

Volume Retardation of Polystyrene. II

Shiro HOZUMI

*Wireless Research Laboratory, Matsushita Electric Industrial Co., Ltd.
Kadoma-shi, Osaka, Japan.*

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ABSTRACT: A semiempirical equation readily applicable to analysis of volume retardation curves is derived from the Bueche theory. The equation is applied to experimental results on polystyrene obtained over a temperature range from the upper limit of the glass transition region, T_g^+ , to 60 degrees below. It is shown that the equation satisfactorily describes the behavior of experimental isotherms. Values of equilibrium volume, diffusion coefficient, and free volume fraction are determined at the temperatures in the above range. In the glass transition region, from T_g^+ to T_g^- , temperature dependence of these quantities is consistent with that predicted from the free volume theory. Below T_g^- , however, the temperature dependence seems to deviate from the extrapolation of the above.

A semiempirical equation for an anomalous isotherm, which has a maximum, is similarly derived and applied to the analysis of the experimental results. The experimental isotherms are fairly well interpreted in terms of the equation.

KEY WORDS Volume Retardation / Free Volume / Diffusion Coefficient / Glass Transition / Polystyrene /

When a polymer equilibrated at a temperature is quenched into another temperature below the glass transition, its volume contracts retardatively to the equilibrium value at the temperature. The phenomenon has been investigated by many authors both theoretically and experimentally with a view to studying retardation phenomena in the glassy state and to clarifying the behavior of free volume in the glassy state.³⁻¹¹

An analytical representation for such a volume retardation will further facilitate those studies. Amongst the attempts to obtain analytical representation, an equation derived by Kavacs⁴ has been well recognized to show close agreement with experimental results.¹¹ Okano derived independently an equation similar to Kovacs and arrived at a free volume theory of glass transition by use of the equation.^{7,9} Both of the equations have been derived with the assumption that the phenomenon possessed a single retardation time mechanism.

Subsequent experimental studies,¹²⁻¹⁴ however, have shown a necessity of taking into account the distribution of retardation times. Bueche has proposed another analytical representation

which involves a concept of a distribution of retardation times.⁸ The representation, however, has some difficulties when applied to experimental results: It does not deal with a time which is necessary, in practice, for quenching from one temperature to another temperature, and it does not completely describe the volume retardation at a relatively low temperature below the glass transition.

In the present report,¹ with a modification of the Bueche theory a semiempirical equation for volume retardation is presented. The equation is successfully applied to experimental results on polystyrene² obtained over a wide temperature range from the upper limit of the glass transition region, T_g^+ , through the lower limit of that, T_g^- , to about 60 degrees below. The parameters included in the equation were determined and are discussed in relation to the free volume theory.^{11,13,15} A semiempirical equation is also derived for an anomalous volume retardation, in which the volume of a polymer goes with time through a maximum towards the value of the normal volume retardation. The equation explains fairly well features of observed anomalous retardation.²

SEMIEMPIRICAL EQUATION FOR VOLUME RETARDATION

Equation for Normal Isotherm

A polymer equilibrated at a temperature T_1 is quenched into a temperature T_2 below T_g^+ . The specific volume of the polymer changes with time t even after the temperature of the polymer reaches T_2 . This specific volume change with respect to time t is called here the isotherm at T_2 .

A semiempirical equation which is readily applicable to analysis of the experimental results was derived from the Bueche theory⁸ (see Appendix).

The equation is

$$V - V_2 = B / [\exp \{E(V - V_2)/V_0\}(t_0 + t)^{1/2}] \quad (1)$$

where V is an instantaneous specific volume, V_2 is the equilibrium volume at temperature T_2 , V_0 is the initial volume at T_2 , t is the observation time, t_0 is a correction constant, and B , and E are the factors relating to the diffusion coefficient and free volume, respectively. Time t is taken as $t=0$ when the temperature of the polymer reaches T_2 . The constant t_0 makes eq 1 applicable to the isotherm around the time range $t \approx 0$. In actual cases, observed isotherms near $t=0$ are usually modified by some transient retardation which arises while the temperature of the

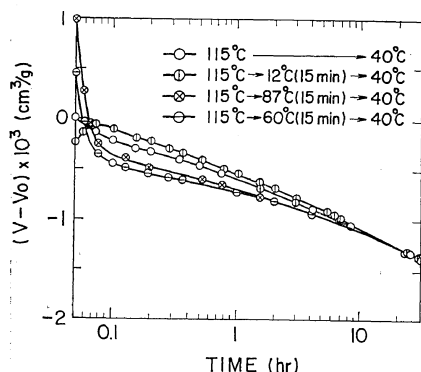


Figure 1. Examples of modifications of isotherms. A temperature of intermediate quenching was varied. The value of V_0 is taken to be the specific volume at 0.05 hr on the isotherm obtained from the direct quenching ($115^\circ\text{C} \rightarrow 40^\circ\text{C}$). The initial part of the curves before $t=0.1$ hr should be ignored since temperature of the polymer does not perfectly attain the equilibrium until that time.

polymer varies from T_1 to T_2 . The amount of such a transient retardation is larger as the quenching rate is smaller around T_g^+ . Examples of the modifications of the isotherms are shown in Figure 1, in which the quenching rate around T_g^+ is varied by providing an intermediate quenching temperature in the quenching from T_1 to T_2 . Experimental details are the same as those of a previous report.² In Figure 1, the initial parts of the curves before $t=0.1$ hr are erroneous since the temperature of the polymer is not perfectly equilibrated at T_2 until that time. The quenching rate around T_g^+ will be larger as the intermediate quenching temperature is lower. One sees in Figure 1 that the contraction velocity of the isotherm at the early stage is slower for the smaller quenching rate around T_g^+ . This feature is reminiscent of a model for the modifications of the isotherms as follows: according to Bueche,⁸ a volume retardation is assumed to consist of a number of elemental retardations with different retardation times, each of which corresponds to each molecular vibration characterized by a mode number n ranging from 0 to N . The smaller the mode number n , the longer is the retardation time. If some retardation corresponding to mode numbers ranging from N to n_0 arise before $t=0$ at T_2 , at an observation time $t=t_a$ the retardation with the mode corresponding to the retardation time $t_0 + t_a$ will start. In the above, the mode number n_0 corresponds to the retardation time t_0 .

