The Viscometric Properties of Polyesters. II. Viscosity in the Range of Low Temperatures near the Glass Transition Point

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The glass transition temperature (T_g) is one of the most important properties of liquid state polymers.[1-3]

Although T_g values vary with individual polymers, the properties at a given temperature share common features; that is, (1) the apparent activation energy for viscous flow[1] ($E^{\neq}$), (2) the free volume fraction[1] (f), (3) the viscosity[2] (η), and (4) the thermal expansion coefficient of the free volume fraction[6,7] (α_f) show similar values irrespective of the nature of the polymers.

Hirai et al.[6] derived a theoretical expression on viscosity near the glass transition point from such empirical formulas as the WLF type,[7] the Fox-Flory type[8] and the Tobolsky-Catsiff type[10] equations, by means of the free volume theory for viscous flow.[5]

The object of the present paper is (1) to represent the viscometric property in the aspect of free volume, (2) to obtain more exact information about the " transition area " for the

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[1] T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

[2] R. F. Boyer and R. S. Spencr, ibid., **16**, 594 (1945).

[3] R. F. Boyer, ibid., **25**, 825 (1954).

[4] R. Kawai, *Kobunshi*, **6**, 348 (1957).

[5] A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951); ibid., **23**, 236 (1952).

[6] N. Hirai, *Kobunshi Kagaku*, **19**, 191 (1962); ibid., **19**, 528 (1962).

[7] M. L. Williams, R. E. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

[8] T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

[9] P. J. Flory, *J. Am. Chem. Soc.*, **62**, 11057 (1940).

[10] A. V. Tobolsky and E. Catsiff, ibid., **76**, 4204 (1954).

TABLE I. RELATIONSHIP BETWEEN CHEMICAL STRUCTURE AND VISCOMETRIC PROPERTIES

	T_s °C	η_s poise	$E_c^{\ddagger}$ kcal./mol.	δ	C. E. D. cal./cc.
DE-Su	− 2	7000	32	0	98
Ad	−23	20000	23	0	86
Az	—	—	—	—	74
Se	—	—	—	—	72
TE-Su	− 8	7000	30	0	92
Ad	−24	13000	23	0	83
Az	−31.5	7000	18	0	74
Se	—	—	—	—	71
DP-Su	5	9000	34	−0.69	85
Ad	−22	20000	25	0	77
Az	−36.5	7000	19	−0.34	68
Se	−37.5	6000	19	+0.22	66
Bu-Su	4	10000	23	−0.34	96
Ad	−28	50000	21	−1.00	85
Az	−39	150000	18	−0.69	75
Se	−39	100000	18	−0.47	73

Note

(1) Chemical

	(Conventional)	(IUPC)
Su :	Succinic acid	Butanedioic acid
Ad :	Adipic acid	Hexanedioic acid
Az :	Azeraic acid	Nonanedioic acid
Se :	Sebacic acid	Decandioic acid
DE :	Diethylene glycol	2, 2′-Dihydroxydiethyl ether
TE :	Triethylene glycol	1, 2-Ethanediol bis(2-hydroxyethylether)
DP :	Dipropylene glycol	2, 2′-Dihydroxydipropyl ether
Bu :	—	1, 3-Butanediol

(2) Physical

T_s, η_s : Constants in the WLF equation
$\ln \eta/\eta_s = -[8.86(T-T_s)]/[101.6+T-T_s]$
$E_c^{\ddagger}$: Average activation energy in the range of temperature −30∼5°C
δ : Corrected value in Eq. 2′ or 8′

$$f(\eta)_{\mathrm{cal}} = 1/(2.3 \log \eta + 10.1 + \delta) \qquad (2')$$

$$E^{\ddagger}_{A\,\mathrm{cal}} = 2.0T(2.3 \log \eta + 10.1 + \delta) \qquad (8')$$

C. E. D.: Cohesive energy density calculated by Kawai's method[4)]

viscous flow mentioned in Part I, and (3) to consider how the viscosity is affected by the difference of a few degrees in chemical structure.

The actual observation of viscosity indicates that (1) linear relationships are obtained in curves of f vs. T, (2) the "transition area" for viscous flow is an intermediate region between the WLF and the Andrade liquid, and (3) some viscometric properties are proportional to the intermolecular force within polyesters of the same glycol series.

Experimental

The Preparation of the Polyesters.—*The Reaction of Long-chain Polyesters* (cf. Part I).

