2}$	f_g (Kovacs) $\times 10^{-2}$	α_f $\times 10^{-4}$	$\Delta\alpha$ $\times 10^{-4}$	$\Delta\alpha T_g$ $\times 10^{-2}$
Se	32.0	6.86	28.6	6.33	4.80	22.1	2.80	8.54
0.00488	31.0	7.74	22.1	5.60	5.03	25.5	2.43	7.39
0.00928	30.3	8.56	27.8	5.07	4.56	18.2	2.25	6.90
0.0100	30.2						2.28	6.93
0.0125	30.6	15.5	68.6	2.80	2.23	4.08	2.16	6.54
0.0128	30.4	16.7	63.5	2.62	2.20	4.09	2.18	6.60
0.0137	31.0	16.4	54.5	2.65	2.43	4.85	2.27	6.89
0.0166	29.2						2.24	6.77
0.0198	29.2	14.5	55.8	2.94	2.69	5.27	2.20	6.65
0.0310	28.6	14.7	55.0	2.96	2.34	5.39	2.22	6.69
0.0588	27.3						2.24	6.72
Usual polymers		17.4	51.6	2.5±0.3		(4.8)		11.3

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[12] T. G. Fox and P. J. Flory, *J. Polymer Sci.*, **14**, 315 (1954).

[13] T. Sekiguchi, *Sci. Papers I. P. C. R.*, **55**, 148 (1961).

the estimated a_T and T_g values, the parameters, C_1^g and C_2^g, in the WLF equation,[14] $\log a_T = -C_1^g(T-T_g)/(C_2^g+T-T_g)$, were calculated to be 6.86 and 28.6 respectively. These values were small compared with those of usual organic polymers (17.4 and 51.6 respectively).

The Isothermal Volume Change of the Chlorinated Selenium. The volume relaxation phenomena of the chlorinated selenium were similar to that of the selenium. The volume-time curves of the chlorinated selenium could superpose upon each other as in the case of the selenium. The values of the C_1^g and C_2^g of the chlorinated selenium were estimated from a_T and T_g.

The glass transition temperatures and the values of C_1^g and C_2^g are listed in Table 1.
Though both the values of C_1^g and C_2^g were small and increased only with an increase in the chlorine content, they were nearly equal to those of usual polymers (17.4 and 51.6 respectively) at chlorine contents above 0.0125%.

Discussion

The retardation phenomena of the volume contractions of the selenium and of the chlorinated selenium were observed as viscoelastic behavior. As the relation between T_g and a_T was shown as the WLF equation, the fraction of the free volume at T_g, f_g, of the selenium can be discussed using the values of the WLF parameters, C_1^g and C_2^g.

Williams, Landel, and Ferry[14] expressed f_g and the expansion coefficient of the free volume, α_f, on the basis of their empirical equation and Doolittle's free space equation for viscosity[15] as follows:

$$f_g = B/2.303C_1^g \qquad \alpha_f = B/2.303C_1^gC_2^g$$

where B is the constant in Doolittle's equation. Therefore, α_f corresponds to the difference, $\Delta\alpha$, between the expansion coefficient of the supercooled liquid state of the polymer, α_l, in the temperature range above T_g and the expansion coefficient of the glassy state, α_g, in the temperature range below T_g. The constant, B, can be ragarded as unity.[15] Bueche[16] supported this assumption by his theoretical treatment. Therefore, f_g and α_f are represented as $1/2.303C_1^g$ and $1/2.303C_1^gC_2^g$ respectively.

The calculated values of f_g and α_f and the empirical values of $\Delta\alpha$ are listed in Table 1.

Kovacs[7] expressed f_g on the basis of the WLF equation as follows:

$$f_g = (\alpha_f[\beta]_g/2.303\Delta\alpha v_g)^{1/2}$$

where $[\beta]_g$ is the slope of the volume-time curve at T_g in Fig. 2, and where v_g is the specific volume at T_g.

