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Effect of Polydispersity on the Shear Rate Dependence of the Intrinsic Viscosity of Flexible Linear Polymers

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ABSTRACT: A multiple-bulb viscometer has been developed enabling the measurement of the specific viscosity of dilute polymer solutions over a shear rate range from 4.8 s^{-1} to nearly 4000 s^{-1}. The shear rate dependence of the intrinsic viscosity has been determined of three polyethylene samples with a polydispersity of the molecular weight of about 2 and of five polyethylene samples with polydispersities between 5 and 7. In the Newtonian range at low shear rates the intrinsic viscosity of these samples varies from 31.8 to 5.2 dL/g. The degree of non-Newtonian behavior increases with molecular weight as well as with polydispersity. A method of analyzing the data is derived which describes these effects for polymers with logarithmic normal molecular weight distributions. Apart from the constants a and K of the Mark–Houwink relation, an additional parameter comes in, viz. in the relation between the shear-thinning relaxation time and the molecular weight M of monodisperse polymers. It appears that for polyethylenes in a good solvent this time is proportional to $M^{a+0.3}$, whereas for polystyrene in a Θ solvent literature data on this time seem to be proportional to M^{a+1}.

Introduction

Polymers with ultrahigh molecular weight, like polystyrene (UHMWPS) and polyethylene (UHMWPE), have attracted strongly increasing clinical and industrial interest in the past decade. The need for a reliable characterization of average molecular weights and molecular weight distributions for specification and control of these materials has grown simultaneously, but the conventional measuring techniques meet with special problems which ask for additional research. Even the complete dissolution of these polymers and the handling of the solutions obtained set some strict restraints on the allowable temperature ranges, stirring rates, dissolution times, and thermal or oxidative stabilization packages. In size exclusion chromatography, solutions with exceptionally low concentrations should be used, and special care should be taken to prevent crystallization and mechanical degradation of the polymer molecules in columns and frits. In viscometry, the intrinsic viscosities are found to be shear rate dependent, so that reproducible methods should be applied to measure or to extrapolate the viscosity at zero shear rate. Besides, problems arise in establishing the constants of the Mark–Houwink relation in the ultrahigh molecular weight range. In all these fields of characterization the distinct polydispersity in molecular weight of these materials gives rise to additional problems.

In this paper we investigate just one of the abovementioned questions, viz. the effect of shear rate on the intrinsic viscosity $[\eta]$, especially for polydisperse UHMWPE. Apparently, this is such a complex phenomenon that there is still no agreement on the systematics of the effect of parameters like molecular weight and kind of solvent, no more than on a complete theoretical treatment of all factors affecting the non-Newtonian viscosity of dilute solutions of flexible polymers. It is obvious to use monodisperse polymers as reference materials for the investigation of the effect of polydispersity, as is described for polystyrene, polybutadiene, or poly(methyl methacrylate), but for polyethylene this procedure is not applicable because monodisperse samples are not available. Therefore, for this polymer the only possible way to record the effects of polydispersity on the shear rate dependence of the intrinsic viscosity is to investigate samples with well-determined, different polydispersities. It is our aim to bring forward new experimental results and to analyze these in a semiempirical way, trying to describe the effects of molecular weight and molecular weight distribution on the shear rate dependence of $[\eta]$ by means of an analytical expression. A complete molecular theoretical interpretation of the results obtained is not achieved, and some presuppositions appear to be unavoidable.