The Fractionation of Polyesters. — Samples were treated at 130°C to remove volatile contaminants and were fractionated under high vacuum (ca. 10^{-4} mmHg) by being distillated two or three times. The distillates at 160°C contained a crystalline substance, while the distillates at 200°C did not.

The Measurement of Viscosity.—A Brookfield-type rotational viscometer was used for the range of 10^{-1}∼10^3 poises, while a Couette-type viscometer was used for the higher range (10∼10^6 poises).

Rotational viscometer (Couette-type) :
Range 1×10∼5×10^6 poise (accuracy ±2%)
Number of revolutions 0.8∼83 r. p. m. (14-stage change)
Rate of shear 63∼0.06 $\sec^{-1}$
Radius of outer cylinder 1.4 cm.
Radii of inner cylinders 1.2, 1.1, and 0.6 cm.
Length of inner cylinders 5.5 cm.

The sample was put in a dry ice-methanol bath and kept for 35∼40 min. until the temperature equilibrium was attained. The viscosity was measured at temperature intervals of 3∼5°C in the ragne from −60 to 30°C.

[11)] J. D. Ferry, "Die Physik der Hoch Polymeren," Ed. by H. A. Stuart, Springer-Verlag, Berlin, Bd 4 (1956), p. 392.

On the basis of this measurement of viscosity, every sample could be regarded as a Newtonian liquid over the whole range of viscosity as had been expected,[8,12] but over 10^3 poises it was difficult to measure the viscocity at a constant temperature except in the case of an extremely low shear rate, because of the great generation of heat by friction during the measurement, and it was also difficult to ascertain the effect of the shear rate on the viscosity.

Results and Discussion

The Temperature Dependence of the Viscosity near the Glass Transition Point. — The amorphous polyesters used in this experiment are listed in Table I. As has been stated in Part I, diethylene azelate, diethylene sebacate and triethylene sebacate were all crystalline, and therefore, their viscosities could not be measured at a low temperature.

In any case, the experimental values fit the WLF equation only within the range of $10^2\sim10^8$ poises; the difference between the experimental and the calculated values becomes evident from the viscosity of $10\sim10^2$ poises.

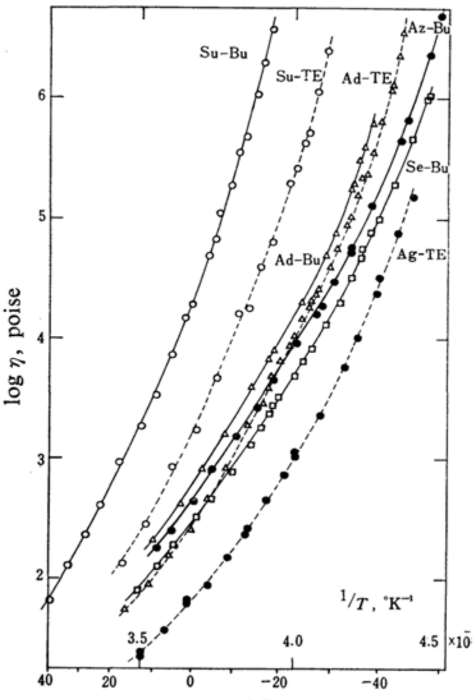
$$\log \eta/\eta_s = -8.86(T-T_s)/(101.6+T-T_s) \qquad \text{WLF eq.}$$

The "transition area" mentioned in Part I corresponds to the range of viscosity where experimental results begin to deviate from the WLF equation.

By applying the experimental values to the WLF equation, the corresponding T_s and η_s are obtained as shown in Table I.

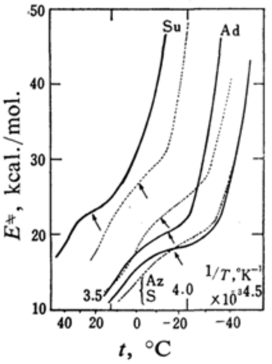
The Temperature Dependence of the Apparent Activation Energy for Viscous Flow ($E^{\ne}$) in the WLF Liquid State. — The relations of $\log \eta$ vs. $1/T$ and $E^{\ne}$ vs. $1/T$ are shown in Figs. 1 and 2. From these relations, it can be observed that the temperature dependence of $E^{\ne}$ behaves peculiarly; over a viscosity range higher than 10^2 poises and within the region of $-30\sim5$°C, most polyesters have a region in which the apparent activation energy for viscous flow becomes nearly constant. In the case of the succinic acid polyester series, however, this region deviates a little towards the high temperature side. The average value of activation energy in this region ($E_c^{\ne}$) is shown in Fig. 2 and Table I.

