High-Shear Capillary Viscosity Studies on Concentrated Copolymer Solutions*

SURESH N. CHINAI and WILLIAM C. SCHNEIDER, *American Cyanamid Company, Stamford Research Laboratories, Stamford, Connecticut*

INTRODUCTION

The flow behavior of rigid and coil-shaped particles of homopolymers has been the subject of many investigations.[1-6] Most of these studies have been undertaken with dilute or moderately concentrated solutions. It is generally agreed that the dependence of the viscosity of concentrated polymer solutions on rate of shear is a difficult subject in so far as the interpretation in terms of exact size and shape of the macromolecule is concerned.

This paper presents measurements and some interpretations of the flow properties of copolymer solutions over a wide range of concentration and shear rate. The Rabinowitsch[7] treatment for the characterization of the absolute flow curves and of viscosity changes as a function of shear rate, concentration, and temperature has been applied. Finally, a qualitative comparison of the experimental results with those calculated by using the rheological equation for non-Newtonian liquids has been made, and a rheological model (fitted to the experimental results only) has been selected and employed in determining the inflection point of the flow curve by computer analysis.

EXPERIMENT

Materials

A copolymer of acrylonitrile–methyl methacrylate (90/10) was prepared in a continuous reactor with a chorate–sulfite redox system as catalyst. The molecular properties of the material were determined by light scattering and viscosity, with the use of reagent-grade sodium thiocyanate (NaCNS), deionized water, and technical-grade dimethylformamide (DMF). The weight-average molecular weight was 115,000, the root-mean-square end-to-end distance in DMF was 500 ± 50 A., and the intrinsic viscosity in 48% aqueous NaCNS was 1.70 dl./g.

Apparatus and Procedure

A stainless-steel capillary viscometer was used for the viscosity measurements. Flow properties were measured at shear rates of up to 200,000 sec.$^{-1}$ with various capillary length-to-diameter ratios (l/d). This apparatus was checked out against a Ferranti cone and plate viscometer at shear rates up to 15,000 sec.$^{-1}$.

Polymer solutions were prepared with 48% NaCNS as solvent. The concentration range covered was between 0% and 16.1% solids. The presence of laminar flow at each concentration was confirmed by Reynolds numbers lower than 2000. All data with higher Reynolds numbers were discarded.

RESULTS AND DISCUSSION

The basic data (uncorrected) of the flow experiments allow one to calculate the consistency variables from the equations:

$$\tau_w = \Delta Pr/2 \tag{1}$$

and

$$D = 4Q/\pi r^3 \tag{2}$$

where τ_w is the maximum shear stress at the capillary wall in dynes per square centimeter, ΔP the applied pressure in dynes per square centimeter, r the capillary tube radius in centimeters, l the capillary tube length in centimeters, D the apparent shear rate in reciprocal seconds, and Q the volume flow rate in cubic centimeters per second.

Unless one uses a capillary of $l/d > 300$, eq. (1) has to be corrected for the viscous resistance encountered during flow in a converging stream, that is, from the wider sample reservoir to the considerably narrower capillary tube inlet. This is the so-called Couette inlet end effect[8] and is usually expressed in terms of a hypothetical addition e to the length of the capillary tube. The net result is that the effective length-to-diameter ratio $(l/d + e)$ is larger than the actual l/d value, e being the total end-effect correction term. The effective shear stress can then be calculated from the equation

$$\tau_w = \Delta P/[4(l/d + e)] \tag{3}$$

It was pointed out by Bagley[9] that the total end effect correction consists of two terms, one each for the viscous part (N) and the elastic part (E) of the total end effects, respectively. Mathematically:

$$e = N + E \tag{4}$$

The Hagenbach kinetic energy correction of the driving pressure[8] becomes important when the rate of flow of polymer solution passing any cross section of a cylindrical capillary tube is high. Thus, when the loss

due to increase in kinetic energy of the fluid in the capillary is taken into account, eq. (3) becomes:

$$\tau_w = \Delta P / [4(l/d + e)] - m\rho Q^2 / [2\pi^2 r^3 d(l/d + e)] \tag{5}$$

where $m = 1.2$ and ρ is the density of the polymer solution.

The ratio of this τ_w to D would give the apparent viscosity μ_a in poises.