The factor B is denoted as

$$B = (v_{f1} - v_{f2}) / D_e^{1/2}, \quad (2)$$

wherein v_{f1} and v_{f2} are the equilibrium specific free volumes at temperatures T_1 and T_2 , respectively, and D_e is the quantity (hr^{-1}) proportional to the diffusion coefficient in the equilibrium state at T_2 . On the basis of the diffusion coefficient obtained by Doolittle,¹⁶ E is given by

$$2E \approx 1 / f f_{e2} \quad (3)$$

where f is an instantaneous free volume fraction and f_{e2} is the fractional representation of v_{f2} . Eq 1 seems to include inconsistency in the sense that Doolittle's diffusion coefficient is introduced into the theory of viscoelasticity accomplished by Bueche.⁸ The inconsistency may be removed

by introducing a modification, which is rather tentative, into the free volume model in the Bueche theory; details are discussed in the Appendix.

Equation for Anomalous Isotherm

Isotherms obtained under more complicated quenching conditions than those mentioned above indicate features which are reminiscent of a wide distribution of retardation times. In a previous report,² one such kind of isotherm, an anomalous isotherm, has been studied experimentally. This isotherm is observed when a polymer is first quenched from T_1 to T_2 , maintained at T_2 during a time z , and then heated up to another temperature T_3 ($T_3 > T_2$) before reaching the equilibrium state at T_2 . The isotherm at T_3 goes to a maximum and then decreases so as to approach the normal contraction isotherm obtained in the direct quenching from T_1 to T_3 .

A semiempirical equation for the anomalous isotherm was also derived from the Bueche theory (see Appendix). The equation for the isotherm placing in the time range $t < t_1 - t_2$ is,

$$V - V_3 = [1/\exp\{E(V - V_3)/V_0\}] \times \{B/(t_1 + t)^{1/2} - C/(t_2 + t)^{1/2} + H\} \quad (4)$$

The equation for the isotherm after passing the time $t = t_1 - t_2$ is,

$$V - V_3 = [B/\exp\{E(V - V_3)/V_0\}]/(t_1 + t)^{1/2} \quad (5)$$

In eq 4 and 5, the origin of time t is taken as the temperature of the polymer reaches T_3 . The constant t_1 has a value relating to the time z , and t_2 is constant, having a character similar to the constant t_0 in eq 1. The volume V_3 is the equilibrium specific volume at T_3 , $B = (v_{f1} - v_{f3})/D_e^{1/2}$, $C = (v_{f3} - v_{f2})/D_e^{1/2}$, and $H = (v_{f3} - v_{f2})/D_e^{1/2}t_1^{1/2}$, where D_e is the quantity (hr^{-1}) proportional to the diffusion coefficient in the equilibrium state at T_3 , and v_{f3} is the equilibrium specific free volume at T_3 . E in eq 4 and 5 is given by

$$2E \approx 1/ff_{e3} \quad (6)$$

where f_{e3} is the fractional expression of v_{f3} .

An anomalous isotherm has a maximum as was mentioned before. The time corresponding to the volume maximum, t_{max} , is calculated from the differential of eq 4 with respect to t .

Then one obtains

$$t_{\text{max}1} = (C^{2/3}t_1 - B^{2/3}t_2)/(B^{2/3} - C^{2/3}) \quad (7)$$

If $t_{\text{max}1} < t_1 - t_2$, $t_{\text{max}1}$ corresponds to an observed t_{max} . If $t_{\text{max}1} > t_1 - t_2$, this value is false and does not give t_{max} ; because eq 4 is valid for only $t < t_1 - t_2$. In the case of $t_{\text{max}1} > t_1 - t_2$, an observed t_{max} corresponds to a time t when $C/(t_2 + t)^{1/2} = H$. Hence, t_{max} corresponds to

$$t_{\text{max}2} = t_1 - t_2 \quad (8)$$

$$= (C/H)^2 - t_2 \quad (8')$$

ANALYSIS OF CONTRACTION ISOTHERMS AT TEMPERATURES ABOVE T_g^-

Application of the Theory of Experimental Results

In a previous report,² contraction isotherms of polystyrene were measured over wide temperature ranges including the glass transition region. The data are presented in Figure 2.

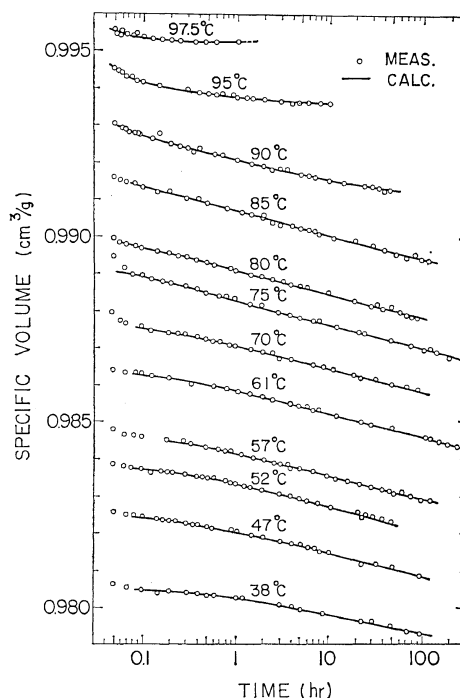


Figure 2. Isotherms of volume retardation for polystyrene obtained after quenching from 115°C to various temperatures shown along side the isotherms.² Circles show experimental values. Solid curves indicate eq 1 adapted for the experimental isotherms.

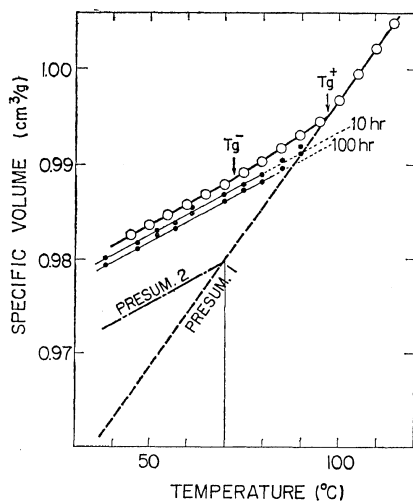


Figure 3. Thermal expansion of polystyrene. The upper limit of the glass transition region, T_g^+ , is about 97°C and the lower limit, T_g^- , is about 73°C. Two thin lines, which are drawn in parallel with volume expansion of glassy polymer, show respective specific volumes at 10 and 100 hr after quenching into various temperatures. Plots indicate experimental data taken from Figure 2. Broken lines and dot-dash-lines represent temperature dependences of equilibrium volume assumed as presumptions 1 and 2, respectively.