The calculated values of f_g, as defined by Kovacs, are listed in Table 1. Because both the values of f_g, that defined by WLF and that defined by Kovacs, were in good agreement with each other, they are likely to be reasonable values. Figure 4 shows the relationship between f_g and the chlorine content. The fraction of the free volume decreased with an increase in the chlorine content, and then reached about a constant value at chlorine contents above 0.0125%, as in the case of usual polymers (2.5×10^{-2}).

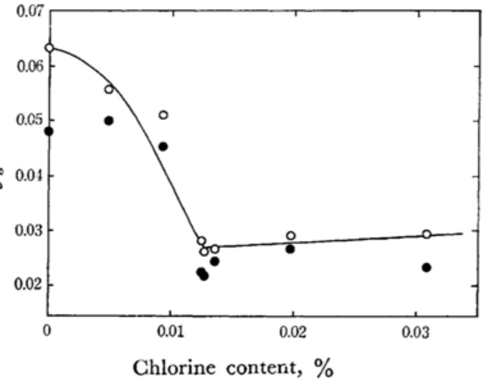

Fig. 4. Plot of f_g against chlorine content.
○: WLF's f_g ●: Kovacs' f_g

The calculated values of α_f, however, were about ten times larger than the empirical $\Delta\alpha$ values of the selenium and of the chlorinated selenium with chlorine contents of less than about 0.0125%, while the order of α_f values were the same as those of $\Delta\alpha$ at chlorine contents above 0.0125%. This notable disagreement of the values of α_f and $\Delta\alpha$ under these conditions may be caused by an abnormal value of B in Doolittle's equation. This has often been observed in usual polymers.[17] Therefore, the values of f_g defined by WLF and by Kovacs under these conditions can not be readily appraised as to their reasonableness.

Simha and Boyer[18] defined the fraction of the free volume at T_g to be $\Delta\alpha T_g$. The calculated values of $\Delta\alpha T_g$ are listed in Table 1. Though the value of $\Delta\alpha T_g$ increased with a decrease in the chlorine content at chlorine contents of less than about 0.0125%, nearly constant values of $\Delta\alpha T_g$ were observed above 0.0125%, as is shown in Fig. 5. The values of $\Delta\alpha T_g$, defined as the fraction of the free volume by Simha and Boyer, gave a curve with the same appearance as that

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14) M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
15) A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
16) F. Bueche, *J. Chem. Phys.*, **24**, 418 (1956).
17) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, New York (1961), p. 226.
18) R. Simha and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).

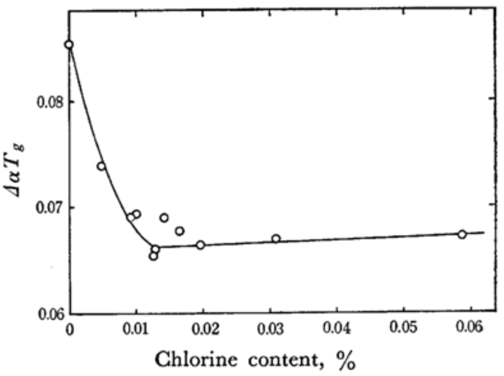

Fig. 5. Plot of $\Delta\alpha T_g$ against chlorine content.

obtained by WLF. This suggests that the f_g values of the selenium and of the chlorinated selenium with chlorine contents of less than 0.125% are larger than that of usual polymers (2.5×10^{-2}) in spite of an uncertainty regarding the values of the WLF f_g under these conditions.

As the number of selenium atoms in an average-length chain of the selenium at 230°C is 7200, the chlorine content corresponds to 0.0125% when all the radicals at both ends of linear chain molecules of the selenium have been dispensed in forming bonds with chlorine atoms. Thus, it may be concluded that the existence of radicals at the molecular ends of selenium chains brings about an augmentation of the fraction of the free volume at T_g. Though the mechanism of the augmentation of the fraction of the free volume at T_g by the existence of radicals has not been established, it may be considered to be due to bond interchange between neighboring selenium chains,[19] or to repulsion between radicals.

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[19] A. Eisenberg and A. V. Tobolsky, *J. Polymer Sci.*, **61**, 483 (1962).