In this study the Rabinowitsch treatment[7] was desirable because it would allow the calculation of the maximum shear rate at the wall, D_w in reciprocal seconds.

According to the differential method of Rabinowitsch, the experimental D of eq. (2) was corrected by the equation

$$D_w = D[(3 + \sigma)/4] \tag{6}$$

where σ is the slope of the $\log D$ vs. $\log \tau_w$ plot at any τ_w.

The material behavior is Newtonian when $\sigma = 1$ and D_w will be equal to D. Viscosity at the wall can be calculated from the equation

$$\eta_w = \tau_w / D_w \tag{7}$$

General Consideration of Flow Curves

The flow curves for a given fluid should be independent of tube dimensions, no matter how complex the connection between shear rate and shear stress, and one should obtain a single flow curve at a given concentration and temperature. However, the fluid and the apparatus must satisfy certain experimental requirements, which are that (1) flow is laminar, (2) heat effects due to fluid friction are negligible, (3) end-effect losses are minor, (4) kinetic energy corrections are negligible, and (5) liquid is non-thixotropic and time-stable. Of these conditions, (1) and (5) are met by the fluid under study. Conditions (3) and (4) have been corrected. Condition (2) is assumed to be small at low flow rates; at high flow rates some
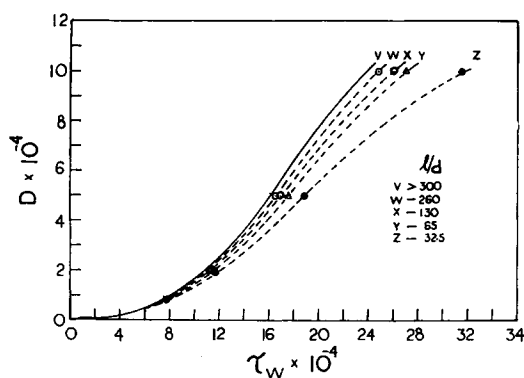

Fig. 1. Effect of length-to-diameter ratio of capillary tube on the flow property of 10% copolymer solution in 48% aqueous NaCNS at 30°C.: (—) single composite curve.
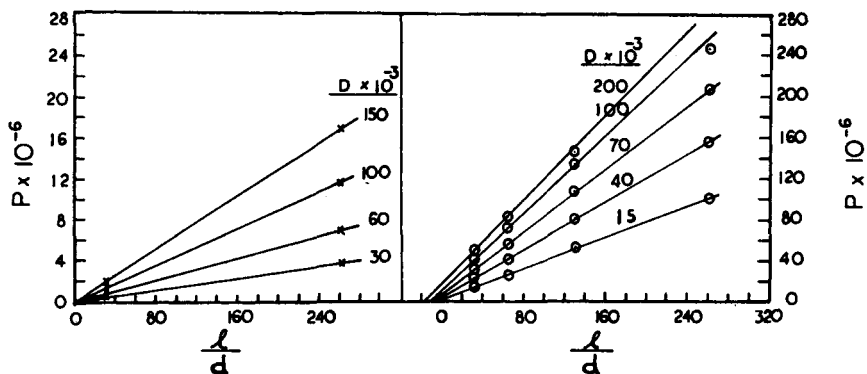
Fig. 2. Pressure versus length-to-diameter ratio at a constant apparent shear rate: (⊙) 10% and (×) 1% copolymer solution at 30°C.

error in the values reported is to be anticipated, since this correction was not applied.

In Figure 1 it is shown that the flow curves obtained with capillaries of different lengths but having the same diameters do not superimpose, the wall shear stress τ_w that corresponds to a given apparent shear rate D being greater, the smaller the length of the capillary tube.

According to the work of Mooney[10] this displacement of the curves cannot be attributed to slip alone, since variations due to slip are primarily dependent upon the tube diameter, which was held constant in this study. An analysis was therefore made in accordance with eq. (3) whereby the pressure required to produce a given apparent shear rate was plotted versus l/d. A typical set of plots for 1% and 10% solutions covering a shear rate range up to 200,000 sec.$^{-1}$ is shown in Figure 2. As expected, the plots are linear since the entrance effects were confined to a region at the entrance small in comparison to the total capillary tube volume, and the x-intercepts (e) for a 1% solution are nearly zero while those for the 10% solution are appreciably higher.

