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On the Viscosity of Liquid Oligotrifluorochloroethylene

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The viscosities and densities of liquid oligotrifluorochloroethylene were measured over a molecular-weight range from 820 to 1090 at temperatures from 40°C to 100°C. The temperature-dependences of the viscosities did not show an Arrhenius-type variation, but were extremely adaptable in the WLF equation; *i. e.*, a viscoelastic behavior was shown under the present experimental conditions. The apparent activation energies, ΔH_a, for the viscous flow of the liquid samples were comparatively large and increased with an increase in the number-average molecular weight. The logarithm of the viscosity, $\log \eta$, varied linearly with the logarithm of the number-average molecular weight, $\log \eta = A \log M_n + B$. The slopes, A, of the linear relationships were estimated to be 11.0, 10.4, 9.3, and 8.4 at 50, 60, 70, and 80°C respectively. The values of the slopes, A, were very much larger than unity in the case of usual organic polymers below the critical values of the molecular weight, and they decreased with an increase in the temperature.

Polytrifluorochloroethylene is a chain polymer with only fluorine and chlorine atoms on the side of the carbon chain, and so the lone-pair electrons surrounding the chain molecules may be expected to have effects on their physical properties. In many respects, polytrifluorochloroethylene has peculiar properties compared with those of usual organic polymers; for example, its thermal and chemical stabilities are unusual. Though a highly-polymerized trifluorochloroethylene is a rigid plastic material and is insoluble in many solvents,[1] the trifluorochloroethylene oligomers are oily, grease-like, and wax-like at room temperature, and they are soluble in various solvents. In this work, the properties of the liquid oligomers will be studied in order to establish those of polytrifluorochloroethylene.

Experimental

Materials. The Daifloil No. 20 and No. 50, which were obtained from the Daikin Kogyo Company, were used as the samples of oligotrifluorochloroethylene.

The precipitation method was employed to fractionate the oligotrifluorochloroethylene using an acetone and water as the solvent and the precipitant respectively. A suitable quantity of water was added to an acetone solution of the sample, and the mixture was stirred at about 30°C. The precipitates were dissolved by again heating the mixture about 55°C, and then the mixture was allowed to stand for about 5 hr at 30°C. The fractionated precipitates were separated, and then a great quantity of methanol was added to them in order to separate the precipitates easily. The precipitates were decanted repeatedly with methanol and were dried at 30°C *in vacuo*. The number-average molecular weights of the fractionated oligotrifluorochloroethylene were estimated to be from 820 to 1090 by the cryoscopic method, using a benzene as the solvent.

Procedure. The viscosities and the densities of the liquid samples were measured at temperatures from 40°C to 100°C in the manner described in a previous paper.[2]

The viscosity, η_θ, at the tilting angle, θ, of the Ubbelohde-type viscometer was calculated by the following equation:

$$\eta_\theta = A_\theta \rho t$$

where A_θ, ρ, and t are the parameter of the viscometer, the density of the liquid sample, and the efflux time respectively. The parameter, A_θ, of the viscometer was estimated by measuring the efflux time of the standard liquid of a known viscosity at 30°C and at various tilting angles, θ. The viscosities, η_θ, of the liquid samples were measured at several tilting angles. The densities of the liquid samples were measured with the U-type densimeter described in a previous paper.[2] The viscosities and densities of the liquid samples were measured at specified temperatures within an accuracy of ± 0.01°C in thermostated baths of silicone oil and water.

The linear expansion coefficient of the densimeter was 7.95×10^{-7}°C^{-1} over the temperature range from 30°C to 50°C, while those of the liquid oligotrifluorochloroethylene were calculated to be about 3×10^{-4}°C^{-1} over the temperature range from 40°C to 100°C. Therefore, the expansion of the densimeter was negligible compared with that found with the liquid samples.

Results

The thermal degradation of the oligotrifluorochloroethylene was considered to result from heating

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[1] H. T. Hall, *J. Am. Chem. Soc.*, **74**, 68 (1952).

[2] S. Hamada, N. Yoshida and T. Shirai, This Bulletin, **42**, 1025 (1969).

