Capillary Viscometry of Molten Polycaprolactam

G. PEZZIN, *Sicedison Laboratory, Institute of Physical Chemistry of the University of Padua, Padua, Italy*, and G. B. GECHELE, *Sicedison Research Center, Bollate, Italy*

Synopsis

A study was made of the rheological behavior of 35 samples of nylon 6 polymers of molecular weights varying from 4,000 to 40,000. A capillary extrusion rheometer was employed, and flow curves extending over a large range of shear rates were obtained. The effect of temperature, shear rate, and molecular weight on viscosity is reported, and some peculiarities of the flow behavior of nylon 6 polymers are discussed.

INTRODUCTION

The rheological behavior of molten polycaprolactam (nylon 6) has been the subject of relatively few investigations.[1–5] Schaefgen and Flory[1] gave a description of the results obtained on measuring the melt viscosity of several nylon 6 polymers at 253°C. with a capillary glass apparatus. One-point viscosity measurements were carried out at unspecified shear rates. The results were described by the equation:

$$\log \eta = A + B(\bar{M}_w)^{0.5} \tag{1}$$

where η is the viscosity of a sample having a weight-average molecular weight $\bar{M}_w$, and A and B are experimental constants.

Fox et al. showed later[2] that a more adequate representation of the Schaefgen and Flory results can be obtained by using the single-constant equation:

$$\eta = K(\bar{M}_w)^{3.4} \tag{2}$$

which is known to have general validity above a critical molecular weight M_c.[2]

Few nylon 6 samples were studies with a falling-ball viscometer by other authors,[3] and a single sample was studied by Kepes[4] with a rotational cone-and-plate viscometer. Another publication deals with the problem of the effect of monomer and water on the viscosity of polycaprolactam.[5] Several flow curves of commercial polymers are collected in the Westover report.[6]

The present paper is intended as a description of the results that were obtained in the study of the rheological properties of molten nylon 6 with a capillary extrusion rheometer. The flow curves of 35 samples, having molecular weight of 4,000–40,000, were obtained at 230°C. in a range of shear rates from 1.7 sec.$^{-1}$ to a maximum of 15,000 sec.$^{-1}$

TABLE I
Characteristics of Nylon 6 Polymers

Sample	Acetic acid used in polymerization[a]	$\bar{M}_{am} \times 10^{-3}$	$\bar{M}_{ca} \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	η_r[b]	$[\eta]$, dl./g.[c]	H_2O, %
P10	—	39.0	46.0	42.50	5.26	—	<0.15
A11[d]	10^{-2}	3.5	3.5	3.50	1.37	—	"
B15	—	7.5	8.6	8.05	1.78	0.60	0.6
D18	—	20.0	19.0	19.50	—	1.28	0.3
B25[e]	10^{-3}	16.1	15.1	15.60	2.43	1.14	0.5
B41[f]	—	19.2	19.0	19.10	2.75	1.10	0.85
B50[g]	10^{-4}	17.6	18.0	17.80	—	1.10	0.8
B54	—	7.5	6.2	6.85	—	—	0.6
B57[h]	—	29.0	31.4	30.20	3.67	1.72	<0.15
D57	10^{-3}	12.2	12.2	12.20	2.12	—	"
D62	"	12.2	11.5	11.85	2.11	—	"
D66	"	15.6	13.7	14.65	2.21	—	"
D69	"	14.8	14.1	14.45	2.29	—	"
E205	"	17.5	17.7	17.60	2.66	—	"
E277C[h]	—	21.3	22.5	21.90	2.94	1.26	0.25
E278C[h]	—	18.8	19.9	19.35	2.80	1.14	<0.15
E279C[h]	—	15.4	18.8	17.10	2.55	—	"
E280B[h]	—	16.3	17.9	17.10	2.61	0.99	"
E280T[h]	—	18.8	21.2	20.00	2.73	1.27	"

Sample	Molar ratio[a]						
D300	5×10^{-3}	11.4	11.0	11.20	2.11	—	"
D301	"	11.1	10.2	10.65	2.06	—	"
D302	"	11.4	10.8	11.10	2.10	1.60	"
E402C[h]	10^{-3}	25.3	25.9	25.60	—	—	"
E410T[h]	—	21.9	22.1	22.00	3.36	—	"
E413T[h]	—	18.8	18.8	18.80	2.96	—	"
E414T[h]	—	21.4	23.2	22.30	3.17	—	"
E415T[h]	—	22.8	23.0	22.90	3.30	—	"
E415C[h]	—	22.4	23.0	22.70	3.22	—	"
E417H[h]	—	17.3	18.2	17.75	2.80	—	"
E418T[a]	—	17.5	16.2	16.85	2.75	—	"
E471T[b]	—	18.8	18.7	18.75	2.86	—	"
E505T[b]	—	25.0	22.7	23.85	3.41	—	"
D575C	3×10^{-3}	14.5	13.8	14.15	2.38	—	"
D579C	"	14.5	13.7	14.10	2.47	—	"
D582C	"	14.5	14.4	14.45	2.41	—	"

[a] Molar ratio acetic acid/monomer.
[b] Relative viscosity of 20°C., concentration 0.01 g./ml., in sulfuric acid.
[c] Intrinsic viscosity in formic acid at 25°C.
[d] Polymerized at 270°C. at low conversion.
[e] Polymerized at 275°C.
[f] Condensation stage of the polymerization at 180°C.
[g] Phosphoric acid as molecular weight control agent.
[h] Polymerization with the condensation stage at reduced pressure (approximately 300 mm. Hg)

EXPERIMENTAL

Polymers

The samples were prepared by hydrolytic polymerization.[7] The polymerizations were carried out under high purity nitrogen at 250°C. in a small stainless steel kettle.   In each run 2000 g. of ε-caprolactam (Sicedison S.p.A.) were mixed with water in the molar ratio 2:1.   Variable amounts of acetic acid were added as molecular weight control agent.   After the initial hydrolytic stage the water vapor was released from the reaction mixture and condensation was completed[7] at a given temperature (usually 250°C.) and pressure.   After condensation the polymer was extruded from the bottom of the kettle into cold water.   The equilibrium mixture obtained in this way is known to contain approximately 8% of residual monomer.[7,8]   Removal of the monomer was accomplished by repeated washing of the polymer with hot water.   In this way the hydrosoluble content HS in the samples was reduced to less than 0.8%.   The polymer was successively dried at 100°C. under reduced pressure.   The hydrosoluble content was determined by extracting the polymer in boiling water for 16 hr. in a Soxhlet apparatus.[9] The determination of the water content was made by the Fisher method on a solution of nylon 6 in a mixture of m-cresol and methanol.   The hydrosoluble content HS of the samples studied in this work was generally lower than 0.4% and the water content was lower than 0.15% except when otherwise indicated.

