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Kinetics of Selenium Spherulite Growth

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The growth rates of spherulites of selenium were estimated by the photomicrographic method in the temperature range from 80°C to 120°C. The selenium was used in the pure and the chlorinated states. At a constant temperature, the spherulite radius increased at a constant rate. The growth rate for pure selenium, log G, varied linearly with $1/T$, and the apparent activation energy for growth, E_A was estimated to be 24.9 kcal/mol. The apparent activation energy for growth is much larger than that for the transport of the chain molecule, which was estimated from the activation energy for the viscous flow. The linear variation in the growth rate, log G, with $1/T$ appeared at temperatures well below the melting point of crystalline selenium, and the apparent activation energy for growth was nearly equal to the enthalpy change for the thermal equilibrium of the opening reaction of the Se_8 ring molecule. These facts indicate that the selenium spherulite growth is not a diffusion-controlled process, but a breaking process of the Se-Se bond in the chain molecule. Moreover, the mechanism of growth at the amorphous-crystalline interface was considered with regard to the variation in the growth rate, in the apparent activation energy for growth, and in the activation entropy change against the chlorine content.

It is well known that a crystalline selenium obtained from an amorphous selenium consists spiral-chain molecules, extending along the C-axis of the hexagonal lattice. Also, it is considered that

the form of the amorphous selenium molecule is similar to that of the crystalline one, while the chain molecules are distributed in disorder.

When a selenium is crystallized, it grows as a spherulite, much as such organic polymers as polyethylene adipate, polyethylene saccinate, and Nylon 6. It is considered that the crystallization of selenium is performed by the reconstruction of the irregularly-distributed chain molecules.[1]

The number-average chain length of a pure selenium at 230°C was estimated to be 7200 by Eisenberg and Tobolsky's calculation[2] and by Shirai and Hamada's measurements.[3] Thus, the chain length of a pure selenium is finite, and there are radicals at both ends of the chain molecule.[4]

In this study, we compared the growth rates of the selenium spherulite with those of organic polymers, and observed the effect of the radicals at the molecular ends on the growth of the spherulite, when the radicals were terminated with chlorine atoms.

Experimental

Materials. The selenium was obtained from the Yokozawa Chemical Company, which guaranteed a purity of better than 99.999%. The sample of pure selenium was made by quenching the molten selenium, which had been heated on a 2 cm×2 cm frost-glass plate at 230°C for 1 hr in an electric furnace, and then storing it in a cooled desiccator. Chlorinated selenium was prepared by passing dried chlorine into the molten selenium; it was uniformalized at 230°C for 1 hr in an electric furnace as dried clean air was being passed into it to remove the remaining chlorine and such low-molecular-weight substances as selenium dichloride and selenium tetrachloride. For the preparation of the chlorinated selenium sample, the melt of the chlorinated selenium was quickly dropped on a frost-glass plate and then stored in a cooled desiccator.

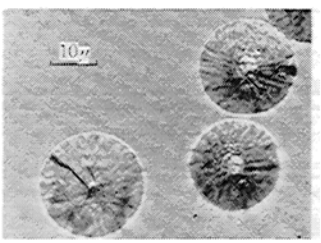
The ferric perchlorate solution was made by dissolving 40 g of freshly-prepared crystals of ferric perchlorate in 44 m*l* of 60% perchloric acid, and then diluting the solution to 100 m*l* with distilled water.

Procedure. An Olympus reflecting microscope, Model PMF, was used to observe the selenium spherulites. The selenium samples were crystallized continually in a small electric furnace, 7 cm in diameter and 4 cm high, mounted on the deck of the microscope. The temperatures of the furnace were regulated by a thermistor controller to ±0.2°C. The spherulites, which were formed on the surface of the samples at temperatures over the range from 80°C to 120°C, were photographed by a camera mounted on the microscope. The radii of the spherulites were estimated by comparing microscopic measurements of the photographs of the spherulites with the standard scale. The radial growth rate of the spherulite was estimated from the slope of the radius time curve.