The upper limit of the glass transition region, T_g^+ , of polystyrene is about 97°C and the lower limit, T_g^- , is about 73°C, as is shown in Figure 3.

Application of eq 1 to those experimental data was accomplished by the least square method with use of an electronic computing system MADIC IIA. Solid curves in Figure 2 represent the results of these computations. As for the three isotherms at 97.5, 95, and 90°C, the curve-fittings were performed in a straightforward manner and the most probable values of the parameters V_2 , B , t_0 , and E were determined. These values are listed in Table I. The values of V_2 are plotted against the temperature in Figure 4 in comparison with those values experimentally obtained and those estimated from vertical shift factors for the isotherms.² Agreement among these three is quite close in the temperature range in question.

Contraction isotherms as a function of $\log t$ have a long, almost linear portion, as is seen in all of the isotherms below 85°C in Figure 2. The isotherms are approximately represented as

$$v-w = -G \log t \quad (9)$$

where w is the specific volume at $t=1$ hr, $-G$ is the slope and t is the time in hours. The

Table I. Values of parameters used for the calculations of eq 1 represented in Figure 2

T_2 , °C	V_2 , cm ³ /g		B , (cm ³ /g)hr ^{1/2} B^\dagger , (cm ³ /g)hr ^{1/2}	t_0 , hr t_0^\dagger , hr	E E^\dagger
97.5	0.99513	Determined from L.S.	7.62×10^{-5}	-3.55×10^{-2}	1.13×10^8
95.0	0.99350	Determined from L.S.	3.20×10^{-4}	-3.51×10^{-2}	9.60×10^2
90.0	0.99089	Determined from L.S.	4.57×10^{-3}	-8.56×10^{-3}	1.16×10^8
85.0	0.98815	Presu. 1	6.87×10^{-2}	4.07×10^{-2}	1.27×10^8
80.0	0.98540	Presu. 1	1.19	1.62×10^{-2}	1.55×10^8
75.0	0.98275	Presu. 1	3.29×10	2.08×10^{-2}	1.56×10^8
70.0	0.98004	Presu. 1	1.68×10^3	6.54×10^{-2}	1.76×10^8
61.0	0.97525	Presu. 1	9.15×10^5	1.14×10^{-1}	1.72×10^8
	0.97762	Presu. 2	9.18×10^3	1.17×10^{-1}	1.69×10^8
57.0	0.97304	Presu. 1	3.43×10^6	1.16×10^{-1}	1.75×10^8
	0.97673	Presu. 2	2.39×10^3	1.19×10^{-1}	1.70×10^8
52.0	0.97036	Presu. 1	1.10×10^8	1.57×10^{-1}	1.76×10^8
	0.97566	Presu. 2	3.70×10^3	1.60×10^{-1}	1.70×10^8
47.0	0.96766	Presu. 1	1.02×10^{10}	1.26×10^{-1}	1.90×10^8
	0.97455	Presu. 2	6.54×10^3	1.29×10^{-1}	1.88×10^8
38.0	0.96286	Presu. 1	5.60×10^{14}	3.95×10^{-1}	2.18×10^8
	0.97261	Presu. 2	8.03×10^4	4.01×10^{-1}	2.09×10^8

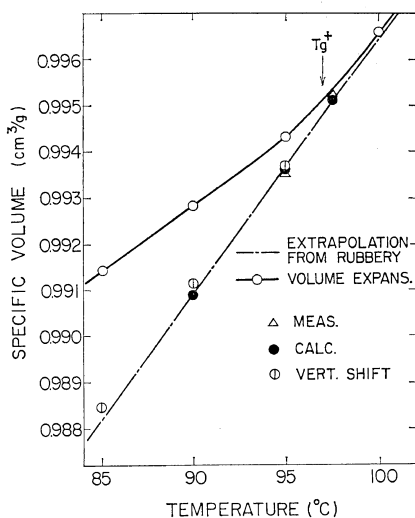


Figure 4. Equilibrium volumes at various temperatures. Calculated values are compared with experimental results which were measured and/or evaluated from vertical shift factors in a previous report.²

logarithmic representation of eq 1, in which t_0 is ignored since $t \gg t_0$, is

$$\log(V - V_2) = -(V - V_2)(E/2.303V_0) - (1/2) \log t + \log B \quad (10)$$

Combining eq 9 and 10, the following equation is obtained;

$$\log \left\{ \frac{(V-w)/(w-V_2)+1}{w-V_2} \right\} + \log(w-V_2) + (1/2G)(w-V_2) = \log B \quad (11)$$

wherein $G \simeq 2.303/(2E/V_0)$, which will be shown in section headed *Slope of Isotherms*. When $(V-w)/(w-V_2) \ll 1$, V_2 and B cannot be determined independently of each other. Thus, in the following, the value of V_2 is first presumed at each temperature, and the temperature dependence of B will be discussed by use of this V_2 value. The presumption 1, shown in Figure 3, was adopted so that V_2 might obey the free volume theory.^{11,13,15} According to the theory, V_2 may be expressed as the linear extrapolation from the rubbery equilibrium in the temperature range from T_g^+ to about 50 degrees below.

The values of parameters B , t_0 , and E were determined by use of the presumed V_2 values at temperatures below 85°C and are listed in

Table I. The following discussion will be made along the presumption 1.

Equilibrium Free Volume

The equilibrium free volume fractions f_{e2} at various temperatures were obtained from the values of E by use of eq 3. The value of f involved in eq 3 was treated as a constant equal to the average of f through the whole observation time, though the actual f varies with V during the retardation. The difference between the averaged f and the actual f may generally be negligible in comparison with f itself.