The number-average molecular weight $\bar{M}_n$ was determined by titration of the endgroups.   Carboxylic groups were titrated with phenolphthalein in a benzilic acid solution and amino groups were titrated with HCl by a conductometric method in a mixture of phenol, ethanol, and water.[10]   The correction for chain ends containing acetyl groups was accomplished, as suggested by Kline,[9] by hydrolysis of these groups with sulfuric acid, recovery of the acetic acid from the system by steaming, and final titration. Accuracy in the molecular weight determination varies from approximately 5% to 10% as molecular weight increases from 4,000 to 40,000.

The intrinsic viscosity [η] was determined in 85% formic acid at 25°C. with a capillary glass viscometer under such conditions that the kinetic energy correction was under 1%.   The relative viscosity η_r was determined in 95.6% sulfuric acid at 20°C. under the same conditions.   The polymer concentration was 0.01 g./ml.   The analytical data on the samples examined in this work are given in Table I.

Rheological Measurements

The rheological measurements were carried out with the Merz-Colwell capillary extrusion rheometer manufactured by Instron.[11]   With this instrument, filling the reservoir and heating the polymer to within 1°C. of the temperature of the rheometer takes about 4 min., after which time measurements can be made.   Flow curves extending over a three-decade range of shear rate can be obtained with nylon 6 polymers in 6–7 min., so that

degradation or post-polymerization can be minimized. However, in this work the molecular weight of the extruded samples was occasionally checked.

Viscosity is defined by:

$$\eta = \tau/\gamma \tag{3}$$

where τ is the shear stress and γ is the shear rate gradient, generally called shear rate. At the walls of a capillary having radius R and length L the shear stress is given by:

$$\tau_w = PR/2L \tag{4}$$

and the shear rate by

$$\gamma_w = 4Q/\pi R^3 \tag{5}$$

where P is the pressure drop along the capillary and Q is the volumetric flow rate. Equation (5) applies strictly only to Newtonian fluids and should be corrected for pseudoplastic fluids. In this case the ratio $\gamma_a = 4Q/\pi R^3$ can be thought of as a kind of volume-average shear rate, and it is often used in rheological work, together with the corresponding viscosity $\eta_a = \tau_w/\gamma_a$.[12,13] It has been demonstrated that the η_a/γ_a curves do not differ substantially from the correct η/γ curves.[12]

Equation (4) applies only if entrance effects are irrelevant. It will be demonstrated later that in this work they can be considered sufficiently low. The pressure drop along the reservoir of the rheometer is negligible,[13] and the total pressure measured on the piston which forces the polymer through the capillary can be inserted in eq. (4), in which case eq. (6) is obtained.

$$\tau_w = FD/\pi L d^2 \tag{6}$$

In this equation $D = 2R$ is the capillary diameter, d the reservoir diameter, and F the force needed to extrude the polymer. Equation (5) can be written for pseudoplastic fluids:

$$\gamma_a = 2Vd^2/15D^3 \tag{7}$$

where V is the piston speed and γ_a the apparent shear rate. The correction for the expansion of the melt in the capillary is usually low.[11] Equations (6) and (7) were used in this work, viscosity being $\eta_a = \tau_w/\gamma_a$. The characteristics of the capillaries used in this work are shown in Table II.

TABLE II
Description of Capillaries

Capillary number	Length, cm.	Diameter, cm.	Entrance angle	L/D
1	15.27	0.1516	90°	100.7
2	10.17	0.1520	"	67.0
3	5.08	0.1510	"	33.7
4	5.04	0.0742	"	68.0
5	10.09	0.0744	"	135.6

It may be noted that most of them have L/D ratios greater than 67, i.e., L/R ratios greater than 134.

RESULTS

Rheological Data

The accuracy with which the flow curves can be reproduced can be seen from the results plotted in Figure 1 and from Table III. A single capillary was used and repeated data were taken on three different samples. The shear rate range extends from 1.7 to 1700 sec.$^{-1}$, and it can be seen that within this range an accuracy of the order of $\pm 5\%$ can be obtained at fixed shear rate in the measurements of the shear stress.
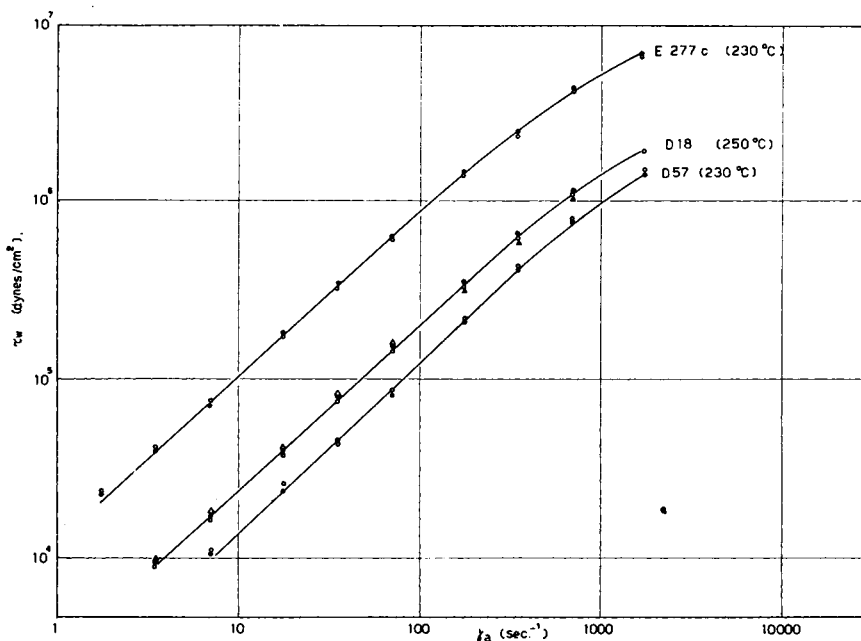
Fig. 1. Reproducibility of rheological data obtained with the extrusion rheometer. Shear stress–shear rate curves obtained with capillary 1 for samples D18 and D57 and with capillary 2 for sample E277C.