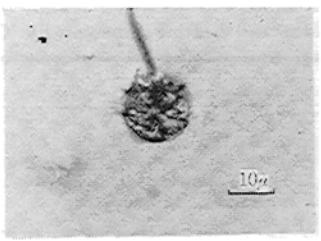
The colorimetric method was employed to determine the chlorine content of a chlorinated selenium.[5,6] A chlorinated selenium (about 2 g) was dissolved in nitric acid, and then a suitable amount of 5% barium nitrate solution was added to the solution. On the neutralization of the mixed solution with ammonia water, a white precipitate of barium selenite was produced. The precipitate was filtered off, and then the filtrate was diluted to a certain volume in a measuring flask. In order to development the color, 2 m*l* of a ferric perchlorate solution and 1.5 m*l* of a mercuric thiocyanate solution (a 0.5% methyl alcohol solution) were added to 10 m*l* of the diluted solution. A Beckman spectrophotometer Model DU was used to measure the absorbances of the colored solutions. The absorbances were measured at the wavelength of 460 mμ and compared with those of the blank solution.

Results

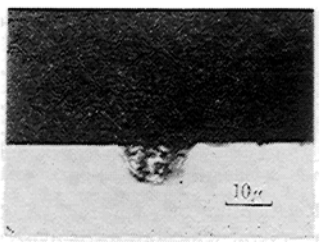
The crystals which were formed on the surface of the amorphous pure selenium sample are shown in Phot. 1. Sections of the crystals which were formed



Phot. 1. Crystals on surface of amorphous selenium.



Phot. 2. Section of crystal in inside of sample.



Phot. 3. Section of crystal on surface of sample.

1) D. Turnbull and M. H. Cohen, *J. Chem. Phys.*, **29**, 1049 (1958).
2) A. Eisenberg and A. V. Tobolsky, *J. Polymer Sci.*, **46**, 19 (1960).
3) T. Shirai and S. Hamada, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 968 (1963).
4) F. G. R. Gimblett, "Inorganic Polymer Chemistry," Butterworths, London (1963), p. 234.
5) S. Utsumi, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **73**, 835 (1952).
6) A. Tomonari, *ibid.*, **83**, 693 (1962).

in the inside and on the surface of the sample are shown in Phots. 2 and 3. These photographs indicate that the crystal was a radial one with a center. Kozyrev[7] reported that the crystal of selenium was grown as a spherulite without forming a single crystal because the kinetics of molecular attachment at the solid-liquid interface was sluggish when amorphous selenium was crystallized under atmospheric pressure. Since the shape of the section of the crystal which was formed on the surface of the sample was hemispheric, as is shown in Phot. 3, all the measurements of the growth rate were made by observing the spherulites which were formed on the surface of the samples.

The Radial Growth Rate of the Spherulite of the Pure Selenium. Since the radii of several spherulites varied linearly with the heating times, and since the slopes of the radius-time curves were nearly all equal with each other, as is shown in Fig. 1, it can be said that the growth rate of the spherulite was not affected by the developing periods of nuclei. Therefore, the radial growth rate was estimated from the relationship between the heating times and the average radii of several spherulites observed in the microscopic field. Figure 2 shows the relationship between the radii of the spherulites and the heating times when the amorphous pure selenium was crystallized at temperatures over the range from 80°C to 120°C. The radial growth rates, G, are given in Table 1.

TABLE 1. GROWTH RATES OF SPHERULITES OF PURE SELENIUM

Temp., °C	G, μ/min	Temp., °C	G, μ/min
80	0.0162	105	0.163
87	0.0300	110	0.246
90	0.0389	120	0.461
100	0.102		

The $\log G$ values varied linearly with the $1/T$ values at temperatures over the range from 80°C to 120°C, as Fig. 3 shows. The apparent activation energy for growth, E_A, was estimated to be 24.9 kcal/mol.

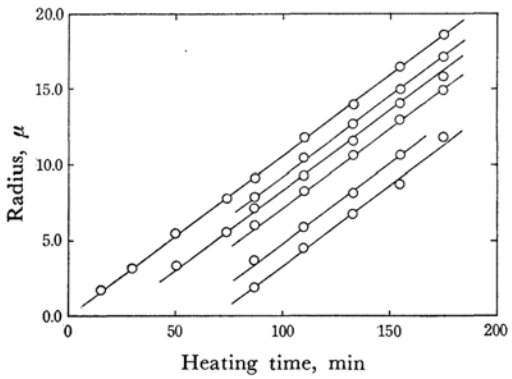


Fig. 1. Relationship between radii of several spherulites and heating times at 100°C in pure selenium.