Over the temperature range 97.5 to 90°C, the difference between f and f_{e2} can be ignored since both f and f_{e2} are much larger than the difference $f - f_{e2}$. Then eq 3 is approximated as

$$2E \simeq 1/f_{e2}^2 \quad (12)$$

The values of specific volumes of each of the isotherms at 10 and 100 hr after quenching were taken from Figure 2 and are plotted in Figure 3. Both lines on the data are drawn in parallel with the volume expansion of the glassy polymer. According to the free volume theory^{11,13,15} the expansion coefficient of the occupied volume is assumed to be the same as that of the glassy polymer. Thus, it may be reasonable to assume that a common f value is adopted for all the

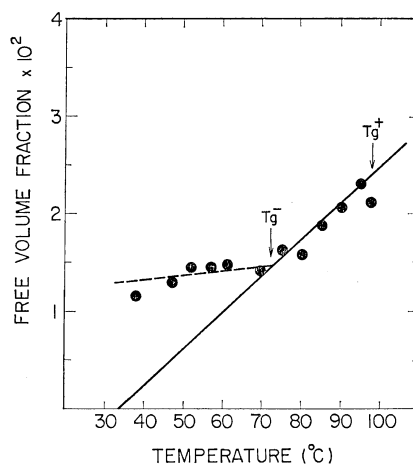


Figure 5. Temperature dependence of equilibrium free volume fractions calculated by eq 12 and 13. Solid line indicates the difference between thermal expansions in rubbery and glassy polymer obtained from Figure 3.

isotherms below 85°C. The value of f_{e2} at 90°C was adopted as this f value. Then one obtains

$$2E \simeq 1 / \{f_{e2}(90^\circ\text{C})f_{e2}\} \quad (13)$$

The values of f_{e2} obtained using eq 12 and 13 are presented in Figure 5. The slope of the solid line in Figure 5 denotes the difference $\Delta\alpha$ in the thermal expansion coefficient between the rubbery state and the glassy state. The value of $\Delta\alpha$ is obtained from Figure 3 to be about 3.7×10^{-4} temperature deg. $^{-1}$. It is seen in Figure 5 that the temperature dependence of f_{e2} in the temperature range from T_g^+ to T_g^- is fairly well manifested in terms of the slope $\Delta\alpha$. It is also seen that the value of f_{e2} is assumed to be about 0.024 at T_g^+ . These features of f_{e2} are in agreement with the prediction of the free volume theory.^{11,13,15}

Temperature Dependence of D_e

Taking account of the results in Figure 5 and the fact that $V_0 \simeq 1 \text{ cm}^3/\text{g}$ as shown in Figure 2,

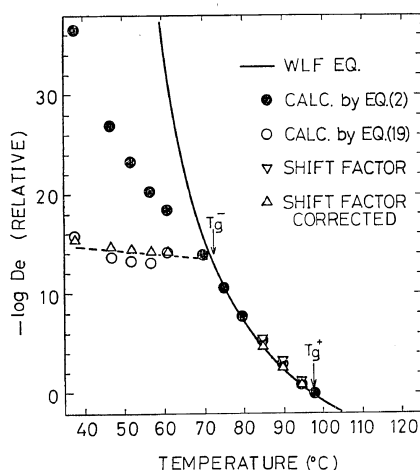


Figure 6. Temperature dependence of diffusion coefficient D_e . Calculated values are compared with values evaluated from horizontal shift factors obtained in a previous report.² For plotting these data from T_g^+ to T_g^- , 97.5°C is regarded as a reference. Corrected shift factors in terms of eq 18 are also shown in comparison. Solid curve indicates the WLF equation adapted for the data on shear creep compliance of polystyrene shown in a previous report.² At temperatures below T_g^- , calculated D_e by eq 19 are also compared with values evaluated from horizontal shift factors. In the latter plotting, the calculated datum at 61°C is taken as a reference point.

($v_{f1} - v_{f2}$) above T_g^- is approximately equal to $\Delta\alpha(T_1 - T_2)(\text{cm}^3/\text{g})$. Then, values of D_e at various temperatures are obtained from the values of B in Table I by use of eq 2. The values of D_e relative to that at 97.5°C are presented in Figure 6. The solid curve in Figure 6 indicates the WLF equation¹⁷ represented in a universal formula;

$$\log a_T = \frac{-8.86(T-139)}{101.6+(T-139)} \quad (T \text{ in } ^\circ\text{C})$$

which was adjusted to a temperature dependence of a shear creep compliance of polystyrene, shown in a previous report.²

As readily seen in Figure 6, the temperature dependence of D_e above T_g^- is fairly well manifested by the WLF equation. It is noted that the WLF equation is based on the concept of a free volume. Features of the free volume are as follows¹⁵: The thermal expansion is almost equal to $\Delta\alpha$, and the free volume fraction at T_g is about 0.025, where T_g is the glass transition temperature and is generally several degrees below T_g^+ . Furthermore, there is the relation $139^\circ\text{C} - T_g = 50 \pm 5^\circ\text{C}$. These features are almost exactly similar to those obtained in the last section.

It is concluded that eq 1 satisfactorily describes the experimental contraction isotherms at temperatures above T_g^- . The obtained values of the parameters satisfy the relations predicted from the free volume theory.^{11,13,15}

Shift Factors

It has been shown in a previous report² that velocity of volume retardation, dV/dt , can be expressed by a product of a function of T_2 and a function of $(V - V_2)$. That is;

$$dV/dt = \theta(T_2) \cdot \chi(V - V_2) \quad (14)$$

The time-temperature reducibility in the volume retardation can be explained in terms of this functional form. The horizontal shift factor corresponds to $\theta(T_2)/\theta(T_{2r})$, where T_{2r} is a reference temperature.