In order to avoid errors due to entrance effects or to other unknown causes it is necessary to compare the rheological data obtained with capillaries having different L/D ratios. Most of the samples studied in this work were extruded through different capillaries. The results are plotted in Figures 2 and 3 in the usual way, that is, as log τ_w versus log γ_a. It can be seen that also when several capillaries are used the accuracy in the measurements is such that the shear stress, at a given shear rate, varies in a range of the order of $\pm 5\%$. In Figures 2 and 3 the range of shear rate explored extends from 1.7 to 15,000 sec.$^{-1}$ for several samples. The corresponding

viscosity–shear rate curves plotted logarithmically for few samples are shown in Figure 4.   From these curves one may obtain the viscosity at any shear rate (within the above-mentioned range) by graphical interpolation. By this procedure the data of Table IV were obtained.   The viscosities of all the samples, at shear rates of 3, 10, 30, 100, 300, 1000, and 3000 sec.$^{-1}$ are collected together, so that any flow curve can be drawn by using these data.

TABLE III
Reproducibility of the Rheological Data (See Figure 1)

Shear rate(sec.$^{-1}$)	Shear stress at various shear rates, dyne/cm.^{2} $\times$ 10^{-3}							
	3.48 sec.$^{-1}$	6.95 sec.$^{-1}$	17.4 sec.$^{-1}$	34.8 sec.$^{-1}$	69.5 sec.$^{-1}$	174 sec.$^{-1}$	348 sec.$^{-1}$	695 sec.$^{-1}$
Sample D18[a]	9.6	17.5	40.0	79.5	154	348	643	1130
	9.9	18.5	41.4	82.5	155	307	575	1010
	9.3	16.4	37.5	76.0	145.	330	630	1120
Sample D57[b]	. . .	10.9	26.2	43.5	85.5	213	417	760
	. . .	10.9	23.5	44.2	81.5	205	397	740
Sample E277C[c]	41.4	74.5	175	325	620	1380	2260	4130
	40.0	73.0	177	340	607	1420	2450	4270

[a] Capillary no. 1, temperature 250°C.
[b] Capillary no. 1, temperature 230°C.
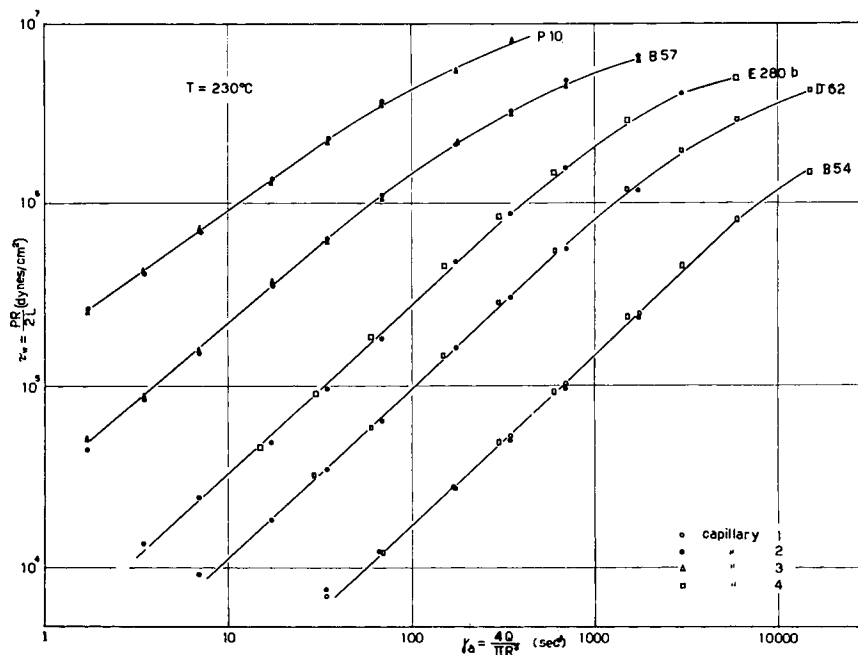[c] Capillary no. 2, temperature 230°C.

