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Viscous Properties of Liquid Oligotrifluorochloroethylene

Naosato Yoshida and Shuichi Hamada
Department of Chemistry, Faculty of Science, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo

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The viscosities of fractionated liquid oligotrifluorochloroethylene were measured in the molecular-weight range from 820 to 2100 at temperatures ranging from 40 to 120°C. While the relationships between log η and log M_n were regarded as being approximately linear in the molecular-weight range smaller than 1090, and their slopes were much larger than unity, a considerable deviation from the approximately linear relationship was observed in the molecular-weight range larger than 1090. The temperature dependence of the viscosities was well explained in terms of the WLF equation under the present experimental conditions. The large slope in the range of the linear relationship may be caused because the reciprocals of the free-volume fractions, $1/f$, increase remarkably with an increase in the molecular-weight. The free-volume per cubic centimeter, F, contributed by chain-ends increased abruptly with an increase in the molecular-weight in the range smaller than about 1200.

In a previous paper,[1] it was reported that the slope of the log η-log M_n relationship for oligotrifluorochloroethylene was much larger than unity in the molecular-weight range from 820 to 1090; a similar behavior in oligostyrene and oligoisobutylene has also been reported by Fox and Flory[2,3] and by Uchida and Hata.[4]

In this work, the dependence of the viscosity on the molecular-weight will be discussed in connection with the free-volume.

Experimental

Materials. Daifloil's No. 20, 50, 100, and 200, which were obtained from the Daikin Kogyo Company, were used as the samples of oligotrifluorochloroethylene. The acetone-soluble part was fractionated in the manner described in our previous paper,[1] while the acetone-insoluble part was fractionated according to whether it was soluble or insoluble in benzene or carbon tetrachloride. The number-average molecular-weight of the oligotrifluorochloroethylene thus fractionated was estimated by cryoscopic and ebullioscopic methods, using benzene and carbon tetrachloride respectively as the solvents.

Procedure. The melting point, T_m, of the sample crystallized was estimated by a dilatometric method. Beforehand, a rough melting point, T_m', of the sample was estimated by a capillary method in order to obtain the crystallization temperature of the sample fractionated. A suitable amount of the sample was crystallized in a container of the dilatometer by allowing it to stand for about 30 hr at a temperature of $(7/9)\ T_m'$. The samples were considered to crystallize sufficiently, since sharp X-ray patterns were observed even with samples obtained by quenching. The sample thus crystallized was sealed in a dilatometer containing mercury. The dilatometer was kept at $T_m' - 20°$ for 30 min to establish a thermal equilibriun, and then it was heated slowly at a heating rate of 0.05°C/min. The melting point was estimated graphically from the specific volume-temperature relationship.

The viscosities and the densities of the liquid samples were measured with an Ubbelohde-type viscometer and a dilatometer respectively in the manner described in a previous paper;[1] they were determined at given temperatures in the range from 40 to 120°C with an accuracy of ±0.01°C in thermostated baths filled with water or silicone oil.

Results

Melting Points of Oligotrifluorochloroethylene. Table 1 shows the melting points of the samples fractionated in the molecular-weight range from 1200 to 3800.

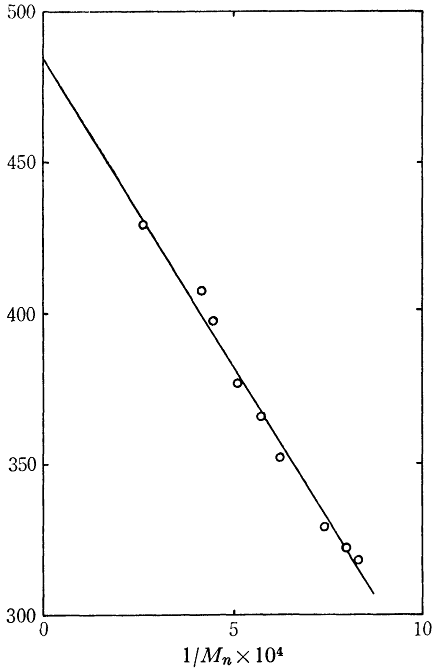

Fig. 1. Relationship between T_m and $1/M_n$.