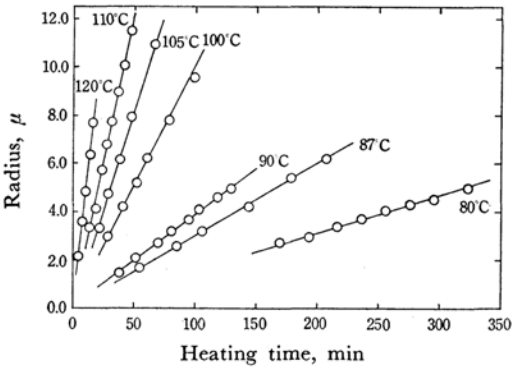


Fig. 2. Relationship between radii and heating times at several temperatures in pure selenium.

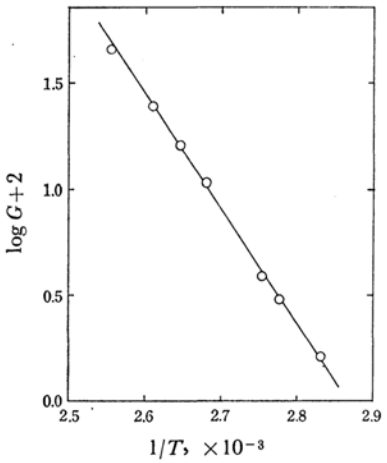


Fig. 3. Plot of $\log G$ of pure selenium against $1/T$.

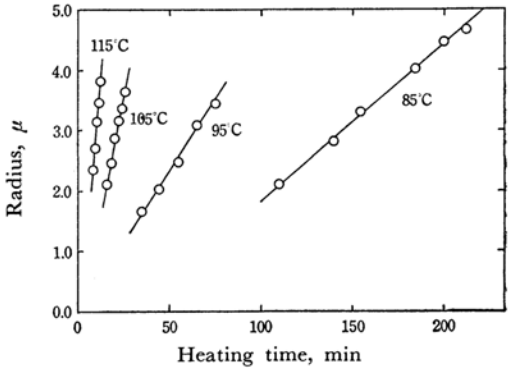


Fig. 4. Relationship between radii and heating times at several temperatures in chlorinated selenium of chlorine content of 0.0252%.

7) P. T. Kozyrev, *Soviet Physics-Technical Physics*, **28**, 470 (1958).

The Radial Growth Rate of the Spherulite of the Chlorinated Selenium. Figure 4 shows the relationship between the heating times and the radii of the spherulite of the chlorinated selenium with a chlorine content of 0.0252% at temperatures over the range from 85°C to 115°C. The radial growth rates, G, of the spherulite of the chlorinated selenium of the chlorine contents over the range from 0.0023% to 0.0287% are given in Table 2.

TABLE 2. GROWTH RATES OF SPHERULITES OF CHLORINATED SELENIUM

Chlorine content, %	G, μ/min			
	85°C	95°C	105°C	115°C
0.0023	0.0270	0.0711	0.152	0.401
0.0053	0.0275	0.0481	0.124	0.324
0.0079	0.0264	0.0482	0.101	
0.0083		0.0428	0.112	0.234
0.0101	0.0197	0.0428	0.107	0.233
0.0112	0.0284	0.0534	0.0931	0.211
0.0121		0.0600	0.106	
0.0124	0.0283	0.0544	0.125	0.288
0.0128	0.0262	0.0513	0.135	0.269
0.0129	0.0306	0.0652	0.125	
0.0143	0.0260	0.0521	0.103	0.322
0.0147	0.0241	0.0515		0.277
0.0161	0.0224	0.0495	0.0880	0.335
0.0175	0.0240	0.0515	0.0988	0.312
0.0189	0.0199	0.0480	0.0890	0.174
0.0222	0.0220			0.241
0.0243	0.0189	0.0407	0.134	0.269
0.0252	0.0262	0.0526	0.157	0.341
0.0287	0.0250	0.0449	0.139	0.240

The $\log G$ values varied linearly with the $1/T$ values except for those of the samples with chlorine contents over the range from about 0.0125% to 0.020%. The $\log G$ values at 115°C for samples with chlorine contents over the above range were larger than expected values which were extraporated from the linear relationship between $\log G$ and $1/T$

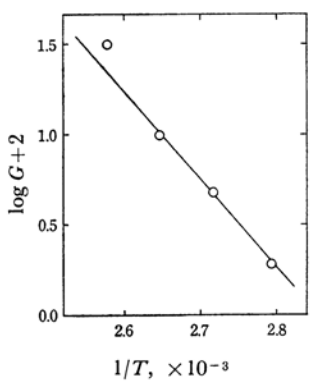


Fig. 5. Plot of $\log G$ of chlorinated selenium of chlorine content of 0.0175% against $1/T$.