Fig. 2. Accuracy of rheological data.   Shear stress–shear rate curves obtained with different capillaries.
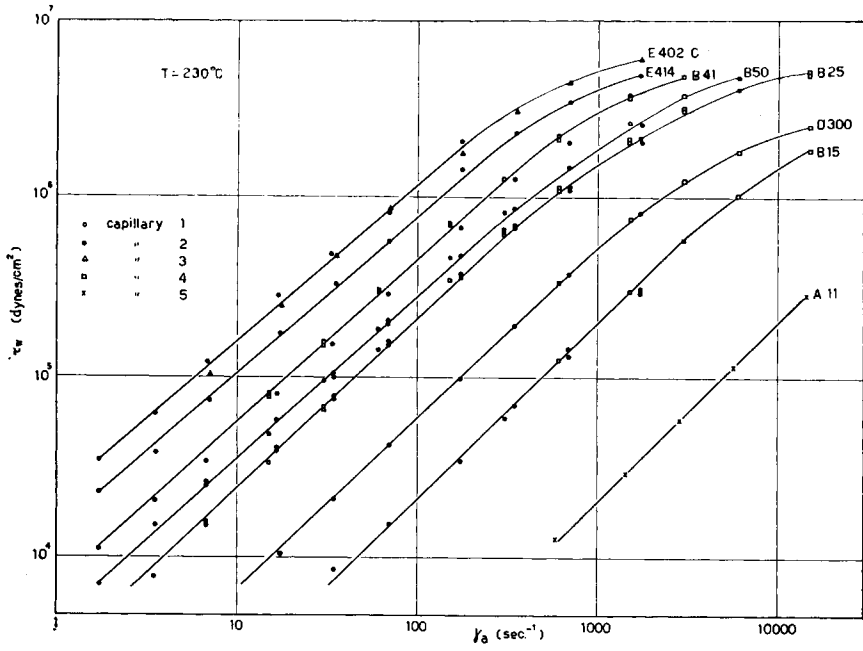
Fig. 3. Shear stress–shear rate curves obtained with different capillaries.
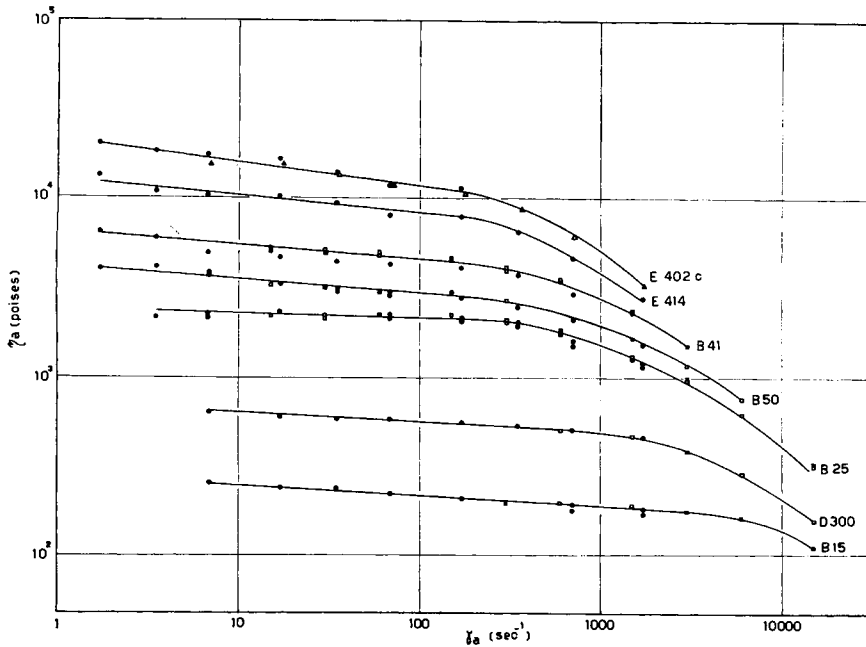

Fig. 4. Viscosity–shear rate curves obtained from data of Fig. 3.

The flow index $n = d \log \tau_w / d \log \gamma_a$, which is also given in Table IV, was calculated in the shear rate range of 2–200 sec.$^{-1}$ for 25 samples and in the range 10–1000 sec.$^{-1}$ for 10 samples.   The temperature coefficient of the viscous flow was determined for few samples in the temperature range of
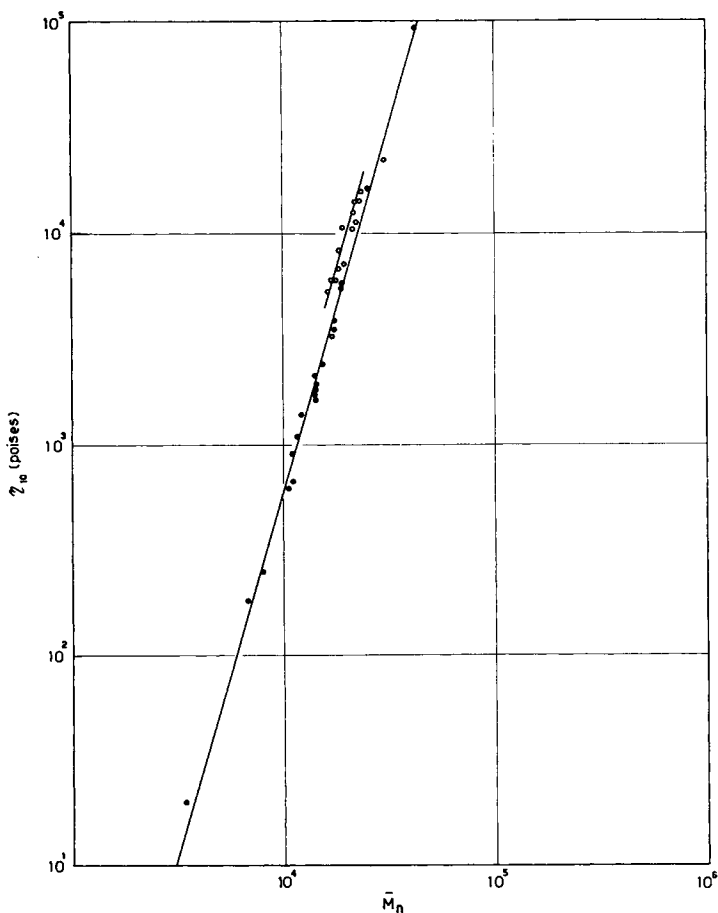

Fig. 5. Viscosity at 10 sec.$^{-1}$ shear rate plotted vs. number-average molecular weight $\bar{M}_n$.   (O) samples polymerized under reduced pressure.   Melt viscosity was measured at 230°C.

230–250°C.   The energy of activation E, defined by $\eta = k \exp \{E/RT\}$, was determined at a shear rate of 10 sec.$^{-1}$; it was found that $E_{10} = 9\text{–}13$ kcal./mole, independent of the molecular weight of the sample.