Table 1. Melting points of oligotrifluorochloroethylene

M_n	1200	1250	1350	1600	1750	1950	2250	2400	3800
T_m, °K	317	321	328	351	365	376	397	407	429

Figure 1 shows the relationship between the melting point, T_m, and the reciprocal of the number-average molecular-weight, $1/M_n$. The linear relationship between T_m and $1/M_n$ can be expressed as follows:

$$T_m = 485 - 2.10 \times 10^5/M_n \qquad (1)$$

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[1] N. Yoshida, S. Hamada, and T. Shirai, This Bulletin, **42**, 3131 (1969).

[2] T. G. Fox and P. J. Flory, *J. Chem. Phys.*, **55**, 221 (1951).

[3] T. G. Fox and P. J. Flory, *J. Polym. Sci.*, **13**, 315 (1954).

[4] Y. Uchida and T. Hata, Preprint of the 13th Annual Meeting of Soc. Polymer Sci., Japan, 222 (1964).

TABLE 2. VISCOSITIES OF OLIGOTRIFLUOROCHLOROETHYLENE

M_n	Viscosities η, poise								
	40°C	50°C	60°C	70°C	80°C	90°C	100°C	110°C	120°C
820	6.39	2.93	1.51	0.855	0.521				
860	10.78	4.71	2.33	1.26	0.730	0.451			
870	18.81	6.68	3.16	1.64	0.916	0.547			
890		9.16	4.23	2.15	1.19	0.698			
1010		29.53	12.28	5.68	2.99	1.63			
1030			16.60	7.59	3.77	2.01	1.14		
1050			21.21	9.49	4.63	2.43	1.36		
1070			23.20	10.39	5.05	2.64	1.47		
1090			26.23	11.66	5.64	2.93	1.62		
1200				24.94	11.20	5.44	2.83		
1600					49.25	22.55	11.14		
2100							23.88	12.20	6.60

The melting point, T_m^0, of a high-polymeric trifluorochloroethylene is expected to be 485°K from the linear relationship. This value is nearly equal to that of polytrifluorochloroethylene, 497°K, as reported by Hoffman and Weeks.[5,6]

Viscosities of Oligotrifluorochloroethylene. The viscosities of the liquid samples fractionated are given in Table 2.

Though the results in the molecular-weight range smaller than 1090 have been reported in the previous paper,[1] they were reexamined for this work.

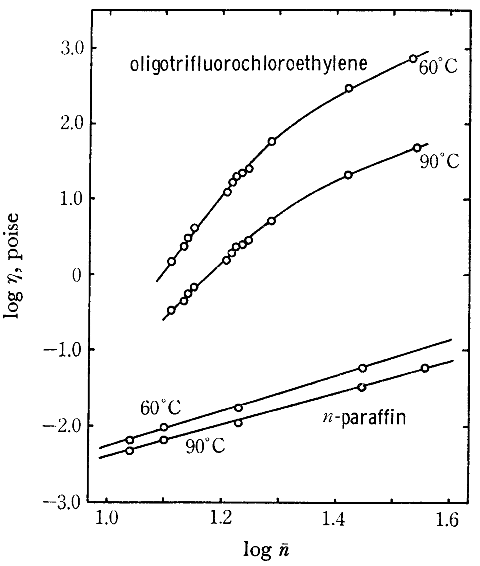

Fig. 2. Chain-length dependence of viscosity.
(The viscosity values for oligotrifluorochloroethylene in the molecular-weight range larger than 1200 at 60°C, and those in the molecular-weights of 820 and 2100 at 90°C were calculated by using WLF equation, respectively.)

Figure 2 shows the relationships between log $\bar{n}$ and log η at 60 and 90°C in the chain-length range from 12.8 to 34.8; the chain-length, $\bar{n}$, shows the number of carbon atoms in the skeleton of oligotrifluorochloroethylene and n-paraffin molecules. An expression, $\bar{n}$, was taken in order to compare the dependence of the viscosities of oligotrifluorochloroethylene on the chain-length with those for n-paraffin. While an approximately linear relationship was obtained between log η and log $\bar{n}$, *i.e.*, between log η and log M_n, in the molecular-weight range smaller than 1090, as was reported in the previous paper,[1] the linear relationship did not hold in the molecular-weight range larger than 1090. On the contrary, in the case of n-paraffin[7,8] log η varied linearly with log$\bar{n}$ in the chain-length range from 5 to 64 (the molecular-weight range from 72.15 to 899.68). The slopes of the linear part were much larger than those found in the usual lower-molecular-weight chain polymers, and they rose remarkably with an increase in the temperature.[1]

Temperature Dependence of Viscosities. The shift factor, a_T, based on an arbitrary fixed temperature, T_0, obeyed well the WLF equation,[9] reported in the previous paper.[1] From the linear relationship between $(T-T_0)/\log a_T$ and $(T-T_0)$, the WLF parameters, C_1^0 and C_2^0, were estimated in the molecular-weight range from 820 to 2100. Table 3 shows C_1^0 and C_2^0 at the fixed temperature of 70°C and their products, $C_1^0C_2^0$.