One may state that concentrated solutions exhibit a highly elastic character, as defined by eq. (4), and this may be visualized as follows. The molecules which are in the form of a coil in the unstressed state become uncoiled when high stress is applied. "Hand-in-hand" type of linkage points between molecules would prevail and act in transmitting stress from one point to the next. Thus, shear stress would increase rapidly from zero to some constant maximum value as the material entered the capillary tube. A tension of some sort is built up, owing to the elastic character of the molecules in solution and, consequently, would require greater input of energy to maintain a given flow rate. At high shear rates, a concentrated polymer solution would be expected to have more difficulty in maintaining its flow pattern because (1) resistance to flow is high at the inlet portion of the capillary tube and (2) the material is accelerated as it enters the capillary tube. The phenomenon would be expected to be dependent upon
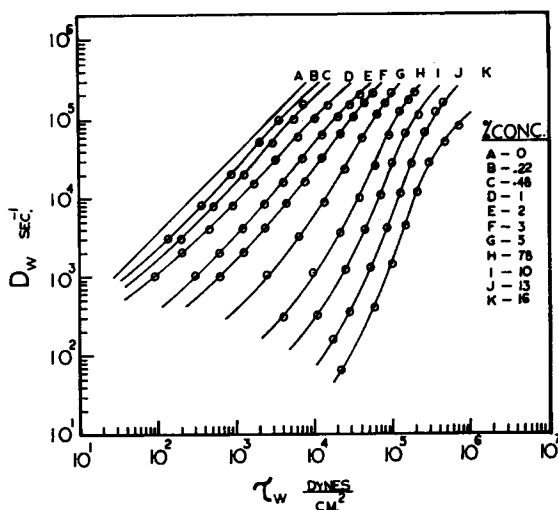
Fig. 3. Concentration dependence of the absolute flow curves at 30°C.

factors such as concentration, molecular weight, and temperature. This variation in concentration is believed to be the cause of variation in the e values of the two solutions.

The absolute flow curves obtained by plotting corrected consistency variables are shown in Figure 3. This, then, represents the graph according to the Rabinowitsch method, where wall shear stress and shear rates are plotted. These flow curves are typical of pseudoplastic fluids; that is, the proportionality factor between shear stress and shear rate is not constant.

Interpretation of Flow Curves

Inflection Point

Schurz[11] has pointed out that in the flow curves of moderately concentrated solutions of polymeric materials the inflection point is a measure of molecular weight. The inflection point occurs at a higher value of the shear rate, the lower the molecular weight of the material. This was explained qualitatively as follows. Structural viscosity (non-Newtonian) sets in earlier, that is, at lower shear rates, as the particle gets larger. In the words of Umstätter,[12] the displacement frequency is inversely proportional to the molecular weight.