Melt Viscosity and Molecular Weight

From the carboxylic number-average molecular weight $\bar{M}_{ca}$ determined by titration of the carboxylic endgroups, and from the correspondent

TABLE IV
Summary of Rheological Data: Polymer Viscosity at Various Shear Rates at 230°C. Obtained from Experimental Curves of the Type Shown in Figure 4

Sample	Viscosity η at various shear rates, poises $\times 10^{-3}$							Flow index n^a
	3 sec.⁻¹	10 sec.⁻¹	30 sec.⁻¹	100 sec.⁻¹	300 sec.⁻¹	1000 sec.⁻¹	3000 sec.⁻¹	
P10	130	93.0	67.0	41.0	23.0	—	—	0.70
B57	26.0	22.0	19.0	14.5	9.7	5.1	—	0.83
E402C	18.6	16.0	13.6	11.4	8.6	4.9	—	0.85
E505T	17.0	15.5	13.8	11.7	8.7	4.8	—	0.88
E415T	15.2	14.0	12.5	10.7	9.0	4.5	—	0.88
E414C	15.2	14.0	13.3	10.5	8.5	4.2	—	0.90
E414T	12.5	10.9	9.8	8.8	6.5	4.3	—	0.87
E410T	13.7	12.5	11.3	10.0	7.6	4.4	—	0.91
E277C	11.4	10.3	9.5	8.6	7.2	5.1	—	0.91
E280T	7.8	7.2	6.4	5.9	5.0	3.5	1.9	0.92
E278C	11.7	10.4	9.0	7.8	6.8	4.2	—	0.90
D18	5.9	5.7	5.3	4.8	4.2	2.9	—	0.94
B41	6.2	5.5	4.9	4.5	3.9	2.7	1.6	0.91
E415T	8.5	7.8	6.9	6.2	5.0	2.3	—	0.91
E471T	7.8	6.9	6.4	5.7	4.6	3.0	—	0.91
E417T	6.7	6.0	5.7	5.2	4.2	2.9	—	0.91
B50	3.9	3.5	3.2	2.8	2.5	1.8	1.1	0.91
E205	4.1	3.9	3.5	3.3	2.7	1.9	—	0.90

Sample								Flow index n[a]
E280B	3.7	3.3	3.0	2.7	2.6	2.1	1.3	0.92
E418T	5.8	5.3	5.0	4.7	3.7	2.4	—	0.92
E279C	6.7	6.0	5.4	4.8	4.4	3.2	0.95	0.92
B25	2.6	2.4	2.3	2.1	2.0	1.5	—	0.94
D66	1.7	1.6	1.5	1.45	1.35	1.10	—	0.92
D582C	2.0	1.9	1.7	1.6	1.45	1.24	—	0.95
D69	1.9	1.8	1.7	1.65	1.6	1.25	—	0.93
D579C	—	2.1	1.9	1.65	1.4	1.10	—	0.92[b]
D575C	—	1.75	1.55	1.4	1.25	1.05	—	0.92
D57	—	1.40	1.30	1.25	1.17	0.98	—	0.96
D62	—	1.10	1.03	0.96	0.93	0.83	0.62	0.94
D300	—	0.66	0.62	0.59	0.55	0.52	0.40	0.95
D302	—	0.90	0.82	0.76	0.69	0.59	—	0.94
D301	—	0.62	0.55	0.50	0.46	0.44	—	0.95
B15	—	0.25	0.22	0.21	0.20	0.20	0.18	0.98
B54	—	0.18	0.18	0.17	0.16	0.15	0.15	0.97
A11	—	—	—	—	—	0.020	0.020	1.00

[a] Flow index $n = d \log \tau_w / d \log \gamma_a$ calculated in the range of shear rate of 2–200 sec.$^{-1}$.

[b] From sample D579C to sample A11 the flow index was calculated in the range of shear rate of 10–1000 sec.$^{-1}$.

amino molecular weight $\bar{M}_{am}$, an average value of the molecular weight was obtained by the relation:

$$\bar{M}_n = (\bar{M}_{ca} + \bar{M}_{am})/2 \qquad (8)$$

When the viscosity of the molten polymers at a shear rate of 10 sec.$^{-1}$ and at 230°C., is plotted against the molecular weight $\bar{M}_n$ on a log-log basis, the results of Figure 5 are obtained. A straight line, described by the equation:

$$\eta_{10} = 1.5 \times 10^{-11}(\bar{M}_n)^{3.4} \qquad (9)$$

where η_{10} is given in poises, represents quite well most of the experimental results. The samples for which the condensation stage during the polymerization was carried out under reduced pressure appear to deviate slightly from eq. (9), having higher viscosity than the other nylon 6 samples at a given $\bar{M}_n$ value.

When the melt viscosity η_{10} is plotted on log-log paper versus the relative viscosity η_r, measured in solution, a straight line is obtained, described by

$$\eta_{10} = 7.0 \ (\eta_r)^{6.4} \qquad (10)$$

which is valid in the range of molecular weight of 6,000–30,000. It can be
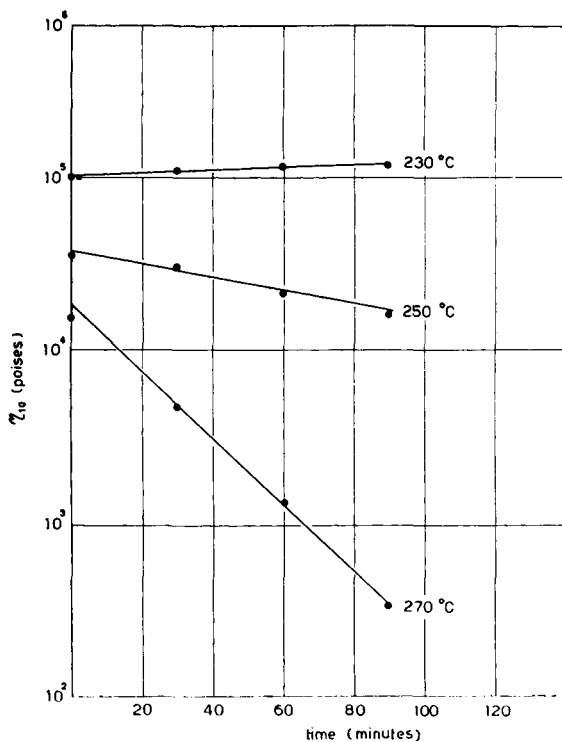

Fig. 6. Viscosity at 10 sec.$^{-1}$ shear rate of sample P10 plotted vs. time of heating at 230, 250, and 270°C. Degradation rate increases rapidly with temperature.

seen that a 5% variation in the solution viscosity gives a 30% variation in the melt viscosity.