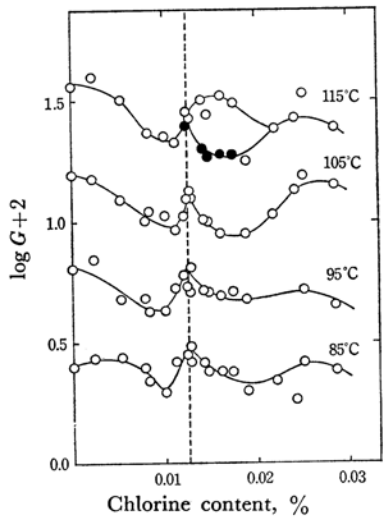


Fig. 6. Plot of $\log G$ against chlorine content at several temperatures.
●; Expected value of $\log G$ from linear relationship between $\log G$ and $1/T$ below 105°C

at temperatures below 105°C, as is shown in Fig. 5. This abnormality was limited to within these range; its cause was not revealed. Figure 6 shows the relationship between the $\log G$ and the chlorine content at several temperatures. The $\log G$ decreased as the chlorine content increased up to near 0.0125%, while a mushroom increase in $\log G$ began at 0.0125%.*1

The apparent activation energies for growth, E_A, which were estimated from the slopes of the linear relationships between $\log G$ and $1/T$, are plotted against the chlorine content in Fig. 7.*2

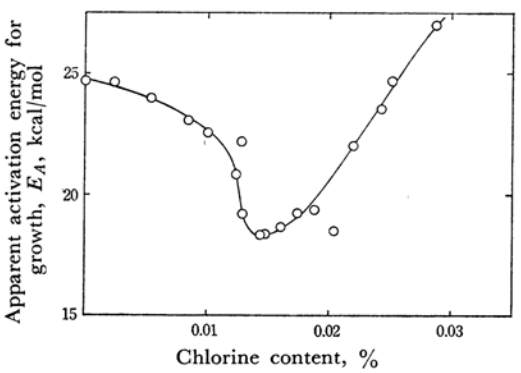


Fig. 7. Dependence of apparent activation energy for growth, E_A, on chlorine content.

*1 If the values of $\log G$ at 115°C, which were expected from the linear relationship between $\log G$ and $1/T$ at the temperatures below 105°C, were be plotted against the chlorine content, the relation was similar to that of below 105°C.

*2 The values which were obtained from the slopes of the linear relationships at temperatures below 105°C were adopted as the E_A values of chlorine contents over the range from about 0.0125% to 0.020%.

There was an abrupt decrease in E_A at the chlorine content of 0.0125%, and then an increase above 0.014%.

Discussion

Takayanagi[8] and Burnet[9] stated that the radial growth rate of such spherulites as polyethylene adipate, polyethylene saccinate and Nylon 6 were governed by the work, ΔF_c, needed to overcome the surface energy of the two-dimensional nucleus which was formed on the surface of the crystal, and by the energy needed for the transport, E_D, of the polymer onto the crystal-amorphous interface from the amorphous phase. Therefore, they showed that the radial growth rate, G, of the spherulite could be indicated as follows:

$$G = G_0 \exp\{-\Delta F_c/\boldsymbol{k}T - E_D/\boldsymbol{k}T\},$$

where G_0 and $\boldsymbol{k}$ are the specific radial growth rate and the Boltzman constant respectively. Since G is governed mainly by the value of $E_D/\boldsymbol{k}T$ at temperatures well below the melting point of the crystalline polymer, the radial growth rate may be shown as follows:

$$\ln G = C - E_D/\boldsymbol{k}T,$$

where C is a constant.

The radial growth rates of the spherulites of the pure and the chlorinated selenium may be governed by the value of $E_D/\boldsymbol{k}T$, because the amorphous samples were crystallized at temperatures well below the melting point of the crystalline selenium (217°C) in our work.