The position of the inflection point is not independent of concentration. For very concentrated solutions, a shift of the inflection point to lower D values takes place, as shown in Figure 4. As one lowers the concentration, the inflection point first rises gradually to higher D and then remains essentially constant. Similar results were found by Schurz with a Vinyon N (copolymer of 60% vinyl chloride and 40% acrylonitrile) solution in
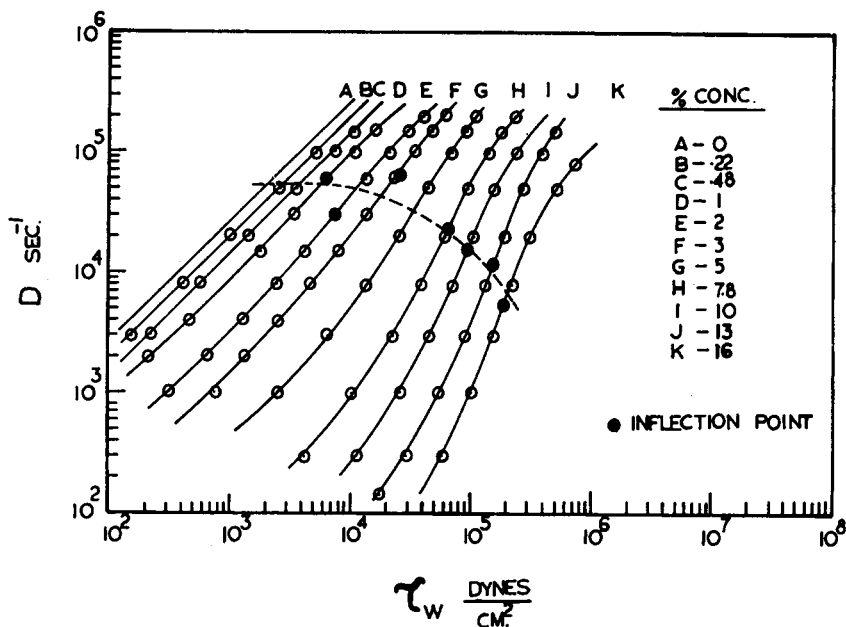
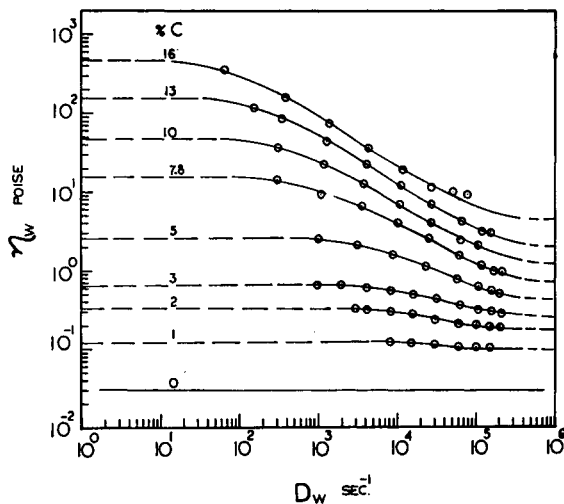Fig. 4. Concentration dependence of the apparent flow curves at 30°C.

Fig. 5. Shear dependence of the viscosity of copolymer solutions at 30°C.

dimethylformamide. The general qualitative interpretation is that at high concentration the formation of micelles or aggregates occurs, and therefore larger particles and a lower value of D. As the concentration is lowered, a level is reached below which the inflection point occurs at constant D. This concentration is assumed to represent the level at which

molecular dispersion has occurred, and a further reduction in the size of the particle is not possible. In this study with acrylonitrile–methyl methacrylate copolymer, molecular dispersion first occurs at a concentration of about 1%.

Initial and Final Absolute Viscosity

Figure 5 shows the shear dependence of the absolute viscosity at 30°C. for several concentrations of solution. The initial viscosity η_i and final viscosity η_∞ represent values obtained by graphical extrapolation of $\log \eta_w$ versus $\log D_w$ to the two extremities $D_{w \to 0}$ and $D_{w \to \infty}$.

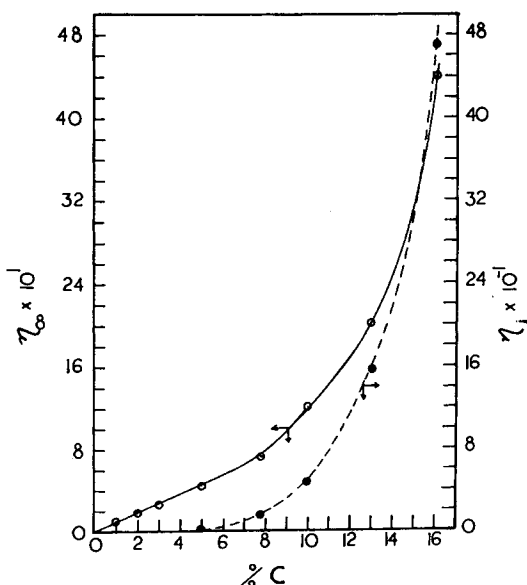Fig. 6. Concentration dependence of initial η_i and final η_∞ viscosity of copolymer solutions at 30°C.

In Figure 6 the η_i and η_∞ values are plotted against concentration. It is apparent that a rapid increase in both the η_i and η_∞ values occurs at about 8% concentration. In this concentration region, molecules having a greater effective radius of gyration in solution due to interaction, association, or aggregation are believed to be present. Also, note that the η_∞ is linear with concentration up to 8%.