Theory

Shear Rate Dependence for Monodisperse Polymers. The molecular theories of the viscoelastic behavior of very dilute solutions of flexible, nonionic polymers have been reviewed in various books (see, e.g., chapter 9 of ref 1, chapter 4 of ref 2, or chapter 8 of ref 3). In these models the frequency dependence of the intrinsic viscosity $[\eta]$ of a linear polymer molecule with molecular weight M in a solvent with viscosity η_s at a temperature T, expressed as the quotient of the intrinsic dynamic loss shear modulus $[G'']$ and the angular frequency ω, is given by

$$[\eta] = \frac{RT}{M\eta_s}\sum_{p=1}^{N}\frac{\tau_p}{1 + \omega^2\tau_p^2} \tag{1}$$

where R is the universal gas constant and N the number of statistical chain segments per molecule. The relaxation times τ_p at short τ, i.e., at large values of p, are much more closely distributed than at small p values. The longest relaxation time τ_1 can be obtained from the limit of $[\eta]$ if $\omega \rightarrow 0$

$$[\eta]_0 = \frac{RT}{M\eta_s}\sum\tau_p = \frac{RT}{M\eta_s}S_1\tau_1 = \frac{RT}{M\eta_s}\tau \tag{2}$$

where S_1 equals 2 ± 0.4, depending on the degree of hydrodynamic interaction (HI) and the quality of the solvent. The characteristic relaxation time τ of the molecule in the considered very dilute solution is defined in terms of macroscopic quantities by

$$\tau = M[\eta]_0\eta_s/(RT) \tag{3}$$

The frequency dependence of the intrinsic viscosity can also be represented by

$$\frac{[\eta]}{[\eta]_0} = \frac{\sum\frac{\tau_p}{1 + \omega^2\tau_p^2}}{\sum\tau_p} = 1 - \frac{1}{\sum\tau_p}\sum\frac{\omega^2\tau_p^3}{1 + \omega^2\tau_p^2} \tag{4}$$

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showing that at very small ω the approximation

$$\frac{[\eta]}{[\eta]_0} = 1 - \omega^2 \frac{\sum \tau_p^{\,3}}{\sum \tau_p} \simeq 1 - \frac{1}{S_1}\omega^2 \tau_1^{\,2} = 1 - \frac{1}{S_1^{\,3}}\omega^2\tau^2 \qquad (5)$$

holds because $\sum \tau_p^3 \simeq \tau_1^3$.

According to the same theories and in line with experimental data,[1-4] at high frequencies $[\eta]$ appears to decrease proportionally to $(\omega\tau)^{-n}$, where under the Doi–Edwards approach $n = {}^1/_2$ for Θ solvents without HI, $n = {}^1/_3$ for Θ solvents with dominant HI, and $n = {}^4/_9$ for good solvents with dominant HI (p 115 of ref 2). The total frequency dependence of $[\eta]$ can be approached by

$$\frac{[\eta]}{[\eta]_0} = \frac{1}{\left\{1 + \frac{2}{S_1^{\,3} n}\omega^2\tau^2\right\}^{n/2}} \qquad (6)$$

If $\omega \rightarrow 0$, the intrinsic viscosity becomes $[\eta]_0$, at low ω eq 5 follows from eq 6, and at very high ω it holds that $[\eta] = [\eta]_0(n/2)^{n/2}S_1^{\,3n/2}\omega^{-n}\tau^{-n}$.

In agreement with much experimental evidence (see, e.g., refs 5–7) we follow Fujita[8] by assuming that for monodisperse polymers the Mark–Houwink relation is valid over very broad ranges of the molecular weight, even up to the ultrahigh molecular weight part. This means that

$$[\eta]_0 = KM^a \qquad (7)$$

where a is related to n through $a = n/(1-n)$. For Θ solvents with dominant HI $a = 0.5$, for good solvents with dominant HI $a = 0.8$, and for Θ solvents without HI $a = 1.0$ is expected. This last value is unrealistic, because the maximum value of a attainable theoretically is 0.77.[8] For polyethylene in decalin at 135 °C we find that $a = 0.725$,[9] leading to $n = 0.42$, and hence decalin is called a good solvent for PE. By use of eq 7 the characteristic relaxation time of eq 3 can be written as