Takayanagi[10] reported that the energy needed for the transport, E_D, of the polymer was proportional to the activation energy for the viscous flow, E_{vis}, and the value of E_D was assessed as one-eighth that of E_{vis}.

Harrison[11] reported that the viscosities of the liquid selenium were as follows:

TABLE 3. VISCOSITIES OF LIQUID SELENIUM

Temp., °K	η, poise	Temp., °K	η, poise
533	5.63	603	1.08
556	3.03	615	0.838
573	2.01	623	0.723
591	1.35		

The values of Table 3 were extremely adaptable in WLF's equation,[12] $\log(\eta_T/\eta_g) = -\alpha(T-T_g)/(\beta+T-T_g)$, which fit with the values of the viscosity of usual molten polymers at temperatures over the range of $T_g < T < T_g+100$, though the temperatures of Table 3 were much higher than the glass transition temperature (T_g) of amorphous selenium (304°K).[13] The constants, α and β, for selenium were estimated to be 12.66 and 118 respectively. These values of constants for selenium were different from those for the usual molten polymers (17.44 and 51.6 respectively); it is probable that this difference arises because the temperatures used in the experiment were much higher than the glass transition temperature of amorphous selenium.

Thus, the activation energies for the viscous flow, E_{vis}, at 80, 90, 100, 110, and 120°C can be calculated from the following equation:

$$E_{vis} = 2.303\boldsymbol{R}\alpha\beta T^2/(\beta + T - T_g)^2$$

The E_{vis} values were estimated to be 30.9, 29.1, 27.5, 26.1, and 23.6 kcal/mol at 80, 90, 100, 110, and 120°C respectively. If E_D were assessed as one-eighth of E_{vis}, E_D could be estimated to be 3.86, 3.64, 3.48, 3.26, and 2.95 kcal/mol at 80, 90, 100, 110, and 120°C respectively. If the spherulite growth of selenium were a diffusion-controlled process at temperatures considerably lower than the melting point of the crystalline selenium, E_A should be about 3—4 kcal/mol and the relationship between $\log G$ and $1/T$ should be a convex curve, even though the ratio of E_D to E_{vis} were larger than one-eighth of Takayanagi's statement. However, $\log G$ varied linearly with $1/T$, and E_A was quite large compared with E_D as is shown in Fig. 3.

The crystal growth of selenium from an amorphous state would be carried out with a reconstruction of the chain molecules, accompanied by a breaking reaction of the Se-Se bond.[1] Since, in general, a potential barrier, ε_0 ($\varepsilon_0 = E_A - \Delta H$ in an endothermic reaction), would be negligible in a reaction concerning two radicals, it is considered that the activation energy for the breaking reaction of the Se-Se bond was nearly equal to the enthalpy change, ΔH, of the thermal equilibrium for breaking of the bond; $Se_n \rightleftarrows Se_i + Se_{n-i}$. Eisenberg and Tobolsky[2] estimated the enthalpy change for the opening reaction of the Se_8 ring molecule, $Se_8 \rightleftarrows \cdot Se_8 \cdot$,*3 to be 25 kcal/mol from the thermal equilibrium relationship between ring molecules and the long-chain molecules of selenium. If the enthalpy change for the thermal equilibrium of the breaking reaction of the bond in a long-chain molecule were nearly equal to that of the ring-opening reaction, it could be considered

8) M. Takayanagi, M. Nakao and S. Machida, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **59**, 549 (1956).
9) B. B. Burnet and W. F. McDevit, *J. Applied Phys.*, **28**, 1101 (1957).
10) M. Takayanagi and T. Kusumoto, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **62**, 587 (1959).
11) D. E. Harrison, "Recent Advances in Selenium Physics," Pergamon Press, Oxford (1965), p. 67.
12) M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
13) B. Wunderlich, *J. Phys. Chem.*, **64**, 1052 (1960).
*3 $\cdot Se_8 \cdot$ is a diradical chain molecule formed by the opening of the Se_8 ring molecule.

that the apparent activation energy for growth was the activation energy for the breaking reaction of the Se-Se bond, since the value of the apparent activation energy for growth (24.9 kcal/mol) was nearly equal to that of the enthalpy change for the thermal-breaking equilibrium of the bond (25 kcal/mol). Therefore, it is probable that the spherulite growth of selenium is not a diffusion-controlled process, but a breaking process of the Se-Se bond for the reconstruction of the chain molecules. Since the apparent activation energy for growth was regarded as that of the breaking reaction, as has been mentioned above, an activation entropy change, $\Delta S^{\ddagger}$, could be calculated from E_A and the growth rate, which was calculated as the radial velocity of the formation of crystalline selenium per unit of area (gram atoms/cm^2 sec) at the amorphous-crystalline interface from the observed radial growth rate, $G(\mu/\text{min})$, when a transmission coefficient was regarded as unity. Figure 8 shows the dependence of $\Delta S^{\ddagger}$ on the chlorine content.