High Temperature Stability of Nylon 6

The viscosity of the molten samples can be measured with the Instron rheometer for a long period of time and its variations can be easily recorded. It is known that the molecular weight of molten nylon 6 can change rapidly due to chemical reactions among polymer and monomer molecules in presence of small quantities of water.[8] The water content of the polymer must be low in order to avoid degradation during processing[14] or the rheometric measurements.[5] The effect of temperature on the time-dependence of viscosity is shown for sample P10 in Figure 6. Measurements were performed at 230, 250, and 270°C. Molecular weight and hydrosoluble content were determined on the samples extruded at 270°C., as can be seen in Table V. The viscosity increases slowly at 230°C., but it decreases rapidly at 250 and 270°C. A parallel decrease of molecular weight is also apparent, as can be seen in Table V for the 270°C. data. The time dependence of viscosity varies from sample to sample at constant temperature. For example, sample E402C has a viscosity that increases 0.6%/min. at 230°C., whereas the viscosity of sample D57 decreases 0.5%/min. under
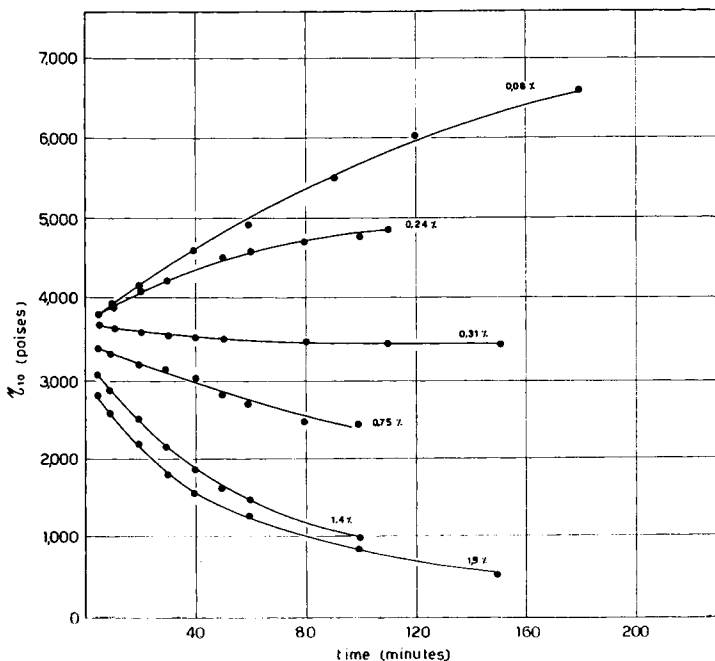

Fig. 7. Effect of the water content on the heat stability of polymer E205. Viscosity at 10 sec.$^{-1}$ shear rate plotted vs. time of heating at 230°C. for samples having different percentages of water content. See Table V for analytical data.

the same conditions.   The direction and the magnitude of such changes seem to be functions of the molecular weight and of the water content of the polymer.   The effect of water was studied in detail on several polymers. The results for sample E205 at 230°C. are reported in Figure 7.   The water content of the samples, determined immediately before the rheological measurements, varied from 0.08 to 1.9%.   At the lowest water content the viscosity increases rapidly with time, while at a water content of the order of 0.3% the viscosity does not change for as long as 150 min.   At larger percentages of water the melt viscosity decreases rapidly.   These changes are paralleled by changes of the molecular weight, as seen in Table VI.   The sample having 0.08% water content shows after 6 hr. a 95% increase in melt viscosity and a 40% increase in molecular weight.   The melt viscosity of the sample having 1.4% water content is reduced, after 5 hr., 7.5 times and the molecular weight 1.25 times the initial values.   In both cases the hydrosoluble content increases.

TABLE V

Decrease of Molecular Weight and Viscosity of Sample P10 after Heating at 270°C.
(See Figure 6)

Heating time, min.	$\bar{M}_{ca}$	$\bar{M}_{am}$	η_{10}, poises	Hydrosoluble content, %
0	46,000	39,000	18,000	0.30
30	23,400	24,800	4,700	1.60
60	—	—	1,300	—
90	15,200	14,400	350	1.15

TABLE VI

Changes of Molecular Weight and Viscosity of Sample E205 after Heating at 230°C.
(See Figure 7)

Heating time, min.	Initial water content, %	$\bar{M}_{ca}$	$\bar{M}_{am}$	η_{10}, poises	Hydrosoluble content, %
0	0.08	17,600	17,500	3900	0.4
360	0.08	22,300	27,400	7600	3.0
300	1.4	13,600	14,400	530	3.2

Flow Curves

From figures 2 and 3 and from Table IV it is seen that at shear stresses less than 10^6 dynes/cm.^{2} the flow index varies in the range 0.80–1.00, increasing as the molecular weight of the samples decreases.   Only when the shear stress τ_w is larger than 10^6 dynes/cm.^{2} does the flow index decrease below 0.80.