Intrinsic Viscosity

From the data in Figure 5 the reduced viscosities as a function of true shear rate were calculated, and the results are shown in Figure 7. It should be noted that within the range of shear rates studied the reduced viscosities at high concentrations dropped to approximately $1/_{100}$ the initial value as D_w changed from low to high values, while at low concentrations
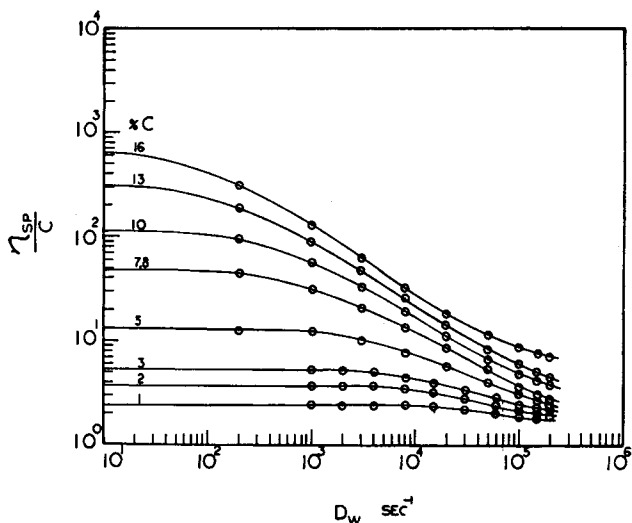
Fig. 7. Reduced specific viscosity as a function of maximum shear rate.

the corresponding drop is only $^2/_3$. This simply indicates that in concentrated solutions the shear rate dependence of the interaction between polymer and solvent molecules is markedly changed as the molecules are deformed or oriented by flow.

The intrinsic viscosity $[\eta]$ was calculated by using the well-known Huggin's equation:

$$\eta_{\text{sp}}/C = [\eta] + k'[\eta]^2 C \tag{8}$$

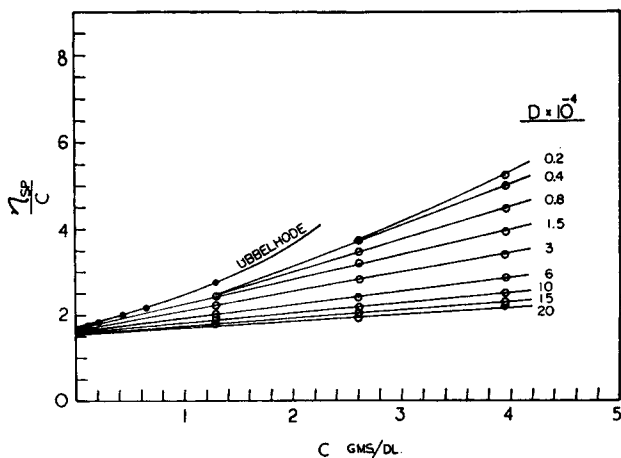

Fig. 8. Concentration and shear dependence of reduced viscosity of copolymer solutions at 30°C.

The value of intrinsic viscosity $[\eta]_{D_w \to 0}$ calculated from the flow curve data agrees well with that obtained with an Ubbelohde dilution viscometer. The reduced viscosity plots and the limiting values at infinite dilution are shown in Figure 8. Table I presents values of η_i and η_∞ for solutions of various concentrations at 30°C., and Table II presents values of $[\eta]_{D_w}$, $[\eta]_{D_w \to 0}$, and the ratio $[\eta]_{D_w}/[\eta]_{D_w \to 0}$.

TABLE I
Initial and Final Viscosities at Various Concentrations

Conc., %	η_i, poises	η_∞, poises
16.1	470	4.4
13	153	2.0
10	47	1.2
7.8	15.5	0.72
5	2.55	0.44
3	0.650	0.288
2	0.325	0.183
1	0.123	0.101
0	0.030	0.030

TABLE II
Shear Dependence of Intrinsic Viscosity

D_w, sec.$^{-1}$	$[\eta]_{D_w}$	$[\eta]_{D_w \to 0}$	$[\eta]_{D_w}/[\eta]_{D_w \to 0}$
4000	1.70	1.70	1.000
8000	1.70		1.000
15000	1.68		0.988
30000	1.66		0.976
60000	1.65		0.970
100000	1.60		0.941
150000	1.55		0.912
200000	1.52		0.894

With the capillary rheometer the precision of measurement was low at 0.22 and 0.5% concentration and, therefore, these values have not been plotted in Figure 8.