The apparent activation energy, E_a, for the viscous flow was estimated from the following equation:[6]

TABLE 3. VALUES OF C_1^0, C_2^0, AND $C_1^0C_2^0$ AT 70°C

M_n	C_1^0	C_2^0	$C_1^0C_2^0$
820	3.50	146.2	511.9
860	4.13	158.8	655.8
870	4.55	164.6	749.7
890	4.61	161.8	744.8
1010	5.76	180.1	1037.1
1030	5.95	179.9	1069.7
1050	6.09	179.7	1094.9
1070	6.27	184.3	1155.6
1090	6.34	185.0	1173.2
1200	7.03	187.1	1314.7
1600	7.51	185.4	1392.0
2100	7.70	179.9	1385.6

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5) J. D. Hoffman and J. J. Weeks, *J. Res. Nat. Bur. Stand.*, **60**, 465 (1958).

6) J. D. Hoffman and J. J. Weeks, *J. Chem. Phys.*, **37**, 1723 (1962).

7) A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).

8) A. K. Doolittle, *ibid.*, **23**, 236 (1952).

9) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).

$$E_a = 2.303C_1^0C_2^0RT^2/(C_2^0+T-T_0)^2 - RT + \alpha RT^2 \quad (2)$$

where R and α are the gas constant and the thermal-expansion coefficient of the liquid sample respectively.

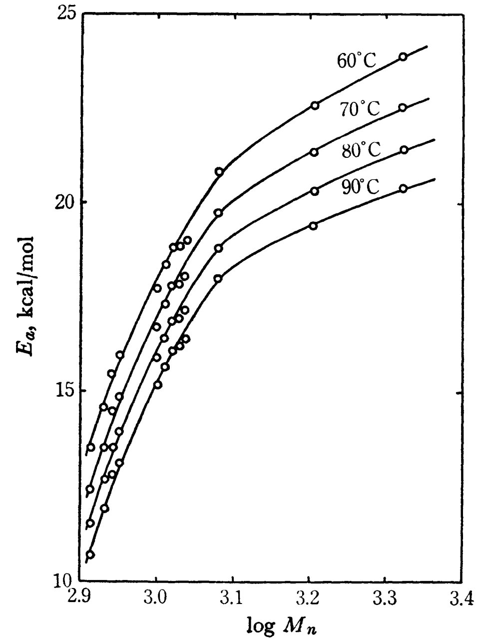

Fig. 3. Dependence of apparent activation energy for viscous flow on log M_n.

Figure 3 shows the dependence of E_a on log M_n. Though the values of E_a increased with an increase in the molecular-weight, they were quite large in comparison with those found in the usual lower-molecular-weight oligomers without branched chains.[10)]

Discussion

According to Doolittle,[7,11)] the viscosity is related to free-volume fraction by the following equation:

$$\ln \eta = \ln P + Q(1/f_T) \quad (3)$$

where P and Q are empirical constants; where f_T is the free-volume fraction at T, and where the parameter, Q, is regarded as being approximately unity.[12)] The reciprocal of the free-volume fraction, $1/f_T$, at a given temperature, T, was calculated from the following equation in conjunction with the WLF equation:

$$1/f_T = 2.303C_1^0C_2^0/(C_2^0+T-T_0) \quad (4)$$

The dependence of $1/f_T$ on the molecular-weight, M_n, and the number of carbon atoms, $\bar{n}$, in the skeletons of oligotrifluorochloroethylene and n-paraffin molecules at given temperatures is shown in Fig. 4. The parameters, C_1^0 and C_2^0, for n-paraffin were estimated from the results reported by Doolittle[7)] by the manner used in the case of oligotrifluorochloroethylene. The reciprocal of the free-volume fraction, $1/f_T$, varied considerably with $\bar{n}$ in the case of oligotrifluorochloroethylene; this is in contrast with the case of n-paraffin, as is shown in Fig. 4. While linear relationships between $1/f_T$ and log M_n were obtained in the molecular-weight range from 860 to 1200, considerable deviations from the linear relationships were observed in the molecular-weight range larger than 1200. In the molecular-weight range from 860 to 1200, the relationship between $1/f_T$ and ln M_n is expressed as follows:

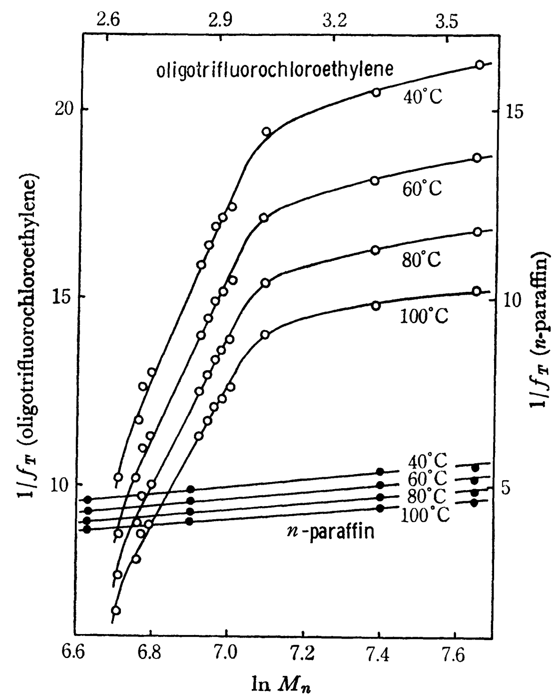

Fig. 4. Relationship between ln M_n and $1/f_T$.

$$1/f_T = \ln h + k \ln M_n \quad (5)$$

The slopes, k, were much larger than unity, and they decreased with an increase in the temperature, as is shown in Table 4.

TABLE 4. SLOPES, k, OF THE LINEAR RELATIONSHIP

Temp., °C	40	60	80	100
k	23.8	22.0	20.0	18.8

The free-volume fraction, f_T, at T is expressed by the following equation:

$$f_T = f_g + \alpha_f(T-T_g) \quad (6)$$

where f_g is the free-volume fraction at T_g, and α_f, its thermal-expansion coefficient. The thermal-expansion coefficient, α_f, of the free-volume fraction is expressed as $1/2.303C_1^0C_2^0$. Figure 5 shows the relationships between α_f and $\bar{n}$ for oligotrifluorochloroethylene and n-paraffin. The α_f values of oligotrifluorochloethylene increased remarkably as the $\bar{n}$ values decreased in the range of $\bar{n}$ smaller than approximately 20; they reached a constant value, 3×10^{-4}°C^{-1}, above an $\bar{n}$ value of 20, though the α_f values for n-paraffin scarcely changed at all.

The glass-transition temperatures, T_g, of the fractionated oligotrifluorochloroethylenes were deduced from their melting points, because the measurement of the glass-transition temperature was difficult because of a tendency toward easy crystallization. The ratio be-

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10) H. Schott, *J. Appl. Polym. Sci.*, **6**, S29 (1962).
11) A. K. Doolittle and D. B. Doolittle, *J. Appl. Phys.*, **28**, 901 (1957).
12) F. Bueche, *J. Chem. Phys.*, **24**, 418 (1956).

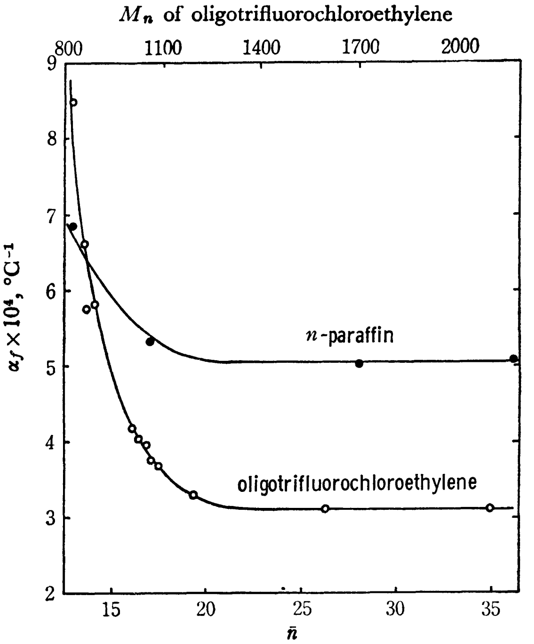

Fig. 5. Relationship between α_f and $\bar{n}$.

tween the glass-transition temperature and the melting point, T_g/T_m, for polytrifluorochloroethylene was reported to be 0.654 by Hoffman and Weeks.[5,6] This ratio was nearly equal to the value, 0.667, found in usual asymmetric polymers.[13] By the use of this value, 0.667, found in usual asymmetric polymers.[13] By the use of this value in the oligomer range, the relationship between the T_g and the M_n of oligotrifluorochloroethylene can be expressed from the relationship of $T_g/T_m=0.654$ and Eq. (1) as follows:

$$T_g = 317 - 1.37 \times 10^5/M_n \qquad (7)$$

Thus, the glass-transition temperature, T_g, of oligotrifluorochloroethylene is considered to rise remarkably as the molecular-weight increases in the oligomer range.

Accordingly, the free-volume fraction, f_T, in the molecular-weight range below 1200 ($\bar{n}=20$) is considered to vary remarkably with the effects of both an abrupt decrease in α_f and a remarkable rise in T_g with an increase in the molecular-weight. The free-volume fractions, f_T, were related only to the variation in T_g depending on the molecular-weight above 1200, because the thermal-expansion coefficient, α_f, of the free-volume was nearly constant.

Bueche[14] pointed out that the chain-ends of the polymer would contribute a certain amount to the total free-volume of the system, because each chain-end would necessarily possess more free-volume than that of a continuous chain. If the free-volume contributed by a chain-end is designated as θ, the total amount of free-volume per cubic centimeter, F, contributed by chain-ends can be expressed as follows:

$$F = \theta(2\rho N/M_n) \qquad (8)$$

where ρ is the polymer density, and N, the Avogadro number. Further, the glass-transition temperature, T_g, in relation to the free-volume contributed by chain-ends, was expressed as follows:

$$T_g = T_g{}^0 - (2\rho N\theta/\alpha_f)(1/M_n) \qquad (9)$$

where T_g^0 is the glass-transition temperature of high-polymeric polymer. From Eqs. (7) and (9), the F and the θ values for polytrifluorochloroethylene are given by the following equations:

$$F = 1.37 \times 10^5\alpha_f/M_n \qquad (10)$$

$$\theta = 1.37 \times 10^5\alpha_f/2\rho N \qquad (11)$$

where α_f is the function of the molecular-weight, as is shown in Fig. 5.

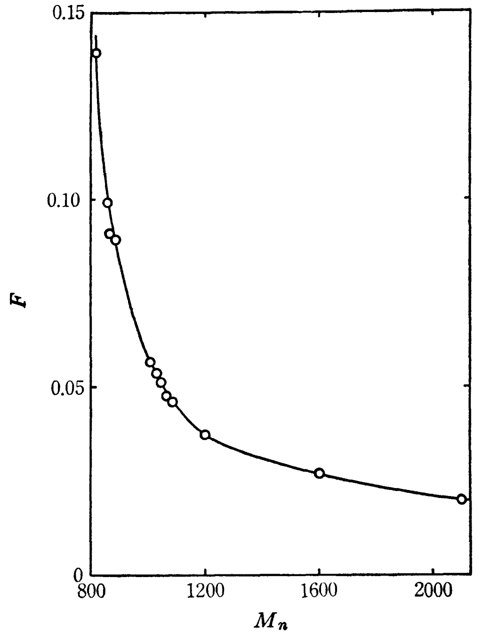

Fig. 6. Relationship between chain-end free volume per cc, F, and M_n at 52°C.

TABLE 5. FREE VOLUME, θ, CONTRIBUTED BY A CHAIN-END, Å^3

M_n	θ	M_n	θ
820	51	1050	24
860	40	1070	23
870	35	1090	22
890	35	1200	20
1010	25	1600	19
1030	24	2100	19

Table 5 shows the free-volume, θ, contributed by a chain-end in the molecular-weight range from 820 to 2100 at 52°C (the glass-transition temperature of polytrifluorochloroethylene[5,6]), when ρ is regarded as approximately 1.9. The θ values decreased with an increase in the molecular-weight up to about 1200.

Figure 6 shows the relationship between the free-volume, F, contributed by chain-ends and the molecular-weight at 52°C. The F value increased abruptly with a decrease in the molecular-weight below about 1200.

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13) R. G. Reaman, *J. Polym. Sci.*, **9**, 470 (1952).

14) F. Bueche, "Physical Properties of Polymers," Interscience Publishers, New York (1962), p. 113.