Differentiating eq 1 with respect to t , and ignoring the weak dependence of E on t , one obtains the following equation;

$$dV/dt = -[1/2B^2\{1 + E(V - V_2)/V_0\}] \times \exp\{2E(V - V_2)/V_0\}(V - V_2)^3 \quad (15)$$

In the vicinity of T_g^+ , $E(V-V_0)V_0 \ll 1$ as shown in Table I, and hence eq 15 is approximated by

$$dV/dt \simeq -(1/2B^2)(V-V_2)^3 \quad (16)$$

The functional form of eq 16 is similar to that of eq 14, and the term corresponding to θ is $-(1/2B^2)$. As the temperature decreases, the value of $E(V-V_2)/V_0$ exceeds unity, and then eq 15 is written as

$$dV/dt \simeq -(1/2B^2)(V_0/E) \times \exp\{2E(V-V_2)/V_0\}(V-V_2)^2 \quad (17)$$

As is seen in Table I and Figure 2, the temperature dependence of (V_0/E) is much smaller than that of B and may be ignored as the first approximation. Furthermore, one must consider that in general shift factors are experimentally determined from superpositions of the isotherms in which each temperature interval of the successive curves is narrow. Hence, the differences between the values of the exponential terms for the successive curves may be insignificant as the first approximation. Thus a term corresponding to $\theta(T_2)$ is

$$1/2B^2 = D_e/2(v_{r1}-v_{r2})^2 \quad (18)$$

in the whole temperature range. Eq 18 indicates that shift factors experimentally obtained in the volume retardation should be multiplied by a factor $(v_{r1}-v_{r2})^2$ to obtain D_e values which are compared with the WLF equation. This procedure was adopted for the data in a previous report² and the results are shown in Figure 6. As is seen in Figure 6, the procedure improves the agreement of the shift factors with the WLF equation.

ANALYSIS OF CONTRACTION ISOTHERMS BELOW T_g^-

Application of the Theory to Experimental Results

Figure 5 shows that the amount of the free volume fraction estimated under presumption 1 is almost constant at the temperatures below T_g^- , which is inconsistent with presumption 1 itself. There seems to be no literature concerned with the behavior of the free volume at temperatures below T_g^- . Here, presumption 2 was tentatively adopted for values of V_2 at temperatures below T_g^- : The value of V_2 begins to deviate from presumption 1 at 70°C and decreases in parallel

with the volume of the glassy polymer, as shown in Figure 3.

By use of these V_2 values, eq 1 was applied to the data in Figure 2 and the values of the parameters B , E , and t_0 were determined. The results are presented in Table I, distinguished by daggers. Calculated isotherms under presumption 2 coincides with those under presumption 1. An example of these calculations under presumption 1 and 2 is presented in Table II. This agreement is quite natural, if account is taken of the fact that B depends on V_2 as shown in eq 11.

One may see in Table I that the values of E^+ agree fairly well with the values of E below T_g^- . In consequence the free volume fractions calculated from E^+ will be similar to those below T_g^- shown in Figure 5. It seems in Figure 5 that the free volume fractions below T_g^- show temperature dependence. This is, however, quite small and may not be considered to be inconsistent with presumption 2.

Table II. Comparison between the calculations based on presumptions 1 and 2, for the isotherm at 38°C

Measured data		Calculated	
V , cm ³ /g	t , hr Meas.	t , hr Presu. 1	t , hr Presu. 2
0.98049	1.0×10^{-1}	9.24×10^{-2}	9.19×10^{-2}
0.98047	1.4×10^{-1}	1.40×10^{-1}	1.40×10^{-1}
0.98045	2.0×10^{-1}	1.93×10^{-1}	1.93×10^{-1}
0.98042	2.8×10^{-1}	2.80×10^{-1}	2.80×10^{-1}
0.98038	4.0×10^{-1}	4.05×10^{-1}	4.06×10^{-1}
0.98033	6.0×10^{-1}	6.10×10^{-1}	6.11×10^{-1}
0.98028	8.6×10^{-1}	8.72×10^{-1}	8.74×10^{-1}
0.98022	1.2	1.25	1.26
0.98015	1.8	1.86	1.86
0.98007	2.8	2.83	2.83
0.98000	4.2	4.13	4.13
0.97992	6.0	5.88	5.88
0.97984	8.6	8.34	8.33
0.97977	1.2×10	1.18×10	1.18×10
0.97971	1.6×10	1.58×10	1.58×10
0.97963	2.3×10	2.27×10	2.27×10
0.97955	3.2×10	3.20×10	3.19×10
0.97948	4.4×10	4.41×10	4.40×10
0.97941	6.0×10	6.01×10	6.01×10
0.97935	8.0×10	8.05×10	8.06×10
0.97929	1.0×10^2	1.03×10^2	1.03×10^2

Shift Factors

On the basis of presumption 2, relative values of the diffusion coefficient are obtained as

$$D_e \propto 1/2B^{12} \quad (19)$$

The results of the calculation are presented in Figure 6. The temperature dependence of the diffusion coefficient D_e is only slight and it deviates from the WLF equation. Horizontal shift factors obtained in a previous report² are also plotted in Figure 6, where 61°C is taken as a reference temperature. The temperature dependence of D_e calculated from B^{\dagger} is fairly close to that of the horizontal shift factors.

Slope of Isotherms

As was mentioned before, at fairly lower temperatures than T_g^+ the isotherms as a function of $\log t$ have a rather long linear portion. Kovacs has called the slope of this portion "the tangent at the inflection point on the isotherm."³ Taking account of that $dV/d \ln t = (dV/dt)t$, one obtains from eq 1 and 17,

$$dV/d \ln t = -V_0/2E + t_0V_0/2E(t_0 + t) \quad (20)$$

Then, the slope of the isotherm plotted against $\ln t$ is equal to $-V_0/2E$ at $t \gg t_0$. Since in most

polymers V_0 is about 1 cm³/g, the slope $dV/d \log t$ is represented as $-2.203ff_{e2}$ (cm³/g) by use of eq 3. Kovacs has assumed the slope to be approximately $-2.303f_g^2$ around T_g ; f_g is f_{e2} at the glass transition temperature.¹¹

The slopes of the isotherms in Figure 2 were calculated from eq 20 and are compared in Figure 7 with the observed values. The data on polystyrene obtained by Kovacs³ are also shown for a comparison in Figure 7. Though the present results are rather scattered above 75°C, a fairly satisfactory agreement between observed and calculated values is obtained below 75°C.

Summary on the Low Temperature Behavior below T_g^-

According to the free volume theory^{11,13,15} the value of V_2 decreases along the extrapolation from the rubbery state, in the temperature range from T_g^+ to about 50 degrees below. However, the several results in this report and also in a previous report² indicate that the value of V_2 may begin to deviate from the rubbery extrapolation at the vicinity of T_g^- . They include:

(1) The temperature dependence of the equilibrium free volume fraction calculated here changes in its slope in the vicinity of T_g^- , as shown in Figure 5.