It is well known that broadening of the molecular weight distribution has a strong effect on the flow index both for polystyrene[15] and for polyethylene.[16]   In this work several attempts were made to see whether nylon 6
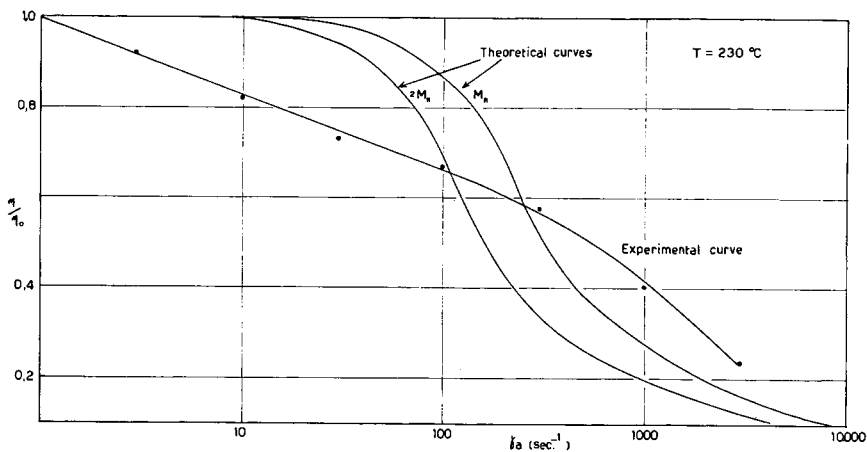
Fig. 8. Comparison between the experimental viscosity–shear rate curve of sample B41 at 230°C. and the theoretical master curve of Bueche.[17]   Two theoretical curves are reported, calculated respectively by assuming for the molecular weight of the sample the value of the number-average molecular weight $\bar{M}_n$ and a value of $2\bar{M}_n$. The zero shear viscosity η_0 was assumed to be 6700 poises.

samples of broad molecular weight distribution show similar behavior. Different mixtures of polymers having very different molecular weight (e.g., samples B54 and D18 or samples D57 and P10) were prepared by carefully mixing thin flakes of the original polymers.   The molecular weight distribution of these mixtures should be very broad compared with that of the unmixed polymers.   The viscosity measurements were done rapidly so that equilibrium reactions in the mixtures were probably avoided. The flow curves of these mixture, however, invariably showed a flow index of the order of 0.80–0.95, so that it can be said that there is no appreciable effect of the molecular weight distribution on the rheological behavior of nylon 6, at least in the range of molecular weight explored in this work.

Another peculiarity of the flow curves of polycaprolactam is their general shape.   According to Bueche,[17] the flow curves of linear thermoplastic materials can be described by a universal master curve, provided the molecular weight and the zero shear (Newtonian) viscosity of the polymer are known. A theoretical treatment which gives a similar master curve was developed by Rouse.[18]   The master curve given by Bueche was applied to polystyrene[13] and to polyethylene[19] with good approximation.   Attempts were made in this work to apply it to nylon 6.   The results for sample B41 at 230°C. are plotted semilogarithmically in Figure 8.   The experimental flow curve is compared with the theoretical curves of Bueche calculated at two different conditions.   In the first theoretical curve the value of the number-average molecular weight $\bar{M}_n$ of the sample was used, whereas in the second curve a value of two times $\bar{M}_n$ was employed.   In both cases the zero shear viscosity of the sample is taken as being $\eta_0 = 6700$ poises, from an approximate extrapolation of the $\eta_a/\log \gamma_a$ curve.

It is seen from Figure 8 that large discrepancies exist between the experimental curve and both the theoretical curves. They cannot be attributed to errors involved in the extrapolation of the zero shear viscosity used because the results do not change by varying η_0 in a large interval. The discrepancies cannot be attributed to the molecular weight distribution, as it was previously noted that this does not influence strongly the shape of the flow curves, nor to the molecular weight assumed in the calculations, as this was varied over a wide range. Therefore it may reasonably be concluded that the flow behavior of nylon 6 cannot be described well by the theoretical master curve of Bueche.

DISCUSSION

It has been shown that sufficiently accurate flow curves, extending over several decades of shear rate, can be obtained on molten nylon 6 in a short time with the above-mentioned capillary extrusion rheometer. By using capillaries with a large L/D ratio (see Table II) flow curves are obtained which are independent of the capillary dimensions with sufficient accuracy, entrance effects and other kind of errors being minimized under these conditions. The energy of activation for viscous flow, at 10 sec.$^{-1}$ shear rate, was found to be of the order of 9–13 kcal./mole, independent of molecular weight. Other authors[3] give a lower value (6–9 kcal./mole) which is claimed to depend on temperature and molecular weight, whereas in two different papers[4,5] values as high as 15–17 kcal./mole are reported.

The effect of molecular weight on melt viscosity [Fig. 5 and eq. (9)] is such that the viscosity is proportional to the molecular weight to the 3.4 power. In viscosity equations usually the proper molecular weight to use is the weight-average molecular weight $\bar{M}_w$ and the proper viscosity is the zero shear viscosity η_0. In the plot of Figure 5 the number-average molecular weight $\bar{M}_n$ and the 10 sec.$^{-1}$ shear rate viscosity were used. It is seen that the polymers for which the condensation stage during the polymerization has been conducted under reduced pressure show differences in the $\eta_{10}/\bar{M}_n$ curve. Their melt viscosities are approximately 35% higher than those of the other polymers having the same $\bar{M}_n$. The effect of branching on melt viscosity seems to be too low to be responsible for these differences,[1] and it can be tentatively supposed that they are due to different molecular weight distributions in the samples. In fact it is easily demonstrated from the results of Schaefgen and Flory[1] that two series of linear nylon 6 polymers having different molecular weight distributions ($\bar{M}_w/\bar{M}_n \cong 1.97$ for the first monochain series and $\bar{M}_w/\bar{M}_n \cong 1.52$ for the second dichain series) give a single $\eta/\bar{M}_w$ equation, but two different curves when η is plotted versus $\bar{M}_n$. The results of Figure 5 could be explained by assuming that the low pressure polymers have a broader molecular weight distribution than the other samples. Work is in progress to confirm this point.

