

The Viscosity of Monomolecular Melts of Poly(vinyl Chloride)

J. LINGAAE-JØRGENSEN, *Instituttet for Kemiindustri, The Technical University of Denmark, Lyngby, Denmark*

Synopsis

PVC melts are predicted to be homogeneous with single molecules as the stable flow units (monomolecular melts) at corresponding values of high temperatures and/or high shear stresses. Under these conditions, it is found that the zero shear viscosity in simple shearing flow of rigid compounds depends on the average molecular weight by weight to the 3.5 power for molecular weights between 24,000 and 100,000. All data measured under conditions where monomolecular melts are predicted fall on a master curve of reduced viscosity versus reduced shear rate when a relaxation time proportional to η_0/c^2T is used. It is, therefore, concluded that monomolecular melts of PVC compounds follow the same structure-viscosity relations as found for other linear melts in viscometric flow.

INTRODUCTION

PVC compounds are often processed below the melting point of the crystalline areas in the sample. The rheological properties of samples containing crystallites show unusual effects such as an abnormally high dependence of molecular weight on zero shear viscosity¹ and transition indelinations of the logarithm of the viscosity against reciprocal temperature.^{2,3}

Even a flow mechanism involving the original particles as flow units has been observed at "low" temperatures.⁴ The rheological phenomena observed in PVC melts have been reviewed by Pezzin.⁵

A model predicting the melting point under continuous shear flow as a function of shear stress and static melting temperature was tested in an earlier publication.⁶ According to this model, simple molecules are the stable flow units at corresponding values of shear stress and temperature involving high temperatures and/or high shear stresses. Melts where simple molecules are the stable flow units will be referred to as monomolecular melts in this paper.

The purpose of this work was to test the prediction and to provide relations between molecular structure and rheological properties of monomolecular melts for PVC compounds. The viscosity function in viscometric flow was used as test parameter.

EXPERIMENTAL

Sample Materials

The materials shown in Table I were used.

Di-2-ethylhexyl phthalate (DOP) from Fluka A. G. was used as plasticizer.

The stabilizer used was Okstán X-OC, a fluid dioctyltin stabilizer from Otto Bärlocher G.m.b.H., München. This was chosen because it has the characteristics of a plasticizer.

Methods

Gel permeation chromatography (GPC) was used for the characterization of molecular weight distribution of the compounds before and after processing. The area under the GPC curve was used as a control of the plasticizer content (together with density measurements).

The GPC apparatus was from Waters Associates, Model 200. The column combination was 10^6 , 2×10^4 , 10^4 , 10^3 Å polystyrene gel. The GPC instrument was run under the following conditions: flow rate, 1 ml/min; injection volume, 2 ml; sample concentration, 2.5×10^{-3} g/ml. Tetrahydrofuran (THF) was used as the solvent. The samples were heat treated at 120°C before measurement.

The columns were calibrated with polystyrene standards from Pressure Chemical Company and from the National Bureau of Standards under the above-mentioned conditions, except for the injection volume which was 0.5 ml.

TABLE I
Sample Materials Used

PVC	\bar{M}_w	\bar{M}_n	Polymerization conditions
Vinnol H 80g	166,000	80,000	commercial suspension polymer from Wacker
Vinnol H 70d	110,000	52,000	commercial suspension polymer from Wacker
Vinnol H 60d	70,000	32,000	commercial suspension polymer from Wacker
U3	51,600	24,000	suspension polymer with cyclohexanone as chain transfer agent; polymerization temp. 50°C
U7	36,000	17,000	
C94-1	28,000	14,000	sample received from Collins, ² prepared at 40°C
U4	23,600	11,000	suspension polymer with tetrahydrofuran as chain transfer agent, polymerization temp. 50°C
S1	100,000	46,000	suspension polymerization at (55°C)

Rheometry

Measurements were performed with a Brabender Plastograph, an Instron capillary rheometer, and the Rheometrics Mechanical spectrometer as covered by reference 6.

Degradation was a problem in this investigation since the measuring temperatures were over 200°C, where the unstabilized samples degrade rather quickly. The stabilizer did prevent severe degradation during the measurements since the molecular weight distribution and the plasticizer content did not change significantly during the time lapsed to establish a single shear rate-temperature data point. The processed samples were, however, discolored to different yellowish shades.

The plasticizer content was controlled by density measurements and by extraction using a Soxhlet apparatus with ethyl ether as extracting liquid. The stabilizer was nearly completely rained in the residue, as shown by atomic absorption measurements (Perkin-Elmer Model 303) for tin in the extract. A maximum of 20% of the stabilizer was extracted.

RESULTS

The values of the zero shear viscosity measured with the cone and plate geometry in the Rheometrics mechanical spectrometer are reported in Table II.

The activation energy of the zero shear viscosity, E_{η_0} , is plotted against weight fraction of polymer in Figure 1. Figure 2 shows a delineation of $\log(\eta/\eta_0)$ against $\log[(\eta_0/(c^2T))\dot{\gamma}]$ for a range of different compounds.

DISCUSSION

Tests of Zero Shear Viscosity Relations

In order to see whether PVC melts above the calculated melting points behaved as monomolecular melts, two equations [eqs. (1) and (3) below] which have been used on melts of linear polymers were tested.

The applicability of a semiempirical equation relating the zero shear viscosity η_0 to the weight-average molecular weight, absolute temperature T , and polymer concentration c (g/cm^3) were first investigated:

$$\ln \eta_0 = 3.4 \ln \bar{M}_w + E_{\eta_0}/RT + a \ln c + K \quad (1)$$

where K and a are constants and a should be approximately 5.⁷ The relation between η_0 and \bar{M}_w seems to be reasonably well fulfilled, as seen in Figure 3.

The exponent found experimentally for the rigid formulations is 3.54 ± 0.11 (S.D.) for the five samples of lowest molecular weight. This value is, therefore, not significantly different from the theoretical value.⁹ At higher molecular weight, a tendency of upward curvature can be seen both in the rigid and in the plasticized samples. The exponent based on the seven samples of rigid components is 3.72 ± 0.08 , which is significantly different from the theoretical value.

TABLE IIa

Compound: PVC/DOP/Stab, parts by weight	Weight fraction <i>w</i>	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	η_0					E_{η_0} , kcal/ mole	T_m , °C	E_{η_0} (Bra- bender) ^a	T_g , °C
				210°C	220°C	225°C	230°C	235°C				
Vinnol H 70d, 100/0/4	0.962	110	52				290,000 ^c		235.2		73.8	
Vinnol H 60d, 100/0/4	0.962	70	32				46,600	36,000			72.8	
Vinnol H 60d, 100/0/4	0.962	70					42,100	32,000	27 ± 7	227		
U3			24				13,700			223.5	71.4	
U7, 100/0/4	0.962	36	17				3,890			222	70.4	
U7, 100/0/4	0.962	36	17				4,170					
C94-1, 100/0/4	0.962	28	14		2,450	1,620	1,460			222 ^b	69.8	
U4, 100/0/4	0.962	23.6	11				1,000			219	67.5	
Vinnol H 60d, 100/50/4	0.6494	70		3,750	2,000		1,420					
Vinnol H 60d, 100/50/4	0.6494	70		3,650	2,200				23.8 ± 2	201 ^b	21.4	
Vinnol H 60d, 100/50/4	0.6494	70		2,270	2,270							
Vinnol H 60d, 100/75/4	0.5587	70		1,000	630							
Vinnol H 60d, 100/75/4	0.5587	70					370			195.4	-16	
Vinnol H 60d, 100/100/4	0.4902	70		450			430					
Vinnol H 60d, 100/200/4	0.3289	70								190 ^b	17.8	
Vinnol H 70d, 100/10/4	0.8772	110									16	
Vinnol H 70d, 100/20/4	0.8065	110		102,600			145,000			227	55	
Vinnol H 70d, 100/20/4	0.8065	110					64,000					
Vinnol H 70d, 100/250/4	0.7752	110		75,200			68,000			220.8	39.4	
Vinnol H 70d, 100/25/4	0.7752	110		79,800						218.0	32	

Vinnol H 70d, 100/333/4	110	0.7282	110	41,000	30,000	25,000	24.7 ± 3	214.4	22
Vinnol H 70d, 100/333/4	110	0.7282	110	44,000	34,000				
Vinnol H 70d, 100/333/4	110	0.7282	110	38,000					
Vinnol H 70d, 100/50/4	110	0.6494	110	27,000	12,000	9,600	23.0 ± 2	208.5 ^b	22, 8
Vinnol H 70d, 100/50/4	110	0.6494	110	27,000	13,400	10,200			4.5
Vinnol H 70d, 100/50/4	110	0.6494	110	28,000					
Vinnol H 70d, 100/50/4	110	0.6494	110	21,000					
Vinnol H 70d, 100/50/4	110	0.6494	110	6,200					
Vinnol H 70d, 100/75/4	110	0.5587	110	3,690		2,680			
Vinnol H 70d, 100/75/4	110	0.5587	110	4,220			20.4 ± 2	202.6	-15
Vinnol H 70d, 100/75/4	110	0.5587	110	3,880					
Vinnol H 70d, 100/75/4	110	0.5587	110	1,820	1,000	860			
Vinnol H 70d, 100/100/4	110	0.4902	110	2,050	1,500	790	21.0 ± 2	198.3	-31
Vinnol H 80f, 100/100/4	166	0.4902	166	80	24,000	8,400	24 ± 4	208.5	-30
Vinnol H 80f, 100/100/4		0.4902		17,500	11,600				
Vinnol H 80f, 100/100/4		0.4902		21,000	10,900				
SI, 100/100/4	46	0.4902	100	1,190					
Utracki(8)	86	0.97	86			158,000			
Utracki(8)	96 ^d	0.97	96 ^d						

^a E_{η_0} (Brabender) is estimated from the expression E_{η_0} (Brabender) = $(1/n)E_{\dot{\gamma}}$, where $E_{\dot{\gamma}}$ is the activation energy at constant shear rate and n is the flow index. The standard deviation on a single determination of zero shear viscosity is found to be 9.5% based on 29 degrees of freedom.

^b Experimental data; other values of T_m are calculated from the Flory expression (ref. 6).

^c The value is extrapolated ($\log \eta_0$ vs. $\log c$).

^d Measured at our Institute with our GPC calibration on a sample of the same type as used in ref. 8, kindly delivered by Dr. Utracki.

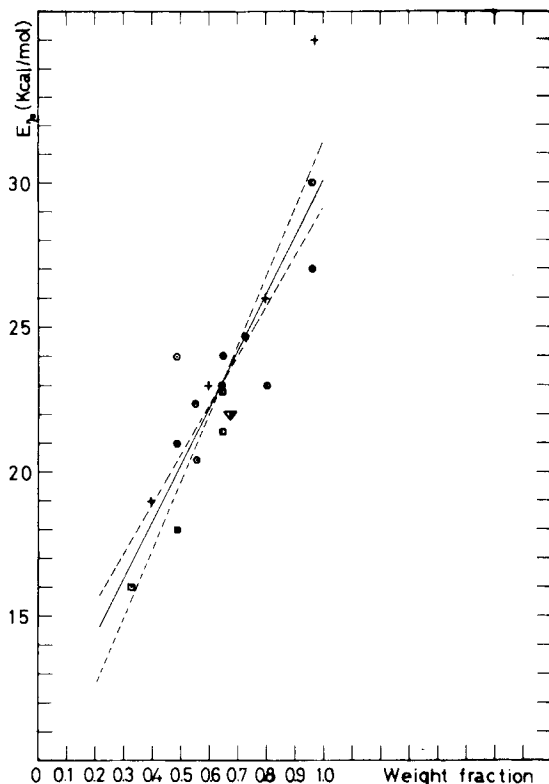


Figure 1. Energy of activation as a function of weight fraction of polymer: (⊙) cone-and-plate data; (◻) Brabender data; (+) data from Utracki⁸; (▽) data from Pezzin.³

E_{η_0} is a function of plasticizer concentration as found by Utracki.⁸ Our own measurements together with those determined by Utracki are shown in Figure 1.

Utracki's E_{η_0} data are based on many more degrees of freedom than our data and show considerably less uncertainty, but the agreement is very satisfactory. The activation energy value found by Utracki for rigid compounds is probably too high because the viscosity data are very close to the melting point. To find an activation energy for the rigid compounds, we extrapolated the data of Figure 1 linearly. A value of 30 ± 1 kcal/mole will be used for rigid compounds. Figure 4 shows $\log \eta_0$ against $\log c$. The constant a in eq. (1) was found to be larger than 5. The most reliable value found for Vinnol H 70d at 220°C was 6.90 ± 0.09 . The constant is a decreasing function of temperature going from ~ 7.5 at 210°C to ~ 6.5 at 230°C.

It is, however, evident that a necessary condition for a constant a value is that the activation energy is independent of the plasticizer concentration. According to Bueche,⁹ one would expect that the activation energy varies with the distance from the glass transition temperature T_g reaching a constant value at a high enough temperature. Plotting E_{η_0} against $T' - T_g$ (Fig. 5), where T' is an average temperature of the activation energy data, one might expect that a limiting value is reached at some higher temperature where the constant a might reach a value close to 5.

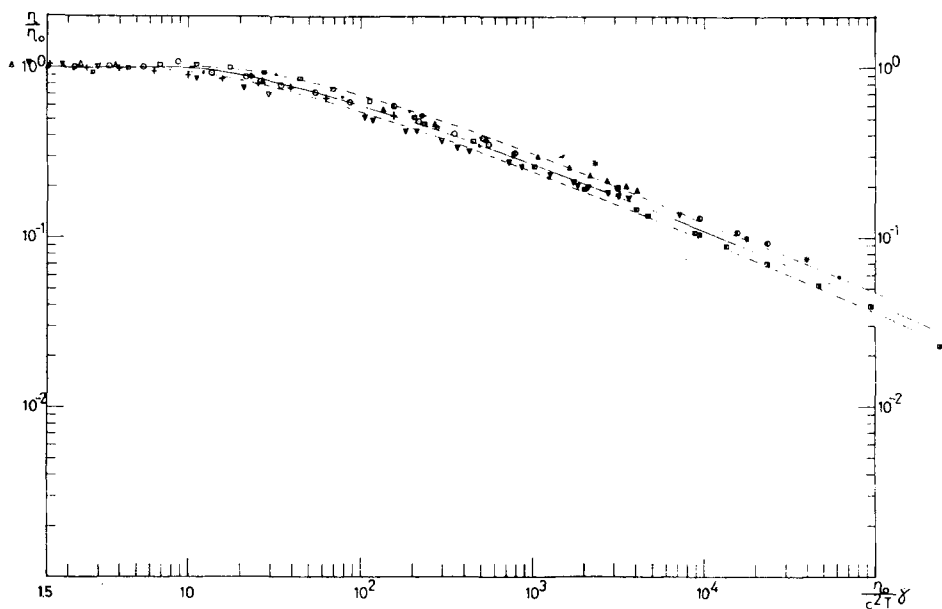


Fig. 2. Reduced plot of $\log (\eta/\eta_0)$ vs. $\log [(\eta_0/c^2T)] \dot{\gamma}$ (master curve). Data measured under the following conditions of weight fraction w and temperature T : (+) Vinnol H60d, $w = 0.962$, $T = 230^\circ\text{C}$; (\blacktriangle) Vinnol H60d, $w = 0.6494$, $T = 210^\circ\text{C}$; (∇) Vinnol H60d, $w = 0.4902$, $T = 195^\circ\text{C}$; (\square) Vinnol H70d, $w = 0.6494$, $T = 210^\circ\text{C}$; (\odot) Vinnol H80f, $w = 0.4902$, $T = 220^\circ\text{C}$; (\bullet) Utracki⁸ data, $w = 0.97$, $T = 239^\circ\text{C}$; (\diamond) Utracki⁸ data, $w = 0.80$, $T = 239^\circ\text{C}$; ($*$) Collins² data, $w = 0.96$, $T = 240^\circ\text{C}$; $\dot{\gamma} = 150 \text{ sec}^{-1}$ and $T = 230^\circ\text{C}$. These symbols are used for cone-and-plate data; symbols with left side filled are Brabender data, symbols with right side filled are Instron data.

For rigid formulation, an empirical equation of the form

$$\log \eta_0 = 3.72 \log \bar{M}_w + \frac{6515}{T} - 26.3248 \quad (2)$$

$\bar{M}_w/M_n \approx 2$ should give reasonable estimates of zero shear viscosities for monomolecular melts.

Thus, eq. (1) did not seem to be exactly fulfilled. The molecular weight relation was, however, in accordance with the behavior found for other linear polymer melts. Since the use of eq. (1) did not give a sufficient basis for concluding that the PVC melts did behave as linear monomolecular melts, the following test was used to elucidate this point.

The best documented work concerning the relation between zero shear viscosity and \bar{M}_w , plasticizer content, and temperature is probably that of Fox et al.¹⁰ According to Fox, the following equation for zero shear viscosity η_0 is valid:

$$\eta_0 = 4.8 \times 10^8 \left(\frac{X}{4.7 \times 10^{-15}} \right)^\alpha \zeta \quad \begin{array}{l} \alpha = 3.4 \text{ for } X \geq 4.7 \times 10^{-15} \\ \alpha = 1 \text{ for } X \leq 4.7 \times 10^{-15} \end{array} \quad (3)$$

where ζ is the friction factor per repetition unit, and

$$X = \left(\frac{\langle S_0^2 \rangle_{AV}}{M} \right) \cdot \left(\frac{Z \cdot \phi_1}{\bar{v}_1} \right)$$

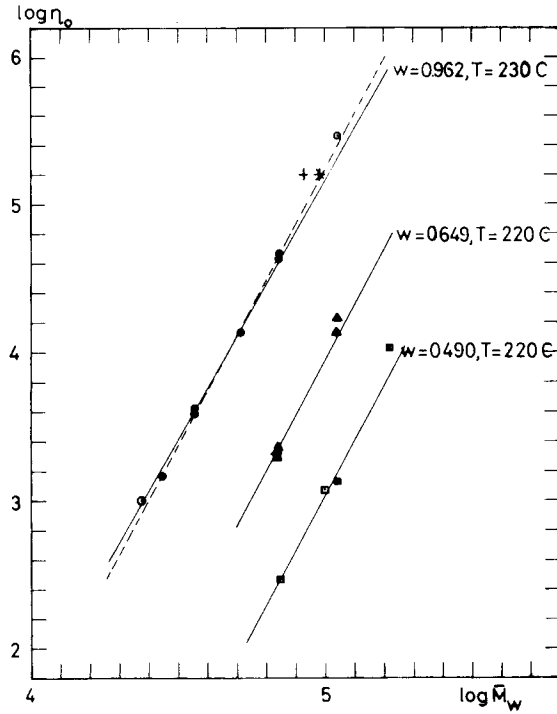


Fig. 3. Effect of weight-average molecular weight on zero shear viscosity: (+) and (*) data from Utracki⁸ with the \bar{M}_w value reported by Utracki and the \bar{M}_w value measured by us, respectively.

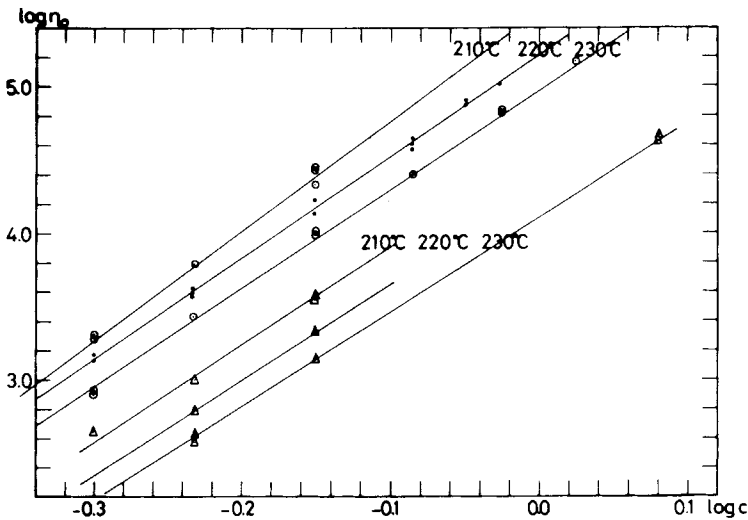


Fig. 4. Effect of concentration and temperature on zero shear viscosity for Vinnol H70 and Vinnol H60, respectively.

where ϕ_1 is the volume fraction of polymer, Z is the number of chain atoms, \bar{v}_1 is the partial specific volume of the sample, $\langle S_0^2 \rangle_{AV}$ is the unperturbed mean-square radius of gyration of the polymer coil, and M is the molecular weight of the polymer. Furthermore, Fox deduced the following expression:

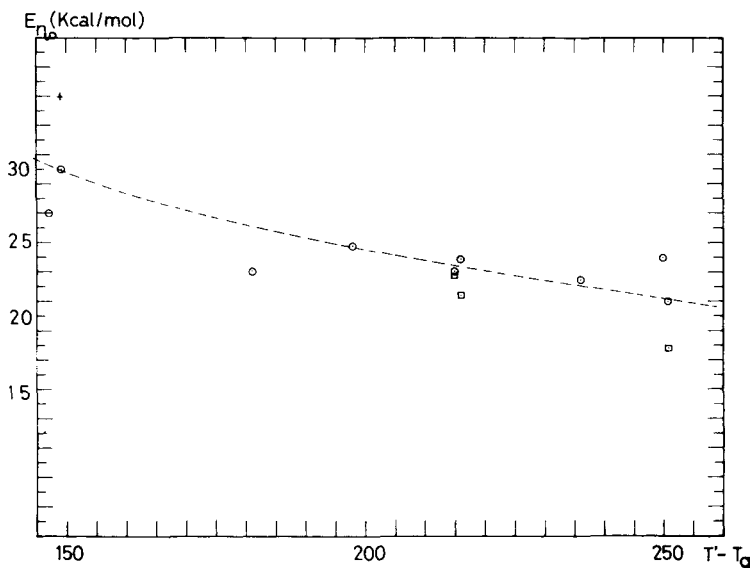


Fig. 5. Effect of $T' - T_g$ on energy of activation of viscous flow, $T' \approx 220^\circ\text{C}$.

$$\log \zeta = -1.2 + \frac{E}{2.3RT} - 11.4 \left(\frac{\Delta\alpha_f(T - T_g)}{0.024 + \Delta\alpha_f(T - T_g)} \right) \quad (4)$$

where T is the absolute temperature, $\Delta\alpha_f$ is the expansion coefficient of the free volume, T_g is the glass transition temperature, R is the gas constant, and E is an activation energy used as an adjusting parameter expected to be in the neighborhood of 4 kcal/mole. Thus, a delineation of

$$\log \zeta = \log \eta_0 - 3.4 \log \left(\frac{\bar{Z}_w \phi_1}{\bar{v}_1} \right) - \log 4.8 - 8 - 3.4 \log \frac{\langle S_0^2 \rangle_{AV} M}{4.7 \times 10^{-15}}$$

against

$$\frac{\Delta\alpha_f(T - T_g)}{0.024 + \Delta\alpha_f(T - T_g)}$$

should give a straight line with slope of approximately -11.4 . This line should superimpose on the general line found by Fox by appropriate selection of E .

The glass transition temperatures of the plasticized compounds were taken from Koleske and Wartman.¹¹ These data were adapted by subtracting the difference between the glass transition temperature reported for pure PVC and the T_g values measured in our laboratory (DTA) which were as follows: Vinnol H80, 83°C ; Vinnol H70, 82°C ; Vinnol H60, 81°C ; 94-1, 78°C ; T_g reference, 85°C .

The reason for not using measured values is that an unambiguous reproducible glass transition temperature on plasticized samples by the DTA technique is difficult if not impossible to obtain.

For PVC compounds, the following values were used:

$$\Delta\alpha_f = (5.2 - 2.1) \times 10^{-4} = 3.1 \times 10^{-4} \text{ (deg}^{-1}\text{)}$$

The following density ρ (g/cm³) and coefficient¹¹ of thermal expansion α (deg⁻¹) values were used

$$\rho_{\text{PVC}} = 1.39(20^\circ\text{C}) \quad \begin{cases} \alpha = 5.2 \times 10^{-4} \text{ for rubber} \\ \alpha = 2.1 \times 10^{-4} \text{ glass} \end{cases}$$

$$\rho_{\text{DOP}} = 0.984(20^\circ\text{C}) \quad \alpha = -7.5 \times 10^{-4}$$

$$\rho_{\text{XOC}} = 1.04(20^\circ\text{C}) \quad \alpha = -7.5 \times 10^{-4}$$

$$\frac{\langle S_0^2 \rangle_{AV}}{M} = 10 \times 10^{-18} \text{ cm}^2 \quad (\text{ref. 12})$$

$$\rho_{\text{PVC}} = 1.28 \frac{\text{g}}{\text{cm}^3} \text{ at } 220^\circ\text{C}$$

$$\rho_{\text{DOP}} = 0.856 \frac{\text{g}}{\text{cm}^3} \text{ at } 220^\circ\text{C}$$

With these values, eq. (3) becomes

$$\log \zeta = \log \eta_0 - 3.4 \log \frac{\bar{Z}_w \cdot \phi_1}{\bar{v}_1} + 0.4036$$

and the critical molecular weight for entanglement formation should be

$$Z_c \simeq \frac{1}{1.28} \cdot \frac{4.7 \times 10^{-15}}{10 \times 10^{-18}} = 367 = > M_c = 11,500$$

Plotted according to eq. (4) (Fig. 6), the slope for the plasticized samples was found to be -12.1 ± 2 which, within experimental error, is in accordance with the value found by Fox, namely, -11.4 .

Thus, the data superimpose on the general relation of Fox when an activation energy of 6.0 kcal/mole for plasticized samples and 4.8 kcal/mole for rigid formulations is used.

Since the Fox equation seems to be followed, this should indicate that the PVC melts above the melting point behave the same way as other linear monomolecular melts.

Test of Relations Between Reduced Viscosity and Reduced Shear Rate

It is important to be able to predict the zero shear viscosity, but it is often necessary to know the viscosity as a function of shear rate.

According to Graessly,¹³ one should expect that the (maximum) characteristic relaxation time (τ_0) for polymer melts should comply to an expression of the form

$$\frac{1}{\tau_0} = \frac{A}{6\eta_0 \bar{M}_w} + \frac{B}{\pi^2 c^2 R T} \quad (5)$$

where A and B are constants and c is the polymer concentration. The last part of the expression should dominate at high entanglement densities.

Thus, since all samples have the same molecular weight distribution

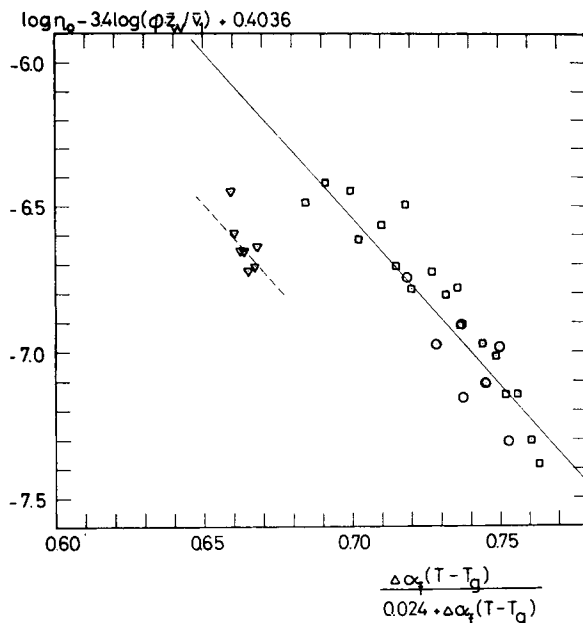


Fig. 6. Double-logarithmic delineation of friction factor vs. $[\Delta\alpha_f(T - T_g)]/[0.024 + \Delta\alpha_f(t - T_g)]$: (∇) rigid compounds ($w = 0.962$); (\odot) and (\square) plasticized compounds based on Vinnol H60d and Vinnol H70d, respectively.

(MWD), a double-logarithmic plot of η/η_0 against either $(\eta_0\bar{M}_w/c)\dot{\gamma}$ or $(\eta_0/c^2T)\dot{\gamma}$ should be generally applicable as limiting cases giving a general representation of the shear rate dependence of the monomolecular melts.

The Rouse-Bueche relaxation time $\tau\alpha$ ($\eta_0\bar{M}_w/cT$) could not reduce all data to a single curve, but the plot $\log(\eta/\eta_0)$ against $\log[(\eta_0/c^2T)]\dot{\gamma}$ did, in fact, give one curve for all tested conditions. As shown in Figure 2, all points coincide on a single curve within experimental uncertainty. Even more convincing is the fact that the only measurements reported in the literature^{2,8} where the temperature or the shear stress used have been high enough to secure monomolecular melt conditions comply to the same curve.

Collins² has reported data measured at 230°C and 240°C on a sample of Geon 101 EP24 with the same composition as our rigid formulations for Vinnol H 70d. Since these two products have approximately the same MWD, we used the extrapolated value at 230°C and 240°C for Vinnol H 70d as zero shear viscosity for the Collins sample.

Since 230°C is below the static melting point of the sample, we used only the data for high shear stresses at this temperature and a value at 240°C. The points of Collins are in accordance with the curve shown on Figure 2.

The cone-and-plate data of Utracki¹⁸ fall on the same curve, except for the high shear rate data of the rigid compound. According to our experience with the cone-and-plate geometry, this is a phenomenon which almost always is caused by the centrifugal forces throwing the material out of the gap between the cone and the plate.

Utracki found that the relaxation times for PVC compounds do not follow Graessly's expression given by eq. (5). The reason for this is, however, quite

simply that Utracki uses data measured on monomolecular melts and on melts containing stable crystallite aggregates in the same plot.

CONCLUSIONS

The experimental evidence indicates that under conditions where monomolecular melts are predicted, the same general structure-viscosity relations as found for other linear materials are followed for PVC compounds.

The author would like to thank F. E. Andersen for assisting with most of the measurements reported here, and Dr. L. L. Chapoy for helpful discussions. The author is grateful to Statens Teknisk-Videnskabelige Forskningsråd for support of this research.

Nomenclature

A	constant
a	exponent in $\eta_0 = A \cdot c^a$
B	constant
c	polymer concentration (g/cm ³)
E	activation energy
E_{η_0}	activation energy of viscous flow
K	constant
M	molecular weight
\bar{M}_n	number-average molecular weight
\bar{M}_w	weight-average molecular weight
R	gas constant
S.D.	standard deviation
$\langle S_0^2 \rangle_{AV}$	unperturbed mean square radius of gyration.
T	absolute temperature
T_g	glass transition temperature
T_m	melting temperature
\bar{v}_1	partial specific volume of the sample
\bar{w}	weight fraction of polymer
Z	number of chain atoms
\bar{Z}_w	weight-average number of chain atoms
$\dot{\gamma}$	shear rate (sec ⁻¹)
ζ	friction factor per repetition unit
η	viscosity
η_0	zero shear viscosity
ρ	density
τ	relaxation time

References

1. G. Pezzin, G. Ajrold, and C. Garbuglio, *Rheol. Acta*, **8**, 304 (1969).
2. E. A. Collins and C. A. Krier, *Trans. Soc. Rheol.*, **11**, 225 (1967).
3. G. Pezzin, IUPAC XXIII Symposium on Macromolecules, 1974, p. 753.
4. A. R. Berens and V. L. Folt, *Trans. Soc. Rheol.*, **11**, 95 (1967); *Polym. Eng. Sci.*, **8**, 5 (1968); *ibid.*, **9**, 27 (1969).

5. G. Pezzin, *Pure Appl. Chem.*, **26** (2), 241 (1971).
6. J. Lyngaae-Jorgensen, *Polym. Eng. Sci.*, **14**, 342 (1974).
7. S. Middleman, *The Flow of High Polymers*, Interscience, New York, 1968.
8. L. A. Utracki, *J. Polym. Sci.*, **12**, 563 (1974).
9. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962, pp. 91-92.
10. V. R. Allen and T. G. Fox, *J. Chem. Phys.*, **41**, 337, (1964); *ibid.*, **41**, 344 (1964); T. G. Fox, *J. Polym. Sci.*, **9**, 35 (1965).
11. J. V. Koleske and L. H. Wartman, *Poly(vinyl Chloride)*, Gordon & Breach, London, 1969, p. 57.
12. A. J. de Vries, C. Bonnebat, and M. Carrega, *Pure Appl. Chem.*, **26** (2), 209 (1971).
13. N. W. Graessley, R. L. Hazleton, and L. R. Lindeman, *Trans. Soc. Rheol.*, **11**, 267 (1967); N. W. Graessley and L. Segal, *Macromolecules*, **2**, 49 (1969).

Received August 25, 1975

Revised November 19, 1975