(2) The temperature dependence of the horizontal shift factor obtained in the vicinity of T_g^+ differs from that below T_g^- , as shown in Figure 6; the former dependence is close to that of D_e calculated under presumption 1 and the latter is close to that of D_e calculated under presumption 2.

(3) As for the equilibrium volumes estimated from the vertical shift factors shown in a previous report,² the conspicuous difference of the temperature dependence has been shown at temperatures around T_g^+ and at temperatures below T_g^- .

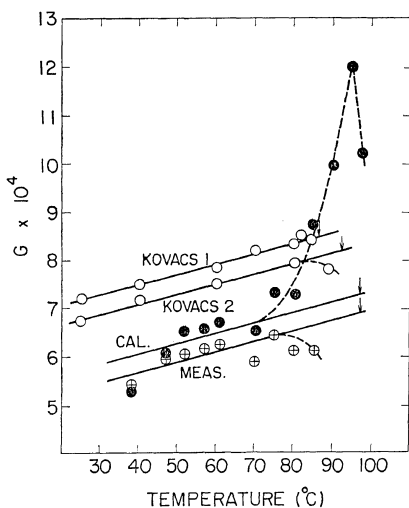


Figure 7. G (cm³/g), slope of linear portion of an isotherm as a function of logarithmic time. Solid circles represent calculated values by eq 20. Circles with cross represent experimental values measured in Figure 2. The results on two polystyrenes by Kovacs³ are shown for comparison. Arrows indicate respective glass transition points of the specimens.

ANALYSIS OF ANOMALOUS ISOTHERMS

Application of the Theory to Experimental Results

The anomalous isotherms were experimentally studied in a previous report,² in which three different quenching conditions were set up:

(1) 115°C → 80 → 88°C; (2) 115°C → 61°C → 75°C; and (3) 115°C → 42°C → 61°C.

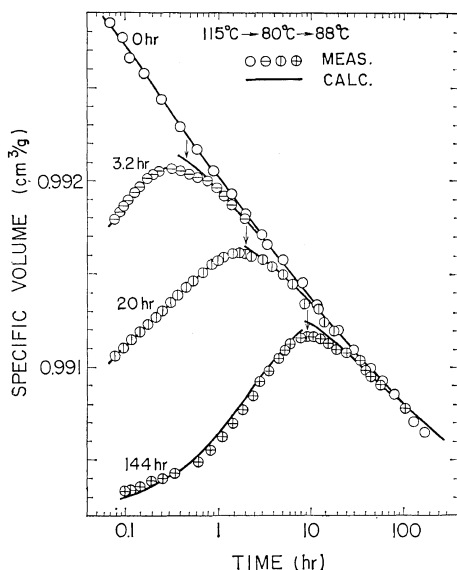


Figure 8. Anomalous isotherms of polystyrene at 88°C. Each of these isotherms was obtained under a quenching condition; polymer has been maintained at 80°C during time z after being quenched from 115°C to 80°C and is then heated up to 88°C. Each z is shown alongside the isotherm.² Solid curves represent eq 4 and 5 adapted for the experimental isotherms. Each arrow indicates a calculated time of maximum by eq 7 and 8'.

Eq 4 and 5 were applied to the experimental data on the anomalous isotherms obtained under conditions (1) and (2), which are presented in Figures 8 and 9. Isotherms obtained under condition (3) could not be analysed because the equilibrium behavior below T_g^- is still not understood.

In application of eq 4 and 5 to the experimental data, the computation in the least square method is very complicated because parameters to be determined are large in number. In practice, the procedure of the computation was divided into three successive steps for the sake of simplification. This might, however, bring some errors in the results. The procedure is:— (1) first, the values of E and B are determined from applying eq 5 to the data on the direct quenching from T_1 to T_3 on the basis of presumption 1; (2) secondly, the value of t_1 is determined from applying eq 5, in which E , B , and V_3 are substituted by the values determined in the step (1),

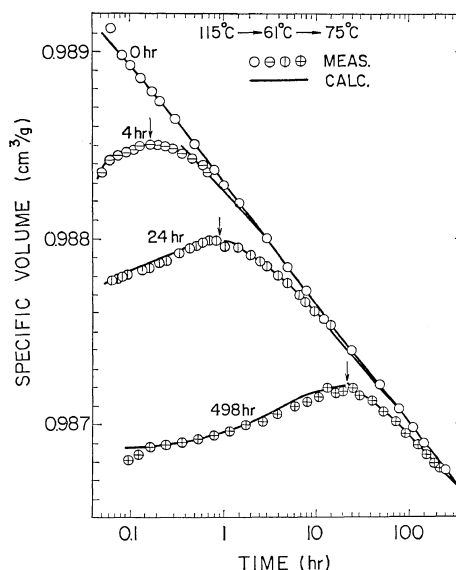


Figure 9. Anomalous isotherms of polystyrene at 75°C. Each of these isotherms was obtained under the condition similar to that in Figure 8 varied in temperature combination; 115°C→61°C, z →75°C.²

to the data on the contraction region of the anomalous isotherm; and

(3) finally, the values of C , H , and t_2 , are obtained from applying eq 4, in which E , B , V_3 , and t_1 are substituted by the values determined in the steps (1) and (2), to the dilative region of the anomalous isotherm.

Eq 4 and 5 thus calculated are represented by solid curves in Figures 8 and 9. The values of the parameters are listed in Table III. The calculated curves by eq 4 explain fairly well the dilative portions of the experimental isotherms. The calculated curves by eq 5 describe the contractive portions of the experimental isotherms rather well, especially those of the isotherms (115°C→61°C→75°C). However, one may see in Figures 8 and 9 that a curve representing eq 4 is not continuous to that representing eq 5. This discrepancy is due to the simplification in the computation described above.