Non-Newtonian behavior is once again evident in the shear dependence of the intrinsic viscosity values. Since the molecular weight of the sample used in this study is relatively low, a marked effect of D_w on $[\eta]$ was not expected. The results of this study have shown an approximate 10% decrease in $[\eta]$ due to shearing action. Consequently, the $[\eta]_{D_w}/[\eta]_{D_w \to 0}$ ratios also decreased with increasing shear rate.

Assuming random-coil configuration for this copolymer sample of a relatively low molecular weight, one can qualitatively state that Bueche's[13] theory for free-draining coils predicts a decrease in $[\eta]$ in accordance with the experimental findings of this study.
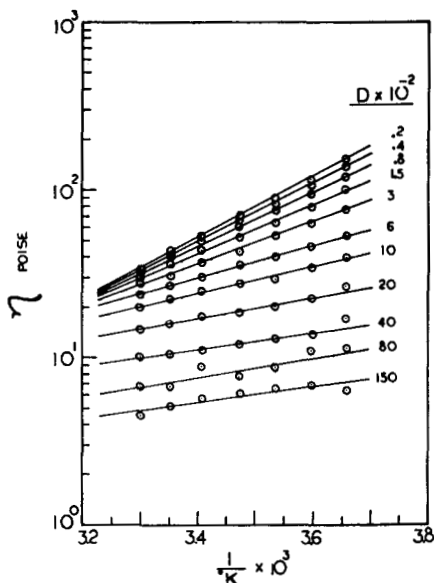
Fig. 9. Arrhenius plots for 10% copolymer solution at indicated shear rate.

The following additional conclusions may be drawn:

1. An upper Newtonian viscosity η^* is observed somewhere in the range of shear rates above 150,000 sec.$^{-1}$.

2. Over the range of concentration up to 1%, and at high shear rate, the value of the upper Newtonian or ultimate Newtonian viscosity is such that the calculated η_{sp}/C was essentially independent of concentration (in contrast to the usually high rate of increase of η_{sp}/C with C at low shear rates). Therefore, this value of η_{sp}/C for any C is identical with the $[\eta^*]$ obtained by extrapolation to infinite dilution. In this study a 10% variation was found between the final $[\eta^*]$ and η_{sp}/C at various concentrations. This is within the precision of the capillary rheometer instrument used. It has been suggested by Merrill[14] that $[\eta^*]$ so obtained is independent of the nature of the solvent, since the configuration at this shear rate represents the unperturbed molecular dimensions in solution. Consequently, the relation between molecular weight and $[\eta^*]$ may be expressed with only one constant, as shown by the equation:

$$[\eta^*] = K\bar{M}_w^{0.50} \tag{9}$$

The value of K was calculated to be 4.5×10^{-3}. This value should be a constant that is independent of both molecular weight and solvent.

Effect of Temperature on Viscosity

The temperature dependence of viscosity is usually examined by the heat of activation for viscous flow according to the equation:

$$\eta = ke^{E/RT} \tag{10}$$

TABLE III
Heat of Activation at Different Shear Rates

D_w, sec.$^{-1}$	E, kcal./mole
20	8.58
40	8.01
80	7.42
150	6.74
300	5.85
600	4.63
1000	3.85
2000	2.95
4000	2.60
8000	2.95
15000	2.75

The expected linear plot between log η and $1/T$ is shown in Figure 9. The values of the heat of activation were found to be dependent upon the shear rate, as shown in Table III.

This clearly indicates that the relative temperature sensitivity of the material varies with the applied stress. Therefore, one may generalize that the kinetic segments which act as a flow unit are varying as a function of applied stress. In this study it was found that at low shear rates the segment length increases as the temperature is lowered at a more rapid rate than the corresponding increment at high shear rates. These values may be compared with the values of about 25 kcal./mole for typical vinyl polymer melts.[15] The rule that high viscosity leads to high activation energy seems to be substantiated inasmuch as a larger unit is involved in the flow process.

Fitting of a Rheological Model to the Experimental Results

A quadratic model was chosen for computor programming of the experimental data. This quadratic model was of the form:

$$Y = A_0 + A_1X^\beta + A_{11}X^{2\beta} \tag{11}$$
$$Y = \log D = \log \text{ (apparent shear rate)}$$
$$\text{and} \quad X = \log \tau_w = \log \text{ (shear stress, corrected for end effects)}$$

The values of the constants A_0, A_1, A_{11}, and β are given in Table IV. The values of $\tau_w\dagger$, $D\dagger$, and $\sigma\dagger$ ($\dagger$ indicates inflection point quantities) obtained mathematically are also included in Table IV.