$$\tau = KM^{a+1}\eta_s/RT \qquad (8)$$

Many viscoelastic fluids show a similarity between the frequency dependence and the shear rate dependence of the viscosity. A well-known empirical interrelation between these dependences for concentrated solutions and melts of flexible polymers is the so-called Cox–Merz rule,[10] but for very dilute solutions such a relationship is unknown. Many molecular theories [see, e.g., ref 3 (book) and 11 (review)] predict that at low shear rates $\dot\gamma$ the intrinsic viscosity can be described by $[\eta] = [\eta]_0[1 - A^2\dot\gamma^2\tau^2 +$ higher powers of $\dot\gamma\tau]$, which is analogous to eq 5. We now presuppose that for the systems we are investigating a relation similar to eq 6 holds, so that the non-Newtonian behavior of the intrinsic viscosity satisfies

$$\frac{[\eta]}{[\eta]_0} = \frac{1}{\left\{1 + \frac{2}{n}A^2\dot\gamma^2\tau^2\right\}^{n/2}} \qquad (9)$$

which is known as the Carreau function (p 172 of ref 12). There is no reason to assume in advance that the values of n in eqs 6 and 9 are equal.

Equations 6 and 9 are able to describe the shape of most of the published curves. This can be demonstrated by means of data of $[\eta]_\omega$ and $[\eta]_{\dot\gamma}$ which have been obtained by McAdams and Williams[13] on dilute solutions of four samples of UHMWPS with narrow molecular weight distributions in Θ solvents consisting of high-viscosity blends of styrene and a low molecular weight polystyrene. We choose these data especially because they reach, as far as we are aware, the highest value of $\dot\gamma\tau$ known in the literature and the most extreme degree of shear thinning without any indication of turn-up effects. In Figure 1 their values of $[\eta]_\omega/[\eta]_0$ for the two highest M PS solutes are plotted against log ω, together with the curves calculated by means of eq 6 with fitted values of the dynamic relaxation time $\tau_\omega = \tau/S_1^{\,3/2}$ and with $n = {}^1/_3$ (Θ solvent). A very reasonable fit can be achieved in this way. In Figure 2 the data of $[\eta]_{\dot\gamma}/[\eta]_0$ for these two PS's, as well as for two lower M PS's, are reproduced and the drawn curves are calculated by means of eq 9, again with $n = {}^1/_3$ and with fitted values of the shear-thinning relaxation time $\tau_{\dot\gamma} = A\tau$. Again the curves describe satisfactorily the non-Newtonian behavior. According to eq 8 in Θ solvents both relaxation times should be proportional to $M^{1.5}$ or $[\eta]_0^3$. Figure 3 shows that it is not impossible to draw a line with a slope of 3 through the fitted values of $\tau_{\dot\gamma}$ vs $[\eta]_0$, but it is more interesting that the values of τ_ω are more than a factor 10 larger than those of $\tau_{\dot\gamma}$. This implies that to get a certain degree of non-Newtonian behavior the shear rate has to be much larger than the angular frequency; this is in contrast to concentrated polymer fluids, where $\dot\gamma$ approximately equals ω at constant η/η_0.

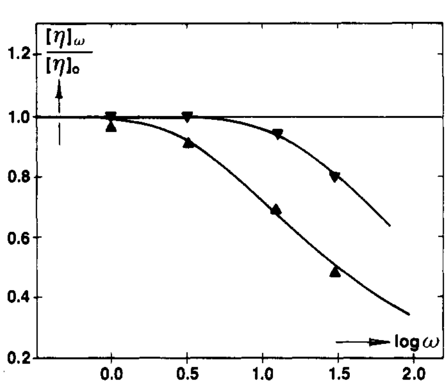

Figure 1. $[\eta]_\omega/[\eta]_0$ for two high molecular weight polystyrene solutes in blended Θ solvents with $[\eta]_0 = 0.84$ (▲) and 0.66 dL/g (▼). Symbols are used only to identify the constant-frequency conditions imposed in the analysis of the data by McAdams and Williams.[13] Curves have been calculated with eq 6 and fitted τ_ω.