For the purpose of elucidating this phenomenon, the same investigation was carried out on several samples of triethylene adipate with different molecular weights ($690\sim3600$), as is shown in Figs. 3 and 4.



t, °C

Fig. 1. Relationship between viscosity and temperature.
(1,3-Butanediol series and triethylene glycol series)
—— Bu series, …… TE series



t, °C

Fig. 2. Apparent activation energy for viscous flow.
(1,3-Butanediol series and triethylene glycol series)
—— Bu series, …… TE series, ↑ $E_c^{\ne}$

Samples 1—3 and 4 were obtained by the conventional method and by molecular distillation at 200°C respectively.

Although polyesters have considerably different molecular weights, they show a similar tendency regarding this peculiarity of $E^{\ne}$: the region where $E^{\ne}$ is considered to be constant is observed in the range of $-30\sim5$°C

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[12] M. Takayanagi and S. Kuriyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kōgyō Kagaku Zassi*), 57, 873 (1954); ibid., 57, 876 (1954); ibid., 59, 49 (1956).

for all samples, and yet the average values of $E^{\ne}$ in this region are equal except for sample 4.

Generally such a special type of curve for the temperature dependence of $E^{\ne}$ has not been observed[8,12] except in the example of a rubber-like polymer.[11]

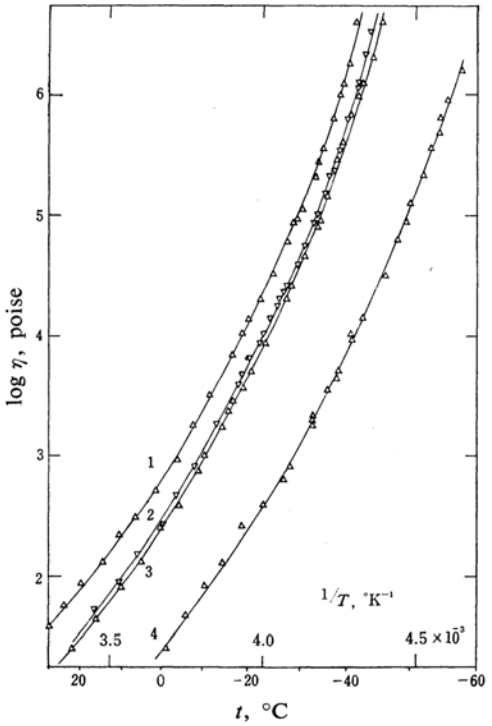

Fig. 3. Effect of molecular weight. (Triethylene adipate)

Sample	$\overline{M}_n$	Sample	$\overline{M}_n$
1	3600	2	1900
3	1200	4	680

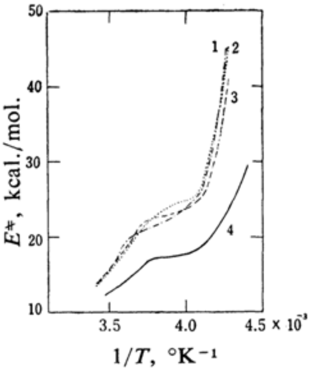

Fig. 4. Effect of molecular weight on activation energy. (Triethylene adipate)

Sample	$\overline{M}_n$	Sample	$\overline{M}_n$
1	3600	2	1900
3	1200	4	680

Even in this region each polyester behaves not as a non-Newtonian body but as a Newtonian liquid, and its molecular weight is too small to cause the so-called intermolecular entanglement; the general properties of the polyesters used in this experiment are very different from those of a rubber-like polymer.

Though it is impossible at present to explain this special phenomenon regarding the temperature dependence of $E^{\ne}$, the author wishes to point out two problems. One is the question whether this is one of the phenomena corresponding to the discontinuous change in the temperature dependence of the thermal expansion coefficient of the free volume fraction of the polyester, and the other is the question whether this depends on the time scale of measurement, for it takes a great deal of time to reach the equilibrium liquid state near the glass transition point. For the moment it can only be said with certainty that this phenomenon has something to do with the "transition area" for viscous flow.