Time of Maximum Volume and Other Parameters

The values of $t_{\max 1}$ and $t_{\max 2}$ were calculated by eq 7, 8, and 8' from the values of B , t_1 , C , t_2 , and H , and are listed in Table III. The smaller one of $t_{\max 1}$ and $t_{\max 2}$ obtained by eq 8'

Volume Retardation of Polystyrene. II

Table III. Values of parameters used for the calculations of eq 4 and 5 represented in Figures 8 and 9, and calculated values of $t_{\max 1}$ and $t_{\max 2}$

$\rightarrow T_2, ^\circ\text{C}, z \text{ hr}$ $\rightarrow T_3, ^\circ\text{C}$	t_1, hr	$C, (\text{cm}^3/\text{g}) \text{hr}^{1/2}$	t_2, hr	$H, \text{cm}^3/\text{g}$	$t_{\max 1}, \text{hr}$	$t_{\max 2}, \text{hr}$ by eq 8 by eq 8'	
$\rightarrow 80, 0 \rightarrow 88$	$\left. \begin{array}{l} V_3 = 0.99010, \\ E = 1077 \\ B = 1.55 \times 10^{-2} \end{array} \right\} \left(\begin{array}{l} \text{cm}^3/\text{g} \\ \\ (\text{cm}^3/\text{g}) \text{hr}^{1/2} \end{array} \right)$	$\left\{ \begin{array}{l} 0.28 \quad 8.5 \times 10^{-3} \\ 1.60 \quad 1.3 \times 10^{-2} \\ 6.9 \quad 3.3 \times 10^{-2} \end{array} \right.$	$\left\{ \begin{array}{l} 2.4 \times 10^{-2} \\ 4.6 \times 10^{-1} \\ 5.3 \end{array} \right.$	$\left\{ \begin{array}{l} 1.1 \times 10^{-2} \\ 8.0 \times 10^{-3} \\ 8.8 \times 10^{-3} \end{array} \right.$	$\left\{ \begin{array}{l} 0.50 \\ 7.7 \\ - \end{array} \right.$	$\left\{ \begin{array}{l} 0.26 \\ 1.1 \\ 1.6 \end{array} \right.$	$\left\{ \begin{array}{l} 0.58 \\ 2.1 \\ 9.2 \end{array} \right.$
$\rightarrow 80, 3.2 \rightarrow 88$							
$\rightarrow 80, 20 \rightarrow 88$							
$\rightarrow 80, 144 \rightarrow 88$							
$\rightarrow 61, 0 \rightarrow 75$	$\left. \begin{array}{l} V_3 = 0.98275, \\ E = 1561 \\ B = 32.92 \end{array} \right\} \left(\begin{array}{l} \text{cm}^3/\text{g} \\ \\ (\text{cm}^3/\text{g}) \text{hr}^{1/2} \end{array} \right)$	$\left\{ \begin{array}{l} 0.24 \quad 8.6 \\ 2.03 \quad 12.4 \\ 27.6 \quad 13.9 \end{array} \right.$	$\left\{ \begin{array}{l} -3 \times 10^{-3} \\ 2.0 \times 10^{-1} \\ 4.8 \end{array} \right.$	$\left\{ \begin{array}{l} 15.1 \\ 11.2 \\ 2.6 \end{array} \right.$	$\left\{ \begin{array}{l} 0.17 \\ 1.60 \\ 25 \end{array} \right.$	$\left\{ \begin{array}{l} 0.24 \\ 1.7 \\ 23 \end{array} \right.$	$\left\{ \begin{array}{l} 0.32 \\ 0.93 \\ 24 \end{array} \right.$
$\rightarrow 61, 4 \rightarrow 75$							
$\rightarrow 61, 24 \rightarrow 75$							
$\rightarrow 61, 498 \rightarrow 75$							

is indicated by an arrow in Figures 8 and 9. The arrows agree fairly well with the observed peaks of the anomalous isotherms. The values of $t_{\max 2}$ obtained by use of eq 8 may involve some errors larger than those involved in $t_{\max 2}$ obtained by use of eq 8'; because the former are directly affected from an error involved in t_1 which was defined by use of eq 5. In addition the agreement of eq 5 with the observed isotherm is not so good as that of eq 4, especially in the case ($115^\circ\text{C} \rightarrow 80^\circ\text{C} \rightarrow 88^\circ\text{C}$).

As for the parameters listed in Table III, one sees that the present results give rather reasonable values at least in the order of magnitude. However, considering the values of the parameters in detail, one can see there are some problems left; the obtained values of C and t_2 vary with the value of z in a temperature combination $T_1 \rightarrow T_2 \rightarrow T_3$, in contrast to the theory leading to eq 4 and 5. Some of these problems may be caused from the simplification in the computation described before; however, others may reflect imperfections in the present theory. In order to achieve a better understanding of anomalous isotherms, it will be necessary to conduct further experimental and theoretical studies on various polymers.

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APPENDIX

Bueche^{8,19} has assumed that a polymer consists of rows of molecules which are mutually joined together with molecular springs. In order to count viscous forces, he has assumed that the rows are immersed in a viscous liquid. On the basis of the model, free volume is ascribed to molecular vibrations occurring between two neighboring molecules joined with the spring. A distribution function for the amount of free volume per a molecule is,

$$P(v) = (\text{const.}) \exp(-v^2/\Omega^2) \quad (\text{A1})$$

where $\Omega = \lambda\sigma$, σ is the cross-section of a molecule, and λ is the averaged amplitude of the inter-molecular vibration; Ω is a measure of average free volume.⁸

In this paper we have assumed that a polymer chain is a tensioned string on which molecules having mass m are arranged and fixed at an identical distance a which is about the diameter of a molecule (Figure A1). A motion of a molecule on such a string is manifested by composing many simple harmonic vibrations. As is well-known,²⁰ a kinetic equation for the motion and its solution are similar to those of the

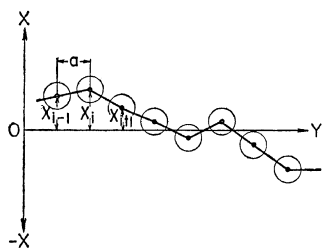


Figure A1. A model of molecular chain. A distance a is almost equal to the diameter of a molecule. Each molecule is joined to neighboring molecules with strings having tension force S .

inter-molecular vibration in Bueche's molecular row.⁸

According to the assumption described above the equation for a motion of a molecule is,

$$m\ddot{x}_i + S\{(x_i - x_{i-1})/a + (x_i - x_{i+1})/a\} = 0 \quad (\text{A2})$$

where S is tension force on the string. Various molecular forces in the polymer chain are lumped into S . If there are N molecules on the string, N equations similar to eq A2 exist. Then the following equation is obtained.