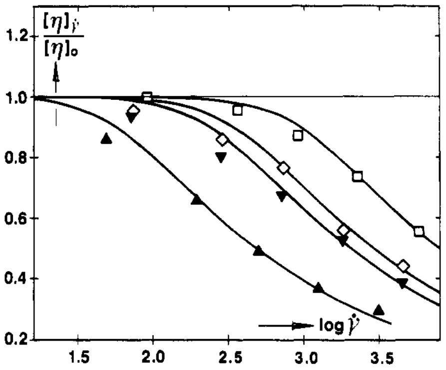

Figure 2. $[\eta]_{\dot\gamma}/[\eta]_0$ for four high molecular weight polystyrene solutes in blended Θ solvents with $[\eta]_0 = 0.84$ (▲), 0.66 (▼), 0.53 (◇), and 0.33 dL/g (□). Symbols are used only to identify the constant-shear-stress conditions imposed in the analysis of the data by McAdams and Williams.[13] Curves have been calculated with eq 9 and fitted $\tau_{\dot\gamma}$.

The idea formulated in eq 9 that $\dot\gamma\tau_{\dot\gamma} = \beta$ determines the non-Newtonian intrinsic viscosity is supported qualitatively by some experimental evidence from the literature, but results of, e.g., Suzuki et al.,[14] Noda et al.,[15] and Yamaguchi et al.[16] on PS solutions demonstrate that $[\eta]/[\eta]_0$ is not really a universal function of β. It does account for the effect of η_s, but at the same β it appears that $[\eta]/[\eta]_0$ is smaller in a good than in a Θ solvent, which might be

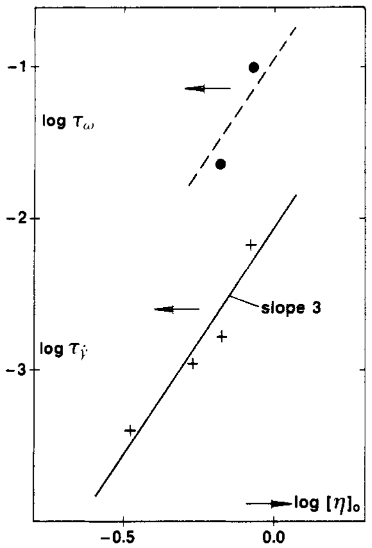

Figure 3. Log τ_ω from Figure 1 and log $\tau_{\dot\gamma}$ from Figure 2 vs log $[\eta]_0$ for four high molecular weight polystyrene solutes in blended Θ solvents. The slope of the line has the theoretical value of 3.

connected with the value of n, and larger for low M than for high M samples. On the other hand, Noda et al.[15] found for poly(α-methylstyrene) solutions that the degree of non-Newtonian behavior decreases with increasing M. Also, several theories predict that not only β determines the degree of non-Newtonian behavior. For instance, Fixman[17] calculates that the shear rate dependence is more enhanced the larger the thermodynamic interaction parameter (proportional to the cluster integral times $M^{0.5}$). In a quite different approach, starting from the physical requirement that the contour length of a polymer molecule remains constant irrespective of shear rate, Noda and Hearst[18] argue that in the Rouse, Zimm, and Harris–Hearst models the shear rate dependence of $[\eta]$ is governed by $\beta M^{-0.5}$. Thus, on experimental as well as theoretical reasons we follow the suggestion of Suzuki et al.[14] and account for this kind of deviation by making A dependent on M, e.g., like

$$A = A_0 M^r \tag{10}$$

where A_0 and r are parameters.

We now introduce a shear-thinning monodisperse relaxation time τ_m, equal to $A\tau$ and defined by

$$\tau_m = KA_0\eta_s M^{a+1+r}/RT \tag{11}$$

by which eq 9 transforms to

$$\frac{[\eta]}{[\eta]_0} = \frac{1}{\left\{1 + \frac{2}{n}\dot\gamma^2\tