

Viscosity of Concentrated Polymer Solutions. I. Polyvinylchloride in Cyclohexanone

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Synopsis

Viscosities of samples of poly(vinyl chloride) in cyclohexanone were measured over a wide range of concentrations, up to polymer weight fractions of the order of 0.4. Polymers with molecular weight from 10,000 to 230,000 and with different molecular weight distributions were studied. The effect of concentration and molecular weight on the solution viscosity is reported and discussed for this system, as well as for other systems for which data are available in literature. The empirical reduction schemes often applied to the viscometric data of concentrated polymer solutions are discussed.

INTRODUCTION

The viscous properties of dilute macromolecular solutions have been successfully interpreted by relatively simple theoretical models, in which the molecules are considered as largely isolated.

In concentrated solutions the domains of the macromolecular chains may overlap, and the molecules may be entangled as in polymer melts, their mobility being severely restricted as a consequence of chain entanglements.

In the past years a number of papers have reported viscometric data for concentrated solutions of high polymers,¹ but they give, in most of the cases, only empirical descriptions for the dependence of viscosity on concentration and on temperature.²⁻⁶

A theoretical treatment of the effect of concentration on viscosity on the basis of free volume has been made by Fujita, Kishimoto, and co-workers.⁷⁻¹⁰ Kelly and Bueche¹¹ have presented a complete theoretical interpretation of the viscometric properties of polymer-diluent systems. Their treatment is based both on the free-volume concept, as extended by Williams, Landel, and Ferry to polymer melts,¹² and on the Bueche model of the mechanism of flow in undiluted polymers.¹³

The main objectives in undertaking this work were, first, to determine experimentally the viscosity-concentration and viscosity-molecular weight dependence for poly(vinyl chloride) (PVC) and, secondly, to test the validity of the Kelley-Bueche equation for this polymer. The first part describes the properties of the system PVC-cyclohexanone.

Several samples of PVC, having widely different molecular weights and molecular weight distributions, were examined, and the effects of aggrega-

tion, of shear rate, and of concentration on their solution viscosity were determined.

The results are compared with earlier measurements on the same system and on other polymer-diluent solutions, and the validity of the empirical reduction schemes often used for such systems is tested.

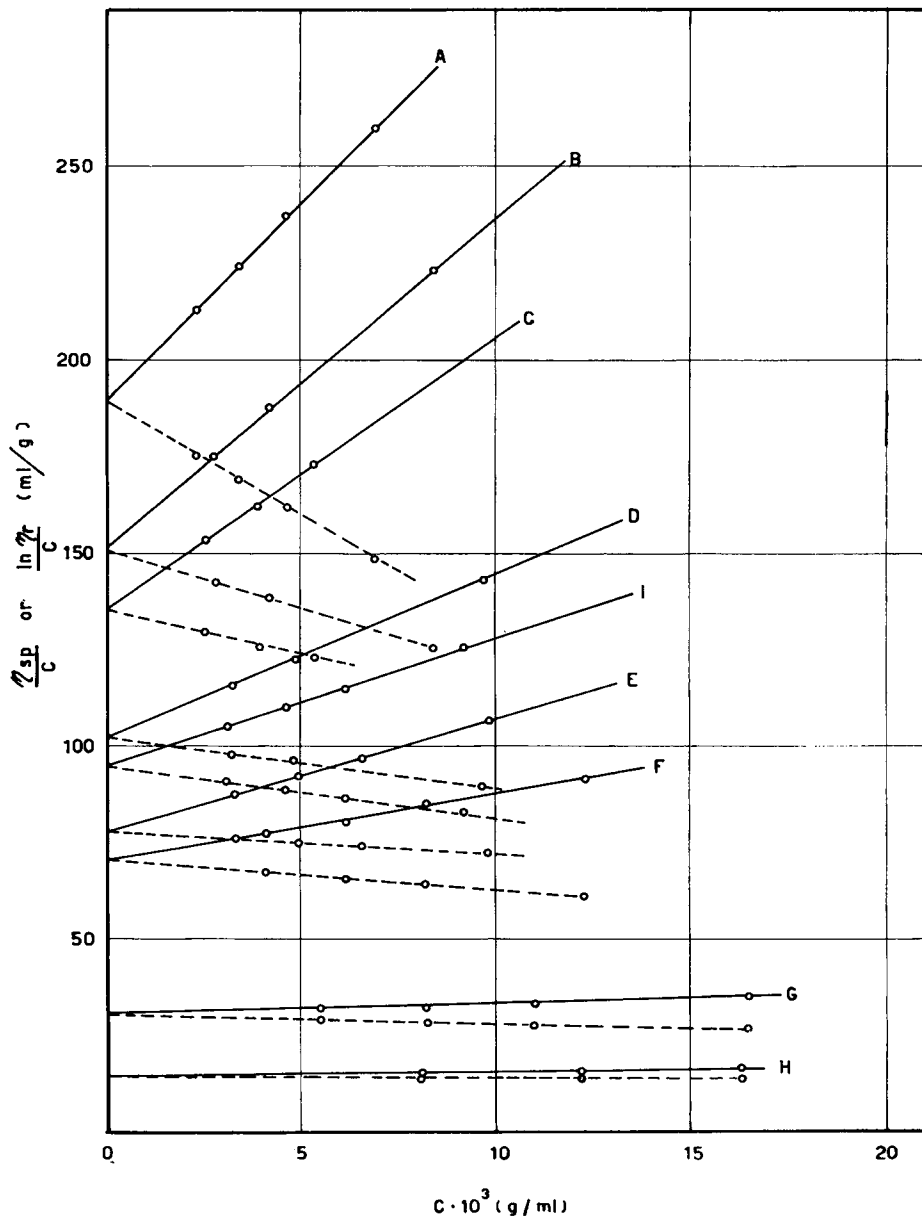


Fig. 1. Dilute solution viscosities of PVC samples A-I. Determination of intrinsic viscosity in cyclohexanone at 25°C.

EXPERIMENTAL

Materials Used

Ten PVC samples were studied. Six were unfractionated polymers, obtained by suspension polymerization methods, having a wide range of molecular weights (samples A–F). Samples G and H were polymerized in suspension in the presence of tetrahydrofuran as chain-transfer agent. Sample I was one of the fractions of narrow molecular weight distribution obtained from sample D by a large-scale fractionation carried out by successive precipitation.¹⁴ Sample L was a mixture of equal weights of polymers A, B, D, F, and H.

The purification of the polymers was accomplished by precipitation from tetrahydrofuran solutions into a mixture of methanol and water, followed by filtration and drying under vacuum at 40–50°C. until constant weight was reached.

Chlorine contents were determined by combustion in oxygen and chlorine titration. Intrinsic viscosity was determined in cyclohexanone solutions with a Desreux-Bischoff low shear-rate viscometer,¹⁵ and molecular weights were calculated by the recently reported¹⁶ relation:

$$[\eta] = 6.0 \times 10^{-3} M_w^{0.84} \text{ ml./g.} \quad (1)$$

The dilute solution viscometric data for samples A–I are shown in Figure 1. The polymerization temperatures, chlorine contents, and molecular weights of polymers are given in Table I.

TABLE I
Characterization of PVC Samples

Sample	Polymerization temperature, °C.	Chlorine, content, %	Intrinsic viscosity, ml./g.	Molecular weight $M \times 10^{-3}$
A	35	—	190	230
B	40	56.3	151	174
C	51	56.4	135	151
D	51	56.2	102	110
E	57	56.3	78	80
F	67	56.2	70.5	70
G	62	55.7	31	26
H	72	54.7	14.5	10.5
I	—	—	95	100
L	—	—	105	112

The solvent used was cyclohexanone of technical grade, purified by fractional distillation. The fraction boiling in the range 155–156°C. was collected and stored in brown glass bottles.

Solutions

The polymers were dissolved in cyclohexanone, under slow stirring, at approximately 85°C., which is just above the temperature of solubilization

of poly(vinyl chloride) in cyclohexanone. In fact, under 80°C. pseudo-solutions containing aggregates can be obtained.¹⁷ In the case of low concentrations and/or low molecular weights, the dissolution was rapid, while for high concentrations and/or high molecular weights it was necessary to continue stirring of the mixture at 85°C. for several hours in order to reach complete solubilization.

The concentrations were determined by weight, but were occasionally checked by diluting the solutions and by precipitating the polymer in methanol, drying, and weighing.

Density Measurements

The density of PVC was found to be 1.390 g./cc. at 30°C. and its thermal expansion coefficient was taken to be $-d \ln \rho/dT = 2.8 \times 10^{-4} \text{ deg.}^{-1}$, as calculated from published data.¹⁸

The density of cyclohexanone at 20°C. was found to be 0.94730 g./cc. and its thermal expansion coefficient, determined in the range 20–50°C., was $9.2 \times 10^{-4} \text{ deg.}^{-1}$.

The densities of several solutions were measured by means of a pycnometer. The results obtained for sample D at 40°C. are given in Table II,

TABLE II
Density of Solutions of Sample D at 40°C.

Weight fraction w_2	Density, g./cc.		Difference, %
	Experimental	Calculated	
0.03850	0.94120	0.94156	-0.036
0.05660	0.94792	0.94724	+0.068
0.07410	0.95333	0.95304	+0.029
0.09090	0.95997	0.95840	+0.157
0.13000	0.97342	0.97136	+0.206

where they are compared with the densities calculated, by assuming no volume changes on mixing, from the equation:

$$1/\rho = w_1/\rho_1 + w_2/\rho_2 \quad (2)$$

where w_1 , ρ_1 and w_2 , ρ_2 are the weight fractions and densities of solvent and polymer, respectively. It may be seen that the volumes are additive within 0.2%, even at relatively high polymer concentrations. Similar results were found also for samples A, G, and H at concentrations up to 30% of polymer by weight.

Therefore the volume fractions can be calculated from the equations:

$$\begin{aligned} \phi_1 &= w_1\rho/\rho_1 \\ \phi_2 &= w_2\rho/\rho_2 \end{aligned} \quad (3)$$

which give volume fractions accurate to within 0.2%. Maximum contractions in mixing of the order of 0.2% have been found for natural rubber and methyl ethyl ketone or ethyl acetate, up to $\phi_2 = 0.6$,¹⁹ while volume contrac-

tions of the order of 1% have been found, at similar concentrations, for polyisobutylene in *n*-pentane.²⁰

The volumes of polymer and diluent have been taken to be additive in several papers, and the results of Table II show that this approximation is reasonable for the system under study.

Viscometric Measurements

Glass capillary viscometers of the Cannon-Fenske type were used. Their dimensions, as measured in this work, are given in Table III. The nominal

TABLE III
Calibration Constants and Dimensions of Viscometers

Viscometer	Capillary radius, cm.	Length, cm.	Reservoir volume, ml.	Calibration constant, cstokes/sec.
N50	0.0210	7.2	3.24	2.99×10^{-3}
N100	0.0325	7.2	5.13	1.282×10^{-2}
N200	0.0508	6.2	3.23	9.96×10^{-2}
N300	0.0622	6.7	3.20	2.417×10^{-1}
N500	—	7.2	—	7.59

calibration constants, reported in Table III, were occasionally checked with several standard viscosity oils and found to be accurate within 0.3%. The measurements were carried out under conditions such that the maximum kinetic energy correction was of the order of 0.3%. Only solutions for which the shear effects were negligible were tested with capillary viscometers, while non-Newtonian solutions were studied with the Rotovisko rotational rheometer manufactured by Gebruder-Haake.

Kinematic viscosities, as obtained from capillary flow data, were converted to absolute viscosities by using the solutions densities calculated from eq. (2).

The temperature of the viscometers was kept constant to 0.05°C. The accuracy with which the viscosities were measured with the capillary viscometers was estimated to be of the order of 1%. With the rotational rheometer, the accuracy obtainable is of the order of 2%, and it was checked with standard viscosity oils.

However, for pseudoplastic fluids the calibration constant given by the manufacturer of the rheometer for the measurement of the shear rate, cannot be applied. In this work, the shear rate at the wall of the inner cylinder was calculated from the rheometer dimensions and from the experimentally determined relation between torque and angular velocity by applying the expanded series given by Kreiger and Elrod for coaxial cylinder viscometers.²¹ Use of the series to the second term was usually sufficient for obtaining data accurate within 4%, and the third term was seldom used. When tested with different combinations of cup and rotor, the corrected viscosities did not differ by more than 4%.

RESULTS

Typical data of the dependence of the viscosity η on the shear rate γ are shown in Figure 2 for sample I at 30°C. at several values of w_2 . It is seen that for this sample the solutions are Newtonian over a large shear rate range. They become slightly pseudoplastic at higher concentrations.

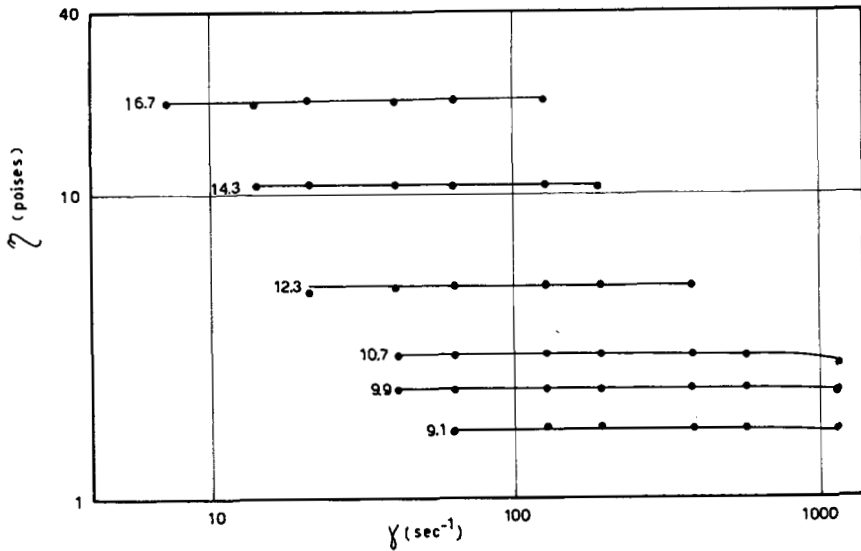


Fig. 2. Rate of shear dependence of the viscosity of solutions of PVC sample I at various weight fractions w_2 at 30°C.

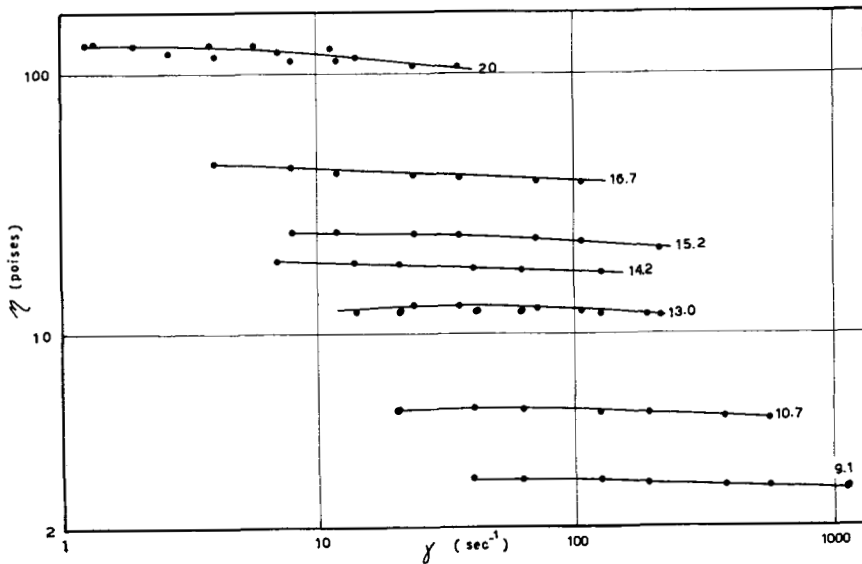


Fig. 3. Rate of shear dependence of the viscosity of solutions of PVC sample D at the weight fractions indicated at 20°C.

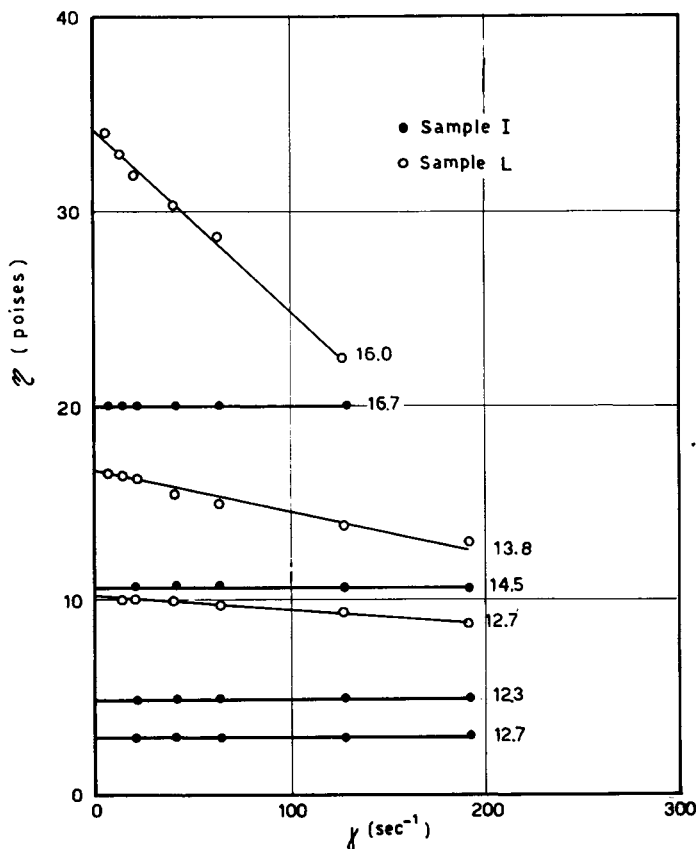


Fig. 4. Viscosity-shear rate curves, at the weight fractions indicated, for PVC sample I (narrow distribution) and for sample L (broad distribution).

Similar data for sample D at 20°C. are plotted in Figure 3. Samples A, B, and C show similar patterns, and their solutions deviate from Newtonian behavior at still lower concentrations and shear rates. It has been confirmed in this work that the solutions begin to be sensibly pseudoplastic (decrease of viscosity of the order of 10%) when the shear stress is of the order of $10^4 C$ dynes/cm.², C being the concentration in grams per milliliter.²²

However, the flow curves are affected also by the molecular weight distribution of the sample, as shown in Figure 4 for sample I (fraction of narrow molecular weight distribution) and for sample L (mixture of polydisperse polymers). This latter shows non-Newtonian behavior at smaller shear rates and concentrations than sample I. When necessary, the zero shear viscosity η_0 was evaluated by extrapolating to zero shear rate curves of the type shown in Figure 4. This procedure was necessary only for sample L and for a limited number of solutions of other samples having high viscosity. It is believed that the inaccuracy introduced in this way is of the order of a few per cent.

TABLE IV
Viscosity of Solutions of Sample D from 20°C. to 50°C. and Activation Energy for Flow

Weight fraction w_2	Viscosity, poises				E , kcal./mole
	$T =$ 20°C.	$T =$ 30°C.	$T =$ 40°C.	$T =$ 50°C.	
0.0909	2.80	2.13	1.70	1.34	4.6
0.107	5.62	4.35	3.30	2.50	5.1
0.130	12.5	10.2	7.8	6.0	5.1
0.142	19.4	15.0	10.0	7.8	5.8
0.152	29.3	21.4	16.2	11.8	6.1
0.167	42.0	29.7	22.5	17.2	5.7
0.200	115	73.2	51.3	36.2	7.0

The measurements were usually carried out at 30°C., but several data were obtained in the range of temperatures from 20 to 50°C. Typical results for sample D, at concentrations up to 20% by weight, are given in Table IV. When $\log \eta_0$ is plotted against reciprocal absolute temperature, straight lines, within experimental error, are obtained, from which the energy of activation for viscous flow E can be calculated. Values of E , defined as $E = R d \ln \eta_0 / d(1/T)$, corresponding to a midrange temperature of 35°C., are listed in Table IV.

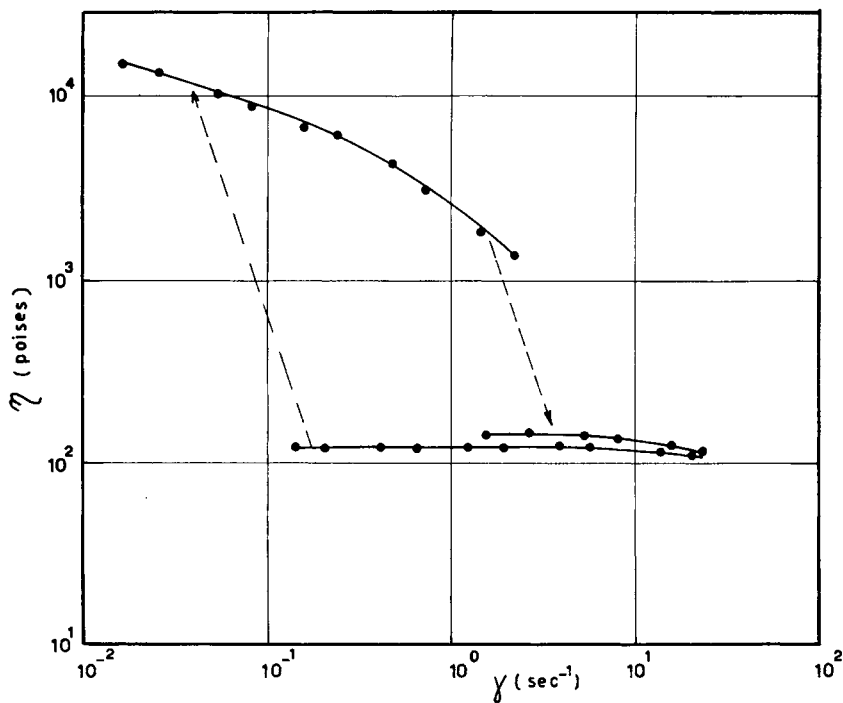


Fig. 5. Effect of aggregation on the viscosity of a solution of PVC sample A at weight fraction $w_2 = 0.1304$ (see text).

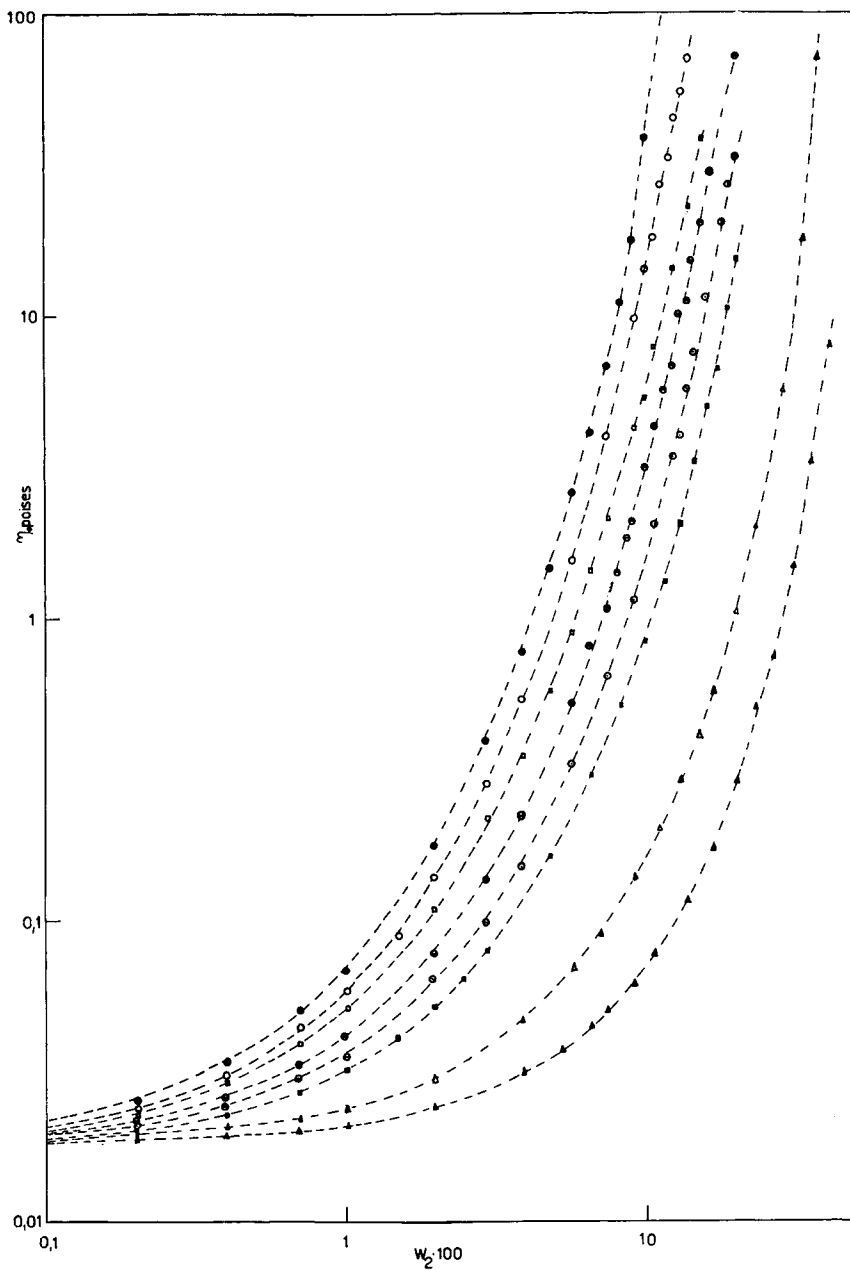


Fig. 6. Zero shear viscosity of solutions of PVC samples A-H at 30°C. plotted against weight fraction w_2 : (●) sample A; (○) sample B; (□) sample C; (⊖) sample D; (⊙) sample E; (■) sample F; (△) sample G; (▲) sample H. The data for samples I and L are similar and have been omitted to avoid superposition.

TABLE V
Zero Shear Viscosities of Solutions of Samples A-L at the Various Weight Fractions w_2 at 30°C.

$w_2 \times 10^2$	Zero shear viscosity, poises											
	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H	Sample I	Sample L		
0.1995	0.0254	0.0235	0.0229	0.0216	0.0209	0.0202	0.0193	0.0191	—	—		
0.395	0.0346	0.0303	0.0297	0.0258	0.0244	0.0228	0.0208	0.0198	—	—		
0.696	0.0513	0.0445	0.0394	0.033	0.0306	0.0271	0.022	0.0201	—	—		
0.990	0.0686	0.0584	0.0513	0.042	0.0355	0.0321	0.024	0.0210	0.040	0.0417		
1.96	0.178	0.14	0.109	0.079	0.064	0.0524	0.0302	0.0242	0.0734	0.080		
2.912	0.391	0.285	0.221	0.136	0.101	0.0793	—	—	0.125	0.141		
3.846	0.778	0.54	0.347	0.225	0.151	—	0.0462	0.0314	0.198	0.229		
4.760	1.48	—	0.572	—	—	0.163	—	—	0.302	0.36		
5.66	2.63	1.58	0.897	0.522	0.334	—	0.0696	—	0.444	0.55		
6.54	4.31	—	1.45	0.812	—	0.303	—	0.0449	0.637	0.80		
7.41	6.97	4.1	2.15	1.09	0.64	—	—	0.0509	0.894	1.15		
8.26	11.07	—	—	—	—	0.517	—	—	1.24	1.65		
9.09	17.9	9.9	4.3	2.13	1.17	—	0.139	0.0626	1.63	—		
9.91	39	14.3	5.33	—	—	0.844	—	—	2.19	3.48		
10.71	—	18	7.93	4.35	2.06	—	—	0.077	2.82	4.80		
11.28	—	27.1	—	—	—	—	—	—	—	—		
11.50	—	—	—	5.73	—	1.34	—	—	—	6.24		
12.28	—	—	14.5	6.85	3.49	—	—	—	4.78	—		

13.04	120	54.7	—	10.2	4.1	2.3	0.293	—	—	—
13.79	—	70.7	23.2	—	5.8	—	—	0.116	—	15.5
14.53	—	—	—	—	7.6	3.3	—	—	10.2	—
14.89	—	—	—	—	—	—	0.409	—	—	—
15.25	—	165	38.3	21.4	—	—	—	—	—	—
16.03	—	—	—	—	—	—	—	—	—	33.2
16.67	—	275	—	29.7	11.5	—	0.565	0.173	20	—
16.87	—	—	—	—	—	—	—	—	—	39
18.70	—	—	—	—	—	10.7	—	—	—	—
19.03	—	—	—	—	27.4	—	—	—	—	—
20.00	—	—	—	73.2	34	15.5	1.06	0.291	—	—
23.07	—	—	—	—	—	—	2.01	0.508	—	—
26.47	—	—	—	—	—	—	—	0.738	—	—
28.58	—	—	—	—	—	—	5.64	—	—	—
31.03	—	—	—	—	—	—	—	1.48	—	—
33.33	—	—	—	—	—	—	18	—	—	—
35.48	—	—	—	—	—	—	—	3.33	—	—
37.50	—	—	—	—	—	—	—	—	—	—
39.40	—	—	—	—	—	—	72	—	—	—
41.18	—	—	—	—	—	—	133	—	—	—
								8		

At high concentrations, some solutions of samples having high molecular weight showed a definite tendency toward aggregation. Their viscosity increased with time, and their behavior became progressively more non-Newtonian. A typical result is shown in Figure 5 for sample A at $w_2 = 0.1304$. The lower flow curve, obtained immediately after dissolution, is almost Newtonian, with a zero shear viscosity of 120 poises.

After a few days standing at room temperature, the low shear viscosity increased to more than 10,000 poises, and strong non-Newtonian behavior was developed also at shear rates as low as 10^{-2} sec. $^{-1}$ (upper curve). When heated at 85°C. for approximately 20 min., the viscosity dropped at 130 poises as a result of disaggregation, as shown in Figure 5. The phenomenon is therefore thermally reversible.

With low molecular weight polymers the increase of viscosity with time occurred only at relatively high concentrations. The solution of sample G having $w_2 = 0.37$ showed, for example, a slow increase of viscosity with time. In these cases the viscosity at zero time was derived by extrapolations from a number of flow data obtained on the same solution over a period of several hours.

When the weight fraction exceeded 0.20 for samples A and B, and approximately 0.5 for the low molecular weight samples G and H (with intermediate values for the other samples), solubilization became possible only at high temperatures, and rapid gelation occurred on cooling of the solutions at 30°C.

In Table V the zero shear viscosities of the majority of the polymer solutions, at the appropriate weight fractions, are given for the temperature $T = 30^\circ\text{C}$. At this temperature the viscosity of the solvent was 0.0178 poises.

The concentration dependence is shown in Figure 6 for samples A-H. (A log-log plot is used for the purpose of compressing the curves, which extend over a large viscosity range, at no sacrifice of detail at the lower concentrations.)

Several data not reported in Table V are also shown in Figure 6. The viscosity concentration curves for samples I and L, which are not plotted in Figure 6 for reason of clarity, are substantially similar and will be discussed in a later section.

DISCUSSION

Aggregation

The range of molecular weights examined in this work is relatively large, extending from 10^4 to 2.3×10^5 . The range of concentrations, on the other side, is limited by the well-known fact that PVC does not give stable solutions in cyclohexanone or in other solvents above some critical concentration range.

The critical concentration, or solubility, cannot however be exactly defined, since the solutions tend to increase their viscosity with time. The increase is more apparent the higher the molecular weight and the more

concentrated the solution. The phenomenon can be ascribed to the formation of aggregates.

Association of macromolecules has been observed in dilute solutions of relatively good solvents for various polymers, e.g., for polyethylene,²³ natural rubber,²⁴ and polybutadiene.²⁵

For the system studied in this work, when the concentration is sufficiently high, the aggregation extends to the whole solution and gelation may occur. A rapid gelation of the solutions when cooled to room temperature after dissolution at 85°C., occurs when the weight fraction w_2 is of the order of 0.5 for low molecular weight polymers and of the order of 0.2 for samples of the highest molecular weight.

The formation of gels from concentrated solutions requires both the presence of an insoluble product and the tendency of the molecules to form aggregates. The more the molecules are extended, the less is the number of them that is necessary to create a network in which all the solvent is immobilized. The effect of the molecular weight of the polymer on the critical concentration range at which rapid gelation occurs may be therefore understood.

Also, insoluble particles of polymer must be present in order to reach gelation. With highly ordered polymers, liquid-crystalline phases may be found in concentrated solutions,^{26,27} and since in poly(vinyl chloride) there is approximately 10% of crystallizable polymer,²⁸ it may be supposed that the insoluble part is formed by this portion of the polymer. This has been confirmed by studying a sample polymerized at -40°C. having $[\eta] = 135$ ml./g. and containing 20% of crystallizable polymer.²⁸ When dissolved in boiling cyclohexanone, this sample showed a strong tendency to aggregate even at a concentration as low as 0.03 (corresponding to an initial viscosity of the solution of 0.3 poises).

At concentrations of the order of 0.06 (corresponding to an initial viscosity of the solution of 4 poises), complete gelation occurred in a few days for this polymer. The increase of viscosity and the gelation can therefore be attributed to the formation of crystallites in the poly(vinyl chloride) solutions, which closely resembles the phenomena occurring in the plasticizer-polymer systems.

When PVC, after being dissolved at high temperature in a plasticizer, is cooled, the polymer forms a three-dimensional network²⁹⁻³² which has been shown³³ to consist partially of a polycrystalline structure. The peculiar properties of plasticized poly(vinyl chloride) have been often ascribed to a small amount of crystallinity in the system; ^{4,34-36} the results obtained in this work can also be so interpreted.

Shear Dependence of Viscosity

While the study of the shear dependence of the viscosity of the PVC-cyclohexanone solutions is beyond the scope of this work, it may be interesting to note the strong effect of the molecular weight distribution of the polymer on the flow curves.

While sample I is a fraction having a narrow molecular weight distribution, sample L is a mixture of a number of unfractionated polymers, the highest average molecular weight of which is 230,000 while the lowest is 26,000.

The difference in molecular weight distribution between samples I and L causes a marked difference in the shear dependence of their solution viscosity, as seen in Figure 4. Similar effects are known for the system polyisobutene-cetane³⁷ and for several polymer melts.³⁸⁻⁴⁴

The non-Newtonian flow behavior of polymer melts or solutions is generally attributed to the presence of entanglements between adjacent macromolecules. The capacity of a molecular chain to form entanglements increases rapidly with increasing molecular weight of the macromolecules.

If we consider two polymers of the same average molecular weight, one of which has a broad molecular weight distribution and the other a narrow one, large macromolecules are present in the first which may contribute to the formation of entanglements, while this is not the case for the second. The shear behavior may therefore vary markedly with the distribution of molecular weights, as shown clearly for the PVC-cyclohexanone system in Figure 4.

Temperature Dependence of Viscosity

The results of Table IV, which show that the energy of activation for viscous flow E increases with increasing concentration, are in agreement with the literature data. It may be shown that E increases from values of 2-4 kcal./mole at low concentration up to values that vary, depending on the glass transition temperature of the polymer T_g , between approximately 10 kcal./mole (for polyisobutylene^{45,46}) and 30-50 kcal./mole [for polystyrene^{1,47} and poly(methyl methacrylate)^{1,48}].

Concentration Dependence of Viscosity

Data on the concentration dependence of the Newtonian viscosity for polymer solutions can be found in several papers.^{1-11, 45-57} Much effort has been spent in describing such data by means of simple mathematical expressions. Several functions have been claimed to be suitable over limited concentration ranges. For example, Simha et al.¹ applied the Baker equation:

$$\eta = \eta_s \{1 + [\eta] (c/a)\}^a \quad (4)$$

where $[\eta]$ is the intrinsic viscosity of the polymer and a is a constant, to moderately concentrated polymer solutions.

Streeter and Boyer⁶ found that the Martin equation:

$$\log (\eta_{sp}/c) = \log [\eta] + k [\eta] c \quad (5)$$

described fairly well their results on polystyrene solutions, up to concentrations of 12%, in various solvents. The data of Flory⁵ on the system poly-

(decamethylene adipate)-diethyl succinate, covering the entire concentration range, have been described respectively by a two-constant empirical equation⁵ and by a logarithmic-decrement empirical equation containing three constants.⁴ Maron et al.^{55,56} used a three-parameter equation for moderately concentrated solutions of poly(methyl methacrylate) in various solvents.

Ferry and co-workers^{22,49-51} found that at moderately high concentrations (approximately 5-40%) the viscosity was proportional to the fifth power of ϕ_2 for a number of polymer-solvent systems, following the relation

$$\eta = K\phi_2^n \quad (6)$$

with $n = 5$. Equation (6) with the concentration expressed in weight fraction w_2 , can also be applied to the data reported by Porter and Johnson³⁷ on polyisobutylene-decalin solutions, at w_2 lower than 0.2, and with the same exponent. However, the validity of this equation is limited at moderately high concentrations, and it fails at very high concentrations, where the exponent n increases to values of the order of 10 or even of 50, depending on the temperature and on the system studied.

In fact, slopes as high as 12 can be calculated, by plotting on log-log paper the viscosity-concentration data of Tager et al.⁴⁶ for the system polyisobutylene-isooctane.

From the results of Fujita et al.⁷⁻¹⁰ it is possible to calculate, at w_2 of the order of 0.9, a maximum slope of 50 for poly(methyl acrylate)-diethyl phthalate at 20°C. and a slope of 60 for the system poly(vinyl acetate)-diethyl phthalate at 10°C. These exponential coefficients are of the same order of magnitude as those found for the concentration dependence of the diffusion coefficients of small molecules in highly concentrated polymer-diluent systems.²²

At higher temperatures, the maximum exponent decreases: it is of the order of 20 for poly(methyl acrylate)-diethyl phthalate at 120°C. and of the order of 25 for poly(vinyl acetate)-diethyl phthalate at 100°C.⁷⁻¹⁰

Reviewing the available data, it may be concluded that the concentration dependence of viscosity shown in Figure 6 for the system under study can be considered typical for all the polymer-solvent systems known at present.

Over a wide concentration range, no simple equation can describe the viscosity-concentration curves, and no attempt was made in this work in trying to interpret mathematically the curves of Figure 6. In relatively dilute solutions, the viscosity depends on a rather low power of w_2 . The slopes of the $\log \eta_0$ versus $\log w_2$ curves increase gradually with increasing w_2 , and in Figure 6 the data at high concentrations are approximately described by eq. (6) with $n = 5$.

There is no evidence in Figure 6 of an abrupt change in the slope at some critical concentration. The corresponding curves for samples I and L have similar shape, which shows that changing the molecular weight distribution of the polymer has no effect on the concentration dependence of the Newtonian viscosity of the solutions.

A thorough analysis of all the available data showed that the $\log \eta$ - $\log w_2$ plots change gradually in slope with increasing w_2 , for all the systems for which a large concentration range is covered,^{1,5,7-10,46-51} and a sudden slope transition was not found at any concentration. The curves reported by Onogi et al.,⁵⁷ in connection with this transition, seem to be rather singular, and the data reported in graphical form by Asai⁵⁸ on the PVC-cyclohexanone system do not find confirmation in the results of this work.

Molecular Weight Dependence of Viscosity

The data of Table V and Figure 6 show the effect of the molecular weight M on the solution viscosity. At low concentrations, the viscosity is proportional to a fractional power of M , while at high values of w_2 the viscosity is approximately proportional to the third power of M for all the polymers, except the low molecular weight samples G and H.

The equation

$$\eta = KM_w^{3.4} \quad (7)$$

has been found to apply universally to polymer melts above some critical molecular weight M_c ,¹ and it applies equally well at high concentrations to various polymer-solvent systems.^{1,22,45-50}

At low concentration and/or low molecular weight the effect of molecular weight on viscosity is less clearly understood, and various reduced parameters have been used for the purpose of superposing the results obtained on solutions of polymers of different molecular weight. Utracki and Simha³ used a concentration parameter which was proportional to the 0.5-0.6 power of molecular weight.

Ferry et al.^{22,49,50} obtained a single composite curve by plotting on a log-log paper the viscosity versus the product $c^5M^{3.4}$, while Hirai⁵⁹ used the product ϕ_2M .

At concentrations higher than 4%, the curves of Figure 6 are almost similar in shape and can possibly be superposed by the use of a reduced variable. Noting that the parameter used by Utracki and Simha is approximately proportional to the intrinsic viscosity $[\eta]$ of the polymers, and that the product $c^5M^{3.4}$ is equivalent, on a log-log plot, to the product $cM^{0.68}$, where $M^{0.68}$ is also almost proportional to $[\eta]$, the data of Table V were plotted, in Figure 7, against the product $w_2 [\eta]$. It may be seen that a master curve can be obtained, from which, however, the low molecular weight samples G and H deviate markedly. Other kinds of reduced concentration give similar results, and the viscosity-concentration curves of samples G and H cannot be superposed to the other curves in any acceptable way. The reduction schemes outlined above^{2,3,22,59} do not apply, evidently, to polymers having molecular weights of the order of 10,000-20,000.

The results of Figure 7 can, however, be expected, since the viscometric properties of concentrated polymer solutions can be interpreted, according

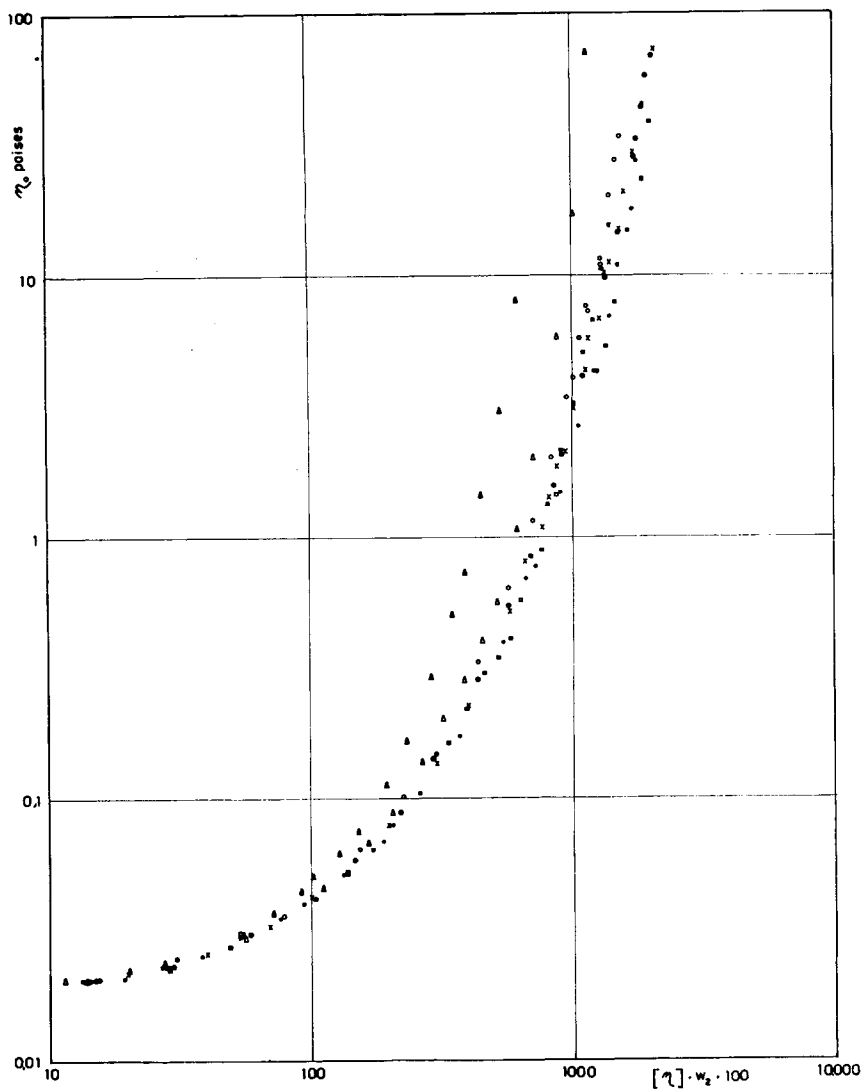


Fig. 7. Zero shear viscosities of solutions of PVC samples A-L at 30°C. plotted against the product $[\eta] w_2$ (see text): (●) sample A; (○) sample B; (□) sample C; (×) sample D; (○) sample E; (■) sample F; (△) sample G; (▲) sample H.

to Bueche, by the same theoretical model which applies to molten undiluted polymers.^{47,48} In the Bueche treatment, the viscosity is proportional to $M^{3.4}$ only when the macromolecular chains entangle each other in a three-dimensional network.

The validity of the reduction schemes described above is therefore limited to molecular weights sufficiently high and to concentration ranges within which eq. (6) can be applied with an exponent of 5.

In the following communication,⁶⁰ the results reported in this paper will be discussed on the basis of the Kelley-Bueche treatment¹¹ of the viscosity of polymer solutions.

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Résumé

Les viscosités d'échantillons de chlorure de polyvinyle dans la cyclohexanone ont été mesurées sur un vaste domaine de concentration jusqu'à des fractions en poids de polymères de l'ordre de 0,4. Des polymères de poids moléculaire variant de 10.000 à 230.000 et de distribution de poids moléculaire différentes ont été étudiés. L'effet de la concentration et du poids moléculaire sur la viscosité de la solution est rapporté et discuté pour ce système aussi bien que pour d'autres systèmes dont les données sont disponibles dans la littérature. Des schémas de réductions empiriques souvent appliqués aux données viscosimétriques de solutions polymériques concentrées sont soumises à discussion.

Zusammenfassung

Die Viskosität von Polyvinylchlorid wurde in Zyklohexan in einem weiten Konzentrationsbereich bis zu einem Gewichtsbruchteil an Polymeren in der Grössenordnung von 0,4 gemessen. Polymere mit einem Molekulargewicht von 10.000 bis 230.000 und mit verschiedener Molekulargewichtsverteilung wurden untersucht. Der Einfluss der Konzentration und des Molekulargewichts auf die Lösungsviskosität wird mitgeteilt und für das vorliegende System sowie für andere in der Literatur beschriebene Systeme diskutiert. Die auf die viskosimetrischen Daten von konzentrierten Polymerlösungen oft angewendeten empirischen Reduktionsverfahren werden diskutiert.

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