$$x_i = \sum_{n=1}^N A_n \sin\left(\frac{in\pi}{N+1}\right) \cos(\omega_n t - \theta_n) \quad (\text{A3})$$

Assuming $\hbar\omega_N \ll kT^*$, the energy distributed in a mode is kT , where \hbar is $h/2\pi$, h is Planck's constant and k is Boltzmann's constant. Then, A_n is presented as

$$A_n^2 \simeq 4kT/Nm\omega_n^2 \quad (\text{A4})$$

A composite amplitude⁸ is then calculated in a similar procedure to Bueche. As a result, the dispersion parameter of the distribution function of the composite amplitudes by N steps is denoted as

$$\lambda^2 = \left(\frac{2akT}{NS}\right) \int_0^N \delta n \quad (\text{A5})$$

and the distribution function of the composite amplitudes is,

$$P(A) \simeq (\text{const.}) \exp(-A^2/\lambda^2) \quad (\text{A6})$$

On the other hand, each molecule on the chain can rotate freely about the Y -axis in Figure A1. If we examine only molecules with larger amplitudes, we may consider the motion of a molecule occupying a space of volume proportional to aA^2 . Here, a polymer is assumed to be packed with the strings. Then, the occupied space of a molecule contacts with those of molecules on the other strings. Based on this model, the total amount of such occupied volumes larger than the volume of a molecule would be proportional to the total amount of free volume defined in the free volume theory; the amount of free volume per a molecule is proportional to aA^2 . The averaged value of this is represented as v_f , and eq A6 is;

$$P(v) = (\text{const.}) \exp(-v/v_f) \quad (\text{A7})$$

* Bueche assumed $\hbar\omega_N \gg kT$. Okano²¹ pointed out that the assumption is not reasonable for a polymer at around room temperature.

This distribution function is similar to that derived by Cohen—Turnbull.¹⁸ Note that Doolittle's diffusion coefficient and the WLF equation can be used in the present theory.

The amount of free volume at a temperature T_1 is given by eq A5 as

$$v_{f1} = \Gamma \left(\frac{2a^2}{S} \right) kT_1 \quad (\text{A8})$$

where Γ is a constant including the number of molecules per gram. According to Bueche,⁸ free volume of a polymer quenched from T_1 to T_2 is obtained from eq A5 and A8;

$$v_f = \Gamma \left(\frac{2a^2}{SN} \right) \left(\int_0^{n_a} kT_1 \delta n + \int_{n_a}^N kT_2 \delta n \right) \quad (\text{A9})$$

where n_a is the mode number corresponding to observation time t . The relation between n_a and t is obtained as¹⁹

$$t = (a^2 N^2) / (3\pi^2 n_a^2 D) \quad (\text{A10})$$

where D is an instantaneous value of the diffusion coefficient. Then one has, from eq A9 and A10,

$$v_f - v_{f2} = (v_{f1} - v_{f2}) / (D_t t)^{1/2} \quad (\text{A11})$$

where $D_t = (3\pi^2/a^2)D$, v_f is an instantaneous free volume, and v_{f1} , v_{f2} are equilibrium free volumes at T_1 , T_2 , respectively. D_t is also a function of instantaneous free volume, and denoted as the following by use of the Cohen and Turnbull diffusion coefficient¹⁸ or Doolittle's diffusion

coefficient¹⁶;

$$\begin{aligned} D_t &= D_e \exp \{2E_c(V - V_2)\} \\ &\equiv D_e \exp \{2E(V - V_2)/V\} \end{aligned} \quad (\text{A12})$$

where D_e is the diffusion coefficient in the equilibrium state at T_2 , $2E_c \simeq \gamma V^*/v_f v_{f2}$, γ is a constant ranging 1 to 1/2, V^* is approximately equal to the volume of a molecule, and $2E \simeq 1/f f_{e2}$. Figure A2 shows a procedure adjusting the relation between the coordinate for the retardation time and that for the observation time. One sees from the figure the following: if the polymer has made some retardations by the n_0 th mode during the quenching, at a time point $t = t_a$ the mode corresponding to $t_a + t_0$ will make the retardation, where t_0 corresponds to n_0 .

An equation for the anomalous isotherm is derived in the procedure similar to the foregoing description on the basis of the following assumption. When a polymer quenched from T_1 to T_2 is heated to T_3 , the modes ranging $N \sim n_a$ -th have passed from the state at T_1 to the state at T_2 and the other modes ranging $n_a \sim 0$ -th still stay at T_1 . At T_3 the modes ranging $N \sim n_a$ -th make retardations from T_2 to T_3 and the modes ranging $n_a \sim 0$ -th make retardations from T_1 to T_3 directly. One then has, from eq A9;

$$\begin{aligned} v_f &= \Gamma \left(\frac{2a^2}{SN} \right) \left(\int_0^{n_b} kT_1 \delta n \right. \\ &\quad \left. + \int_{n_b}^{n_a} kT_3 \delta n + \int_{n_a}^{n_c} kT_2 \delta n + \int_{n_c}^N kT_3 \delta n \right) \end{aligned} \quad (\text{A13})$$

and then,

$$\begin{aligned} v_f - v_{f3} &= \Gamma \left(\frac{2a^2}{SN} \right) \{n_b k(T_1 - T_3) \\ &\quad - n_c k(T_3 - T_2) + n_a k(T_3 - T_2)\} \end{aligned} \quad (\text{A14})$$

where n_b and n_c are variables defined in the ranges n_0 to 0 and N to n_a , respectively. The quantities n_b , n_c , and n_a representing the mode numbers are substituted by times corresponding to them, respectively, on the basis of eq A10. A time t_1 corresponding to n_a is introduced. Taking account of the range for n_b , $t + t_1$ is substituted for the time corresponding to n_b . A constant t_2 is introduced in a similar sense as to t_0 in eq 1.

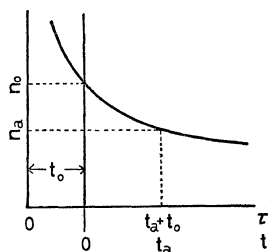


Figure A2. Relation between coordinates for retardation times and observation times. The ordinate represents a mode number corresponding to a retardation time. Two abscissa axes indicate time axes for retardation times τ and observation times t , where each axis is measured in the same unit as the other.