Estimation of the Free Volume Fraction. — The Doolittle equation is generally applicable to the actual liquid, especially in the non-Andrade liquid state:

$$\ln \eta/\eta_g = B(1/f - 1/f_g) \tag{1}$$

The relationship between the free volume fraction (f) and the temperature (T) can be calculated from the results of the temperature dependence of the viscosity:

$$f = B/(\ln \eta/\eta_g + B/f_g) \tag{2}$$

The WLF equation and its function of the free volume fraction, $f(T)$, are deduced[7] from Eq. 1.

$$\ln \eta/\eta_g = [(T - T_g)/f_g]/[T - T_g + f_g/\alpha_{fg}] \tag{3}$$

$$f(T)_{\mathrm{WLF}} = f_g + \alpha_{fg}(T - T_g) \tag{4}$$

The functions of $f(T)_A$ and $E_A^{\ne}$ in the Andrade equation have been shown to be as follows by Hirai et al.:[6]

$$\ln \eta/\eta_g = (E_A^{\ne}/\boldsymbol{R})(1/T - 1/T_g) \tag{5}$$

$$f(T)_A = \alpha_l T \tag{6}$$

$$E_A^{\ne} = B\boldsymbol{R}/\alpha_l \tag{7}$$

$$E_A^{\ne} = \boldsymbol{R}T(\ln \eta/\eta_g + 1/f_g) \tag{8}$$

Equations for calculating the free volume fraction, $f(\eta)_{\mathrm{cal}}$ and $E_{A\,\mathrm{cal}}^{\ne}$ are obtained by substituting the following empirical values in Eqs. 2 and 8; a correction term δ is also added at the same time in order to assure the validity of this mathematical treatment.

$$f(\eta)_{\mathrm{cal}} = 1/(2.3 \log \eta + 10.1 + \delta) \tag{2'}$$

$$E_{A\,\mathrm{cal}}^{\ne} = 2.0T(2.3 \log \eta + 10.1 + \delta) \tag{8'}$$

In Eq. 1—8, the constants are termed as follows:

R: gas constant 1.987 cal./mol. deg.
η_g: viscosity at glass transition point (T_g) about 10^{13} poises[2)]
B: a constant about 1[5,6)]
f_g: Doolittle's free volume fraction at T_g about 0.025[7)]
α_{fg}: thermal expansion coefficient of f at T_g about 4.8×10^{-4} (°K^{-1})[7)]
α_l: thermal expansion coefficient of f in Andrade liquid
$E_A^{\ast}$: activation energy for viscous flow in Andrade liquid

The correction term δ can be obtained from Eq. 8′ by comparing the calculated value of the activation energy with the observed value, because the latter value for every polyester is almost constant (about 7.3 kcal./mol.) in the range between 370 and 420°K, as has already been shown in Part I.

The correction term δ is listed in Table I; this value depends on the molecular weight and the chemical structure of the polyester. In this table, all the δ values of the diethylene or triethylene glycol polyester series are zero.

In this manner, it is possible to discuss the temperature dependence of the f of amorphous polyesters as shown in Figs. 5—6.

The curve virtually consists of three straight-line part.

A typical pattern of the relation between f and T is represented in Fig. 7. We can divide the viscous flow state into three parts; (1) the Andrade liquid state ($T_1<T$; $f_1<f$), (2) the "transition area" for viscous flow ($T_2<T<T_1$; $f_2<f<f_1$), and (3) the WLF liquid state ($T_g<T<T_2$; $f_g<f<f_2$).

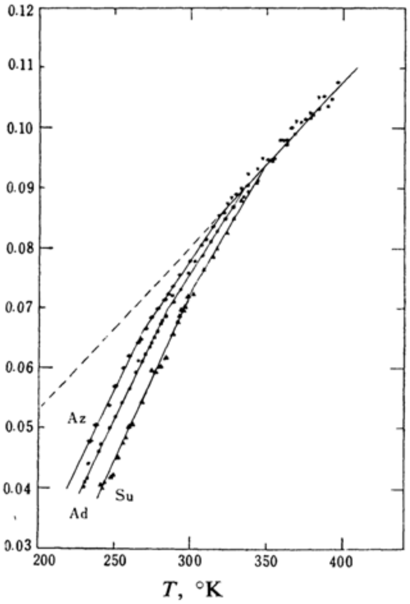

Fig. 5. Relationship between free volume fraction and temperature.
(Triethylene glycol series)