From these results the following conclusions may be drawn. *1*. The values of shear stress at the inflection point $\tau_w\dagger$ is independent of the measurement temperature (Fig. 10). Thus, the value of apparent shear rate at the inflection point $D\dagger$ is greater, the higher the temperature, while the values of shear stress $\tau_w\dagger$ are all at about the same level. *2*. The values of $D\dagger$ were found to be greater, the lower the concentration of the solution. It appears that the value of $D\dagger$ would reach a maximum value at a certain low concentration (1% in this study) and thereafter would remain approximately constant even upon further decrease in concentration.

TABLE IV

Variables and Parameters of Mathematical Model

Condition	τ_w†	D†	σ†	A_0	A_1	A_{11}	β
16.1%, 30°C.	192,300	5,365	2.821	1.151	3.22×10^{-6}	-7.19×10^{-13}	8.325
13%, 30°C.	158,692	14,193	2.577	1.246	5.63×10^{-5}	-1.97×10^{-10}	6.727
10%, 30°C.	94,190	14,700	2.375	1.792	3.43×10^{-5}	-8.83×10^{-11}	7.110
7.8%, 30°C.	67,450	23,740	1.987	1.771	9.75×10^{-4}	-6.33×10^{-8}	5.171
5%, 30°C.	—	—	—	1.506	0.0672	-0.0000848	2.548
3%, 30°C.	27,251	72,777	1.291	1.940	0.0802	-0.000338	2.554
2%, 30°C.	7,671	30,356	1.184	2.079	0.101	-0.000648	2.486
1%, 30°C.	6,926	62,257	1.058	2.146	0.245	-0.00307	1.898
10%, 45°C.	99,540	28,040	2.244	1.809	2.11×10^{-4}	-2.97×10^{-9}	6.022
10%, 30°C.	94,190	14,700	2.375	1.792	3.43×10^{-5}	-8.83×10^{-11}	7.110
10%, 15°C.	106,900	11,220	2.361	1.025	5.13×10^{-4}	-1.52×10^{-8}	5.534
7.8%, 30°C.	67,450	23,740	1.987	1.771	9.75×10^{-4}	-6.33×10^{-8}	5.171
7.8%, 1°C.	95,500	13,170	2.022	1.446	6.97×10^{-4}	-3.16×10^{-8}	5.297
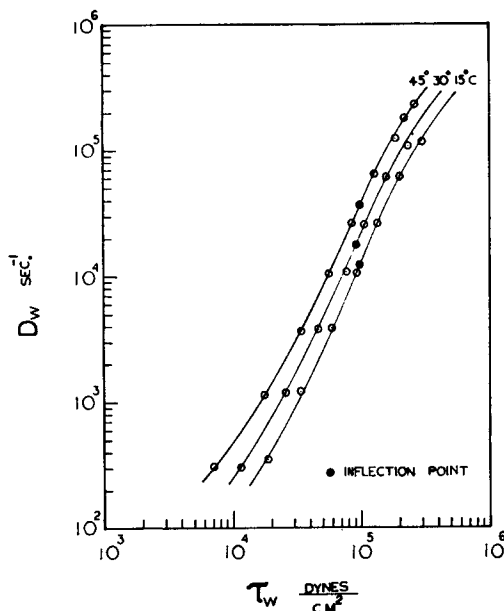
Fig. 10. Temperature dependence of the absolute flow curves of 10% copolymer solution.

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Synopsis

Flow behavior of ten copolymer solutions of polyacrylonitrile and polymethyl methacrylate in concentrations up to 16% was studied at 30°C. with the use of capillaries of constant diameter but different lengths. The shear rate and shear stress range covered were up to 200,000 sec.$^{-1}$ and 800,000 dynes/cm.^{2}, respectively. A rheological model of the form $\log D = A_0 + A_1 (\log \tau)^\beta + A_{11} (\log \tau)^{2\beta}$ was employed in determining the

inflection point of the flow curve by computer analysis.   A marked dependence of the flow curve upon the length-to-diameter ratio was observed when l/d ratio decreased to below 300.   At shear rates above 50,000 sec.$^{-1}$ the capillary "end effect" corrections and the kinetic energy corrections were found to be large for the concentrated and dilute solutions, respectively.   The flow curves were characterized in terms of the inflection point in accordance with the treatment of Schurz.   An upper Newtonian viscosity η^* was observed at shear rates above 150,000 sec.$^{-1}$.   Up to a concentration of about 1%, the value of the upper Newtonian viscosity was such that the calculated η_{sp}/C was essentially independent of C and equal to $[\eta^*]$ obtained by extrapolation to infinite dilution.   The values of the heat of activation for viscous flow were found to be dependent upon the applied shear stress.

Résumé

Le comportement à l'écoulement de dix solutions de copolymères de polyacrylonitrile et polyméthylenéthacrylate de concentrations variant jusqu'à 16% a été étudié à 30°C en utilisant des capillaires de diamètre constant mais de longueur variable.   La vitesse de cisaillement et le domaine de tension de cisaillement considéré allaient respectivement jusqu'à 200.000 sec^{-1} et 800.000 dynes/cm². Un modèle rhéologique de la forme log $D = A_0 + A_1 (\log \tau)^\beta + A_{11} (\log \tau)^{2\beta}$ a été employé pour déterminer le point d'inflexion de la courbe d'écoulement par analyse à la machine à calculer.   Une nette dépendance de la courbe d'écoulement vis-à-vis de la longueur du capillaire a été observée lorsque le rapport l/d tombe en-dessous de 300.   À des vitesse de cisaillement supérieures à 50.000 sec^{-1} on a trouvé que les corrections dues à l'effet terminal du capillaire et à l'énergie cinétique sont importantes respectivement pour les solutions concentrées et pour les solutions diluées.   Les courbes d'écoulement ont été caractérisées en termes de point d'inflexion en accord avec le traitement de Schurz.   À des vitesses de cisaillement supérieures à 150.000 sec^{-1}, une viscosité η^* supérieure à la viscosité newtonnienne a été observée. Jusqu'à une concentration d'environ 1%, la valeur de la viscosité sub-newtonnienne est semblable à celle calculée; η_{sp}/C est fondamentalement indépendante de C et égale à $[\eta^*]$ obtenu par extrapolation à dilution infinie.   On a trouvé que les valeurs de la chaleur d'activation pour un écoulement visqueux sont dépendantes des forces de cisaillement appliquées.

Zusammenfassung

Das Fliessverhalten von zehn Copolymerlösungen von Polyacrylnitril und Polymethylmethacrylat wurde bei Konzentrationen bis hinauf zu 16% und bei 30°C. unter Verwendung von Kapillaren konstanten Durchmessers aber verschiedener Länge untersucht.   Es wurde ein Schergeschwindigkeitsund Scherspannungsbereich bis zu 200000 sec.$^{-1}$ bzw. 800000 dyn/cm.² erfasst.   Eine rheologische Modellbeziehung der Form

$$\log D = A_0 + A_1 (\log \tau)^\beta + A_{11} (\log \tau)^{2\beta}$$

wurde zur Ermittlung des Wendepunkts der Fliesskurve durch Computeranalyse benützt.   Eine merkliche Abhängigkeit der Fliesskurve vom Verhältnis Länge zu Durchmesser ergab sich beim Absinken von l/d unterhalb 300.   Bei Schergeschwindigkeiten oberhalb 50000 sec.$^{-1}$ traten grosse Korrekturen für den kapillaren "Endeffekt" und die kinetische Energie bei konzentrierten bzw. verdünnten Lösungen auf.   Die Fliesskurven wurden in Übereinstimmung mit der Behandlung nach Schurz durch den Wendepunkt charakterisiert.   Eine obere Newtonsche Viskosität, η^*, wurde bei Schergeschwindigkeiten oberhalb 150000 sec.$^{-1}$ beobachtet.   Bis zu einer Konzentration von etwa 1% lag der Wert der oberen Newtonschen Viskosität derart, dass das berechnete η_{sp}/C im wesentlichen unabhängig von C und gleich dem durch Extrapolation auf unendliche Verdünnung erhaltenen $[\eta^*]$ war.   Die Werte der Aktivierungswärme des viskosen Fliessens zeigten eine Abhängigkeit von der angewendeten Scherspannung.