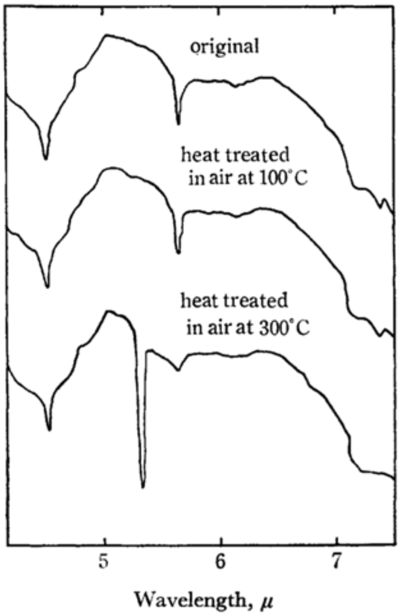

Fig. 1. IR spectra of original and heat-treated samples.

in the atmosphere.[3] Figure 1 shows the IR spectra of the sample with the molecular weight of 1090. A sharp absorption band assigned to an acid fluoride group at 5.31 μ coming from the thermal degradation was not observed in the sample heated at 100°C for 10 hr, as is shown in Fig. 1. Therefore, the measurements were carried out below 100°C, since the influence of the thermal degradation was considered to be negligible under these conditions.

The Viscosities of the Liquid Oligotrifluorochloroethylene. The viscosities, η_θ, of the liquid samples at several tilting angles were measured at temperatures from 40°C to 100°C. Table 1 shows the viscosities, η_θ, of the fractionated sample with the number-average molecular weight of 1090 at 70, 85, and 100°C, and at several tilting angles, θ_n.

The tilting angles, θ_n, represent the relative angles of the capillary of the viscometer to the vertical line, and they increase with an increase in the subscript, n; the difference between θ_5 and θ_1 is 45°. The viscosities, η_θ, were nearly constant regardless of the variation in θ_n, *i. e.*, the variation in the rate of shear. The viscosities of the other fractionated liquid samples showed the same appearance as that of the sample, $M_n=1090$. Therefore, liquid oligotrifluorochloroethylene are considered to behave as a Newtonian liquid under these experimental conditions.

TABLE 1. DEPENDENCE OF VISCOSITIES ON TILTING ANGLES

Tilting angle, θ_n	Viscosities, η_θ, poise		
	70°C	85°C	90°C
θ_1	11.8_1	4.03_1	
θ_2	11.8_0	4.03_1	1.61_0
θ_3	11.8_1	4.03_9	1.60_9
θ_4		4.03_0	
θ_5	11.8_0	4.02_9	

TABLE 2. VISCOSITIES OF OLIGOTRIFLUOROCHLOROETHYLENE

Molecular weight, M_n	Viscosities, η, poise						
	40°C	50°C	60°C	70°C	80°C	90°C	100°C
820	6.43	3.04	1.51				
860	10.78	4.73	2.33	1.42	0.717		
870	15.81	6.65	3.15	1.88	0.916		
890	22.39	9.18	4.23	2.13	1.17	0.698	
1010		29.53	12.61	5.90	2.98	1.63	
1030		40.52	16.60	7.52	3.77	2.01	1.14
1050		55.90	21.62	9.49	4.61	2.44	1.36
1070			23.20	10.31	5.03	2.63	1.51
1090			27.45	11.81	5.64	2.94	1.61

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

The Temperature-dependences of the Viscosities. The temperature-dependences of the viscosities, η, did not show an Arrhenius-type variation under these conditions. Therefore, the temperature-dependences of the viscosities, ,η were treated with the WLF equation, $\log a_T=-C_1{}^0(T-T_0)/(C_2{}^0+T-T_0)$.[4]

Figure 2 shows the relationships between $(T-T_0)$ and $(T-T_0)/\log a_T$. The shift factors, a_T, which were expressed to be $\rho_0\eta T_0/\rho\eta_0 T$, were calculated

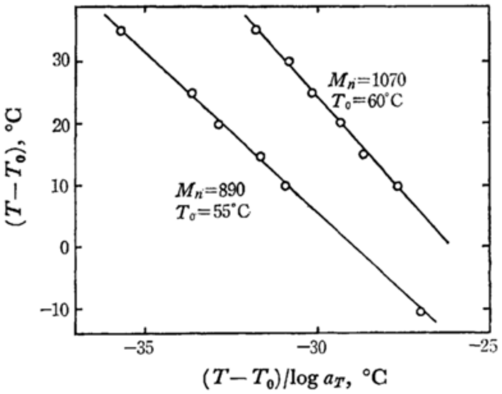

Fig. 2. Relationship between $(T-T_0)$ and $(T-T_0)/\log a_T$.

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[3] M. Iwasaki, M. Aoki and R. Kojima, *J. Polymer Sci.*, **25**, 377 (1957).

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

on the basis of a voluntary fixed temperature, T_0, because the glass-transition temperatures, T_g, of the fractionated samples were not known. The linear relationship shown in Fig. 2 makes it obvious that the temperature-dependences of the viscosities were extremely adaptable in the WLF equation. Therefore, the viscoelastic behavior was shown in the viscous flow of the liquid samples over the temperature range from 40°C to 100°C. The WLF parameters, C_1^0 and C_2^0, were estimated on the basis of T_0 from the linear relationships in Fig. 2, while the apparent activation energies, ΔH_a, for the viscous flow were estimated from the following equation:

$$\Delta H_a = 2.303 R C_1^0 C_2^0 T^2/(C_2^0 + T - T_0)^2$$

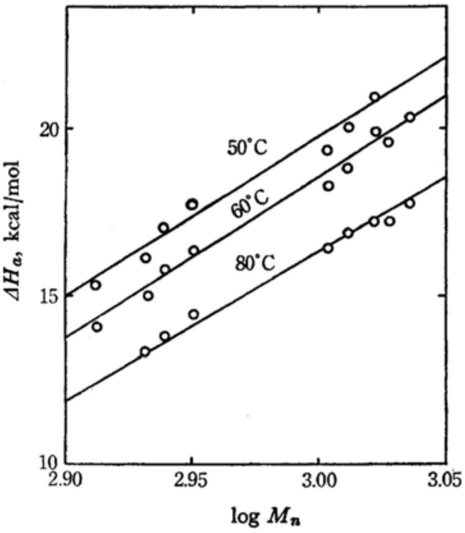

Fig. 3. Dependence of apparent activation energy for viscous flow on log M_n.

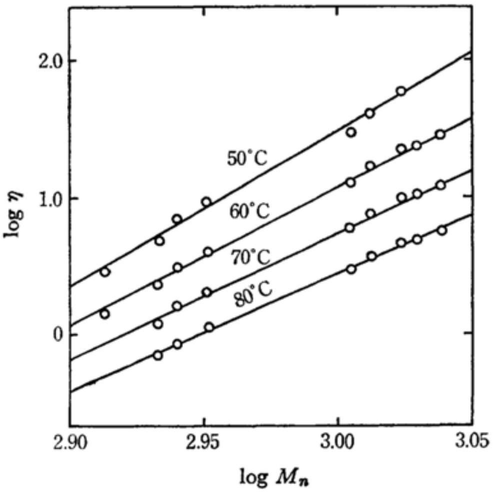

Fig. 4. Dependence of log η on log M_n.

Figure 3 shows the dependence of ΔH_a on the molecular weight. The apparent activation energy, ΔH_a, for the viscous flow increased linearly with an increase in the logarithm of the molecular weight, log M_n.

The Molecular-weight Dependences of the Viscosities. The dependences of the viscosities on the molecular weight are shown in Fig. 4. The logarithm of the viscosity, log η, varied linearly with the logarithm of the number-average molecular weight, log M_n. The linear relationships at the specified temperatures could be expressed as follows:

$$\log \eta = A \log M_n + B$$[5]

The slopes, A, of the linear relationships were very much larger than unity at lower temperatures, unlike the case of usual organic-polymers below the critical values of the molecular weights, and they decreased with an increase in the temperature, as is shown in Table 3.

TABLE 3. SLOPES, A, OF LINEAR RELATIONSHIPS

Temp., °C	50	60	70	80
A	11.0	10.4	9.3	8.4

Discussion

The relationship between the viscosity and the free volume is satisfactorily described by the Doolittle equation:[6,7]

$$\ln \eta = \ln P + Q(v - v_f)/v_f$$
$$= \ln P + Q/f$$

where P and Q are the empirical constants; v, the specific volume; v_f, the free volume, and f, the fraction of the free volume. The fraction of the free volume, f, at T is expressed as follows:

$$f = f_g + \alpha_f(T - T_g)$$

where f_g is the fraction of the free volume at T_g, and α_f, the thermal expansion coefficient of the free volume. All the oligotrifluorochloroethylenes used in the study are quite small in number-average molecular weight; $M_n \leq 1090$. In general, the melting points of the lower-molecular-weight oligomers rise remarkably with an increase in the molecular weight; also, their glass-transition temperatures, T_g, are considered to show a tendency similar.[8] Particularly the glass-transition temperatures of the oligotrifluorochloroethylene rise remark-

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

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

[7] A. K. Doolittle and D. B. Doolittle, *J. Appl. Phys.*, **28**, 901 (1957).

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

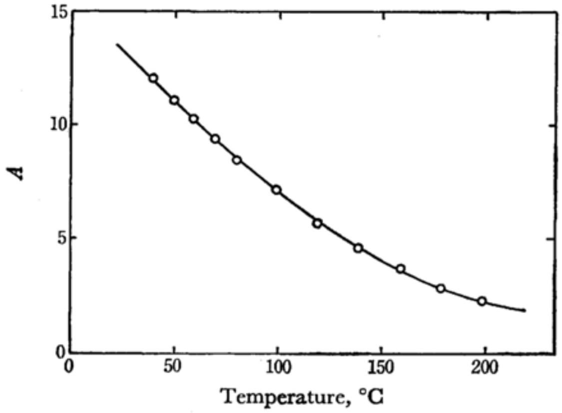

Fig. 5. Temperature dependence of slope, A, of linear relationship.

ably as the molecular weights increase; in fact, the states of the samples at room temperature depend notably on the molecular weight. They are all oily, grease-like, and wax-like, in spite of the small range of molecular weight (from 820 to 1090).

Thus, since a large dependence of the fraction of the free volume, f, on the molecular weight at specified temperatures may be expected, the viscosity will rise remarkably with an increase in the glass-transition temperature in the lower-molecular-weight range. The slopes, A, of the linear relationships in Table 3, which indicated the dependences of the viscosities on the molecular weights, show large values at lower temperatures. The large values of A are caused by the large dependence of the fraction of the free volume on the molecular weight. Though the slopes, A, were very much larger than unity at the lower temperatures, they gradually decreased as the temperature was elevated; they were considered finally to approach a certain value, A_0, as is shown in Fig. 5. The values, A, above 100°C were calculated from the WLF equation. The decrease of A with an increase in the temperature is caused by the decrease in the dependence of the fraction of the free volume on the molecular weight as the temperature is elevated.

Large dependences of the viscosities on the molecular weights have also been reported for the oligostyrene and oligoisobutylene.[5,9] For example, the A values of the oligoisobutylene over the molecular-weight range from 530 to 2190 were estimated to be 5.45, 3.08, and 1.75 at 0, 30, and 217°C respectively.

The liquid organic-chain polymers, in general, show comparatively small values of the apparent activation energies for the viscous flow, though they increase with an increase in the bulk of the side chains.[10] The comparatively large values of ΔH_a for oligotrifluorochloroethylene, with no branched chain, are considered to be caused by a high rotational barrier about carbon-carbon bonds which is to be attributed to the lone-pair electrons of fluorine and chlorine atoms.

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9) T. G. Fox and P. J. Flory, *J. Polymer Sci.*, **13**, 315 (1954).

10) H. Schott, *J. Appl. Polymer Sci.*, **6**, S29 (1962).