Several studies of the shear dependence of the viscosity/molecular weight function for molten polymers indicate that the exponent of the η/M equation, which is usually close to 3.4 for zero shear viscosity, decreases very

rapidly with increasing shear rate.[20,21] The results obtained in this work indicate that for nylon 6 the decrease of the exponent is very slow. At a shear rate of 10 sec.$^{-1}$ the exponent is still 3.4 (see Fig. 5), and it can be demonstrated from the data of Table IV that at a shear rate of 10^3 sec.$^{-1}$ the exponent of the η/M curve is of the order of 2.8. For comparison it will be remembered that for polystyrene at $\gamma = 10^2$ sec.$^{-1}$ the exponent is approximately 1 and for polyethylene at $\gamma = 10^3$ sec.$^{-1}$ it is less than 1.[20]

It can be concluded that as far as the viscosity/molecular weight function is concerned, the flow behavior of nylon 6 differs substantially from that of the above mentioned polymers. The rate at which the melt viscosity of nylon 6 changes at high temperature is such that the fractional decrease, or increase, in viscosity is an exponential function of time (see Fig. 6), as is known to occur also for other polymers.[22] The effect of water on the process is particularly important (see Fig. 7). When the water content is high, the decrease in melt viscosity can be attributed to hydrolysis reactions[23] and to equilibrium depolymerization, while at low water content the increase in viscosity can be due to post-condensation and to other reactions[23] which increase the molecular weight of the polymer. The changes in melt viscosity are invariably accompanied by similar changes in the molecular weight and always by an increase of the monomer content (see Tables V and VI). The viscosities of the degraded samples are lower than the values calculated from their molecular weights by means of eq. (9) due to the effect of this monomer and possibly to the effect of chemical reactions in which the aminic and carboxylic endgroups disappear and branched molecules are formed.[23]

It was previously noted that at moderately high shear stresses (τ_w less than 10^6 dynes/cm.^{2}) the flow index n for the samples studied in this work is generally larger than 0.80, which means that there is only a relatively slight deviation from Newtonian flow. The above-mentioned particular behavior of the η/M function, the exponent of which remains close to 3.4 also at high shear, is clearly due to the fact that the value of n is relatively constant and close to unity up to high shear. The insensitivity of the flow index n to a broadening of the molecular weight distribution of the polymers may have the same origin.

The peculiarity of the flow curves of nylon 6 was also seen from the comparison with the theoretical master curve predicted by Bueche for molten polymers. The nylon 6 polymers show a small deviation from Newtonian flow at lower shear rates than is predicted by the theory. However at high shears the flow is more newtonian than predicted by the Bueche theory. It is known that the requirement for non-Newtonian flow are orientation of the molecules and chain disentanglement due to a shear field. From the broad pattern of the flow behavior established in this work for nylon 6 polymers it seems reasonable to suppose that the molecular mechanism which has been postulated for the theoretical interpretation of the non-Newtonian flow of polymer melts may be perhaps inadequate to explain the peculiarity of the rheological properties of molten polycaprolactam.

References

1. Schaefgen, J. R., and P. J. Flory, *J. Am. Chem. Soc.*, **70**, 2709 (1948).

2. Fox, T. G, S. Gratch, and S. Loshaek, *Rheology*, Vol. 1, F. R. Eirich, Ed., Academic Press, New York, 1956.

3. Kokhomskaya, T. N., and A. B. Pakshver, *Kolloid. Zh.*, **18**, 188 (1956).

4. A. Kepes, Thesis, University of Strasbourg, 1958.

5. Mukouyama, E., and A. Takegawa, *Kobunshi Kagaku* **13**, 323 (1956).

6. Westover, R. F., *Processing of Thermoplastic Materials*, E. C. Bernhardt, Ed., Reinhold, New York, 1959.

7. Hanford, W. E., and R. M. Joyce, *J. Polymer Sci.*, **3**, 168 (1948).

8. Canthon, T. M., and E. C. Smith, paper presented at 138th American Chemical Society Meeting, New York, Sept. 1960.

9. Kline, G. M., *Analytical Chemistry of Polymers*, Part 1, Interscience, New York, 1959.

10. Waltz, J. E., and B. G. Taylor, *Anal. Chem.*, **19**, 448 (1947).

11. Merz, E. H., and R. E. Colwell, *ASTM Bull.*, **No. 232**, 63 (1958); R. L. Ballman and J. J. Brown, Instron Application Series SA-2.

12. Cox, W. P., and E. H. Merz, *ASTM Special Techn. Publication*, **No. 247**, American Society of Testing Materials, Philadelphia, 1958.

13. Pezzin, G., *Materie Plastiche*, **28**, 1042 (1962).

14. Kessler, J. F., paper presented at International Congress on Plastics Processing, Amsterdam, October 1960.

15. Rudd, J. F., *J. Polymer Sci.*, **44**, 459 (1960).

16. Tung, L. H., *J. Polymer Sci.*, **46**, 409 (1960).

17. Bueche, F., *J. Chem. Phys.*, **22**, 1570 (1954).

18. Rouse, P. E., *J. Chem. Phys.*, **21**, 1272 (1953).

19. McKelvey, J. M., *Polymer Processing*, Wiley, New York, 1962.

20. Schreiber, H. P., E. B. Bagley, and D. C. West, *Polymer*, **4**, 355 (1963).

21. Bagley, E. B., *J. Appl. Phys.*, **30**, 597 (1959).

22. Schott, H., and W. S. Kaghan, *SPE Trans.*, **3**, 145 (1963).

23. Kamerbeek, B., G. H. Kroes, and W. Grollo, *Thermal Degradation of Polymers*, Soc. Chem. Ind. Monograph No. 13, Society of Chemical Industry, London, 1961.

Résumé

On a effectué une étude sur le comportement rhéologique de 35 échantillons de nylon-6 possédant des poids moléculaires variant de 4000 à 40000. On a employé un rhéomètre d'extrusion capillaire, et on a obtenu des courbes d'écoulement couvrant une large gamme de vitesses de cisaillement. On a décrit l'effet de la température, de la vitesse de cisaillement et du poids moléculaire sur la viscosité, et certaines particularités du comportement de l'écoulement des polymères nylon-6 sont discutées.

Zusammenfassung

Das rheologische Verhalten von 35 Nylon-6-polymerproben mit einem Molekulargewicht von 4000 bis 40000 wurde untersucht. Ein Kapillarextrusionsrheometer wurde verwendet und Fliesskurven über einen grossen Bereich der Schubgeschwindigkeit erhalten. Über den Einfluss von Temperatur, Schubgeschwindigkeit und Molekulargewicht auf die Viskosität wirde berichtet und die Besonderheiten des Fliessverhaltens von Nylon-6-polymeren werden diskutiert.