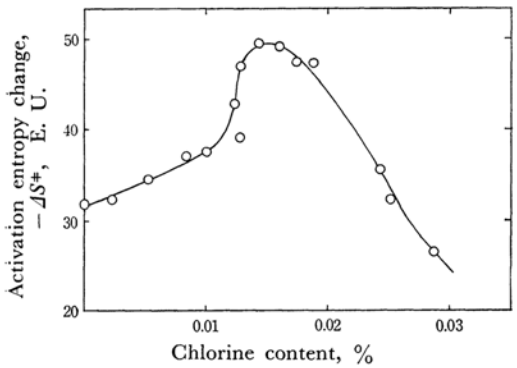


Fig. 8. Dependence of activation entropy change, $\Delta S^{\ddagger}$, on chlorine content.

The activation entropy change decreased with an increase in the chlorine content up to 0.0125%. In particular, an abrupt decrease in $\Delta S^{\ddagger}$ appeared at the chlorine content of 0.0125%. On the contrary, $\Delta S^{\ddagger}$ increased with chlorine contents of more than 0.014%.

Eisenberg and Tobolsky[2] estimated the number-average chain length of pure selenium at 230°C to be 7200; this value agreed with that obtained from the viscosity method by Shirai and Hamada.[3] Briegleb[14] reported that the molar fraction of the Se_8 ring molecule in selenium was 0.40 at 230°C, which was only 0.22% of the weight percentage. Therefore, the chlorine content corresponded to 0.0125%, when all the diradical molecules in pure selenium were terminated with chlorine atoms. The abrupt decrease in $\Delta S^{\ddagger}$ and in E_A shown in Figs. 7 and 8 suggests that the spherulite growth is affected by the presence of the radicals at the molecular ends, and that a rate-determining step was the settlement of the chain molecule on the amorphous-crystalline interface rather than the migration of the segment for the transport of the molecules.

The two-dimensional nuclei would be formed preferentially at active points formed by the radicals at the molecular ends on the amorphous-crystalline interface. It is considered that the chain molecules, which were transported onto the amorphous-crystalline interface from the amorphous phase, should be transformed to a considerably-confined form proportionately with an increase in the chlorination. The abrupt decrease in $\Delta S^{\ddagger}$ at the chlorine content of 0.0125% is likely to have resulted from a confined attachment of molecules onto the amorphous-crystalline interface. The increase in $\Delta S^{\ddagger}$ at chlorine content of more than 0.014% may be attributed to an increase in the probability of molecular attachment after all the radicals at the molecular ends have been terminated with chlorine atoms, and to an easier transformation of shorter chain molecules cut off with chlorine atoms at chlorine contents of more than 0.0125%.

The transformation of the chain molecules to the crystalline form would be extended not overall, but partially, in the molecule, as the viscosity was quite large. The severance of an amorphous part from the settled molecule would be needed to make the growth progress. The thermal-breaking equilibrium relationship is likely not to be affected by the termination of the radical ends. Therefore, the activation free-energy changes, $\Delta G^{\ddagger}$, at the activated state should be nearly constant, without regard to the chlorine content. E_A (nearly equal to $\Delta H^{\ddagger}$) should be varied in order to offset a variation in the term of $-T\Delta S^{\ddagger}$, since $\Delta S^{\ddagger}$ varied with the degree of chlorination. This is supported by the fact that an increase in the term of $-T\Delta S^{\ddagger}$ (6.8 kcal) was offset by a decrease in E_A (6.6 kcal) at the chlorine content of 0.0143% and at 105°C compared with the pure state, as is shown in Figs. 7 and 8.

14) G. Briegleb, *Z. Phys. Chem.*, **A144**, 321 (1929).