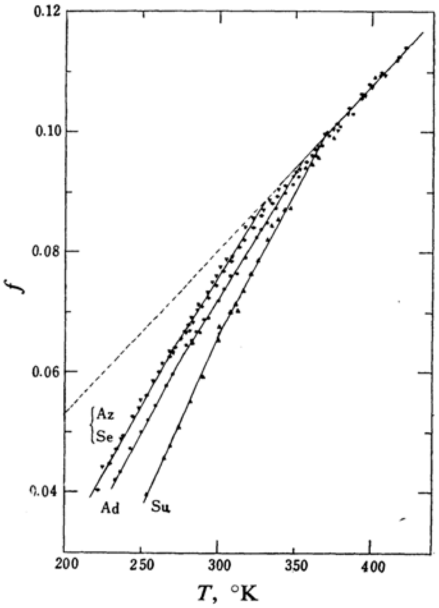

Fig. 6. Relationship between free volume fraction and temperature.
(1,3-Butanediol series)

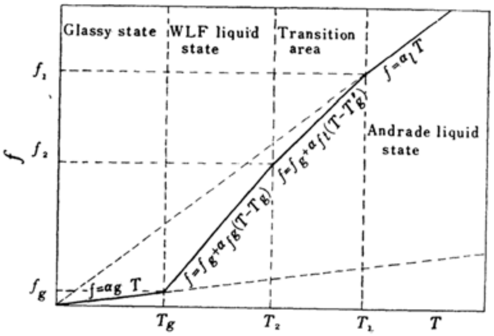

Fig. 7. Relationship between free volume fraction and viscous flow state.
(Schematic)

In the Andrade and the WLF liquid states, the values of f estimated from η are in good agreement with Eqs. 6 and 4 respectively, and the constants of these equations can be estimated for every polyester (cf. Table II).

The experimental values of f_1, f_2, α_l and α_g are approximately 0.10, 0.07, 2.69×10^{-4} and 4.8×10^{-4} respectively, independent of the type of polyester.

In the "transition area" ($0.10>f>0.07$), the relationship between f and T can be represented by Eq. 4′, the form of which is similar to Eq. 4:

TABLE II. RELATIONSHIP BETWEEN CHEMICAL STRUCTURE AND TEMPERATURE DEPENDENCE OF FREE VOLUME FRACTION

	T_g' °K	T_g °K	α_{ft} $\times 10^{-4}$ °K^{-1}	α_{fg} $\times 10^{-4}$ K°$^{-1}$	T_1 °K	T_2 °K	f_1	f_2
DE-Su	191	221.5	4.03	5.62	386	303	0.108	0.071
Ad	175	205	3.94	5.27	346	293	0.093	0.072
Az	159	—	3.71	—	329	(280)	0.088	(0.070)
Se	159	—	3.71	—	329	(308)	0.088	(0.080)
TE-Su	193	216	4.31	5.63	347	303	0.094	0.074
Ad	174	203	4.01	5.63	335	288	0.090	0.072
Az	166	193	3.94	5.93	321	269	0.099	0.071
Se	166	—	3.94	—	321	(318)	0.099	(0.085)
DP-Su	213	228.5	4.58	5.53	374	319	0.101	0.075
Ad	148	203.5	3.45	5.17	367	313	0.099	0.085
Az	148	189	3.45	4.57	367	298	0.099	0.075
Se	148	189	3.45	5.22	367	298	0.099	0.075
Bu-Su	214	226.5	4.77	5.70	372	305	0.101	0.068
Ad	115	196.5	4.14	5.77	359	276	0.097	0.063
Az	172	191.5	3.95	4.60	342	267	0.092	0.063
Se	172	188.5	3.95	4.94	342	268	0.092	0.063

Note

T_g, α_{fg}: Constants in the WLF liquid state $f(\eta)_{\mathrm{cal}}=f_g+\alpha_{fg}(T-T_g)$

T_g', α_{fg}: Constants in the "transition area" $f(\eta)_{\mathrm{cal}}=f_g+\alpha_{ft}(T-T_g')$

T_1, f_1: Boundary between the Andrade liquid state and the "transition area"

T_2, f_2: Boundary between the WLF liquid state and the "transition area"

$$f=f_g+\alpha_{ft}(T-T'_g) \qquad (4')$$

This shows that the WLF-type equation is also applicable to the "transition area," but that the estimated value of the glass transition point in this area is different from that in the WLF liquid state.

Nevertheless, even in crystalline polyesters with structures similar to those of amorphous polyesters, f at the melting point exists in the range of about 0.07∼0.10 and this range of f corresponds to the "transition area" for viscous flow in amorphous polyesters.

The range corresponding to the "transition area" for viscous flow has been observed near the respective melting points of several n-paraffines by Miller.13)

Moreover, even though the estimated value of f only in the range of high temperature changes considerably as a result of a little change in α_l or $E_A^{\ne}$, the relation between f and T would not be significantly changed.

Influences of Chemical Structure on Viscometric Properties.—The influences of chemical structure can be elucidated more clearly by comparing the cohesive energy density,4) calculated from the structural unit of polyesters, with such viscometric properties as f, $E_c^{\ne}$ or T_g.

It follows from these results that there is a linear relation between the cohesive energy density and the viscometric properties in a certain kind of glycol polyester series; i.e., the plots of these straight lines are those

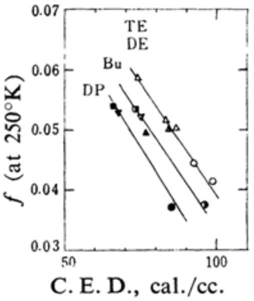

Fig. 8. Relationship between cohesive energy density and free volume fraction.

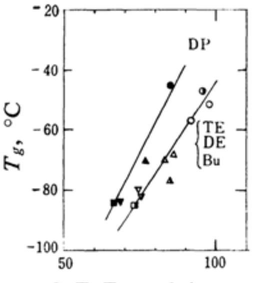

Fig. 9. Relationship between cohesive energy density and glass transition temperature.

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13) A. A. Miller, *J. Chem. Phys.*, 67, 1031 (1963).

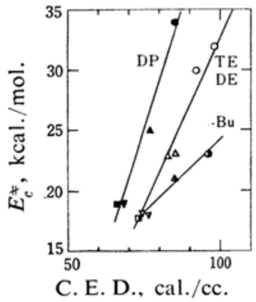

Fig. 10. Relationship between cohesive energy density and average activation energy for viscous flow (cf. Fig. 2).

from the following series respectively;

(1) Ether-type polyesters without side chains (TE and DE series)

(2) Ether-type polyesters with side chains (DP series)

(3) Ordinary-type polyesters with side chains (Bu series).

It seems probable that the viscometric properties are not perfectly represented by only the intermolecular forces because these tendencies are different according to the kinds of gylcol; a similar relation for many polymers has been obtained by Kawai.[4)]

It is observed that, with an increasing intermolecular force, the free volume fraction (f) decreases, while the activation energy for viscous flow ($E_c^{\neq}$) in a peculiar region (cf. Fig. 2) and the glass transition point (T_g) increase.

As Figs. 8—10 show, in the series of dipropylene glycol (with the side chains) the above tendencies between the cohesive energy density and the viscometric properties are more strongly recognized than the expected tendencies from the series of diethylene- and triethylene glycols (without side chains); therefore, this shows that the intramolecular rotation in the liquid state was remarkably disturbed by the existence of side chains. In contrast with the dipropylene glycol series, the 1,3-butanediol polyester series (without ether bond) show a different pattern of viscometric properties.

Since the tendencies of the 1,3-butanediol polyester series are too complex to be explained clearly, at present it can be said with certainty only that the ether- and the methylene-bond in the main chain of polyesters behave remarkably differently in terms of viscosity.

Summary

The viscosities of amorphous long-chain polyesters have been measured in the range of $10\sim10^6$ poises and between -60 and 30°C, and the following results have been obtained (cf. also Part I).

(1) Within the limit of $10^2\sim10^6$ poises, all the polyesters are consistent with the WLF equation. At the "transition area" which was described in Part I, the observed viscosity begins to deviate from the WLF equation.

(2) The apparent activation energy for the viscous flow ($E^{\neq}$) is nearly constant within the range of $-30\sim5$°C, and over the range of viscosity beyond 10^2 poises for all the polyesters.

(3) The estimated curve of the temperature dependence of the free volume fraction (f) can be divided into three straight-line parts, corresponding to the WLF liquid state, the "transition area" for viscous flow, and the Andrade liquid state respectively.

(4) The relationship between the chemical structure and the viscosity can be represented in connection with intermolecular force, intramolecular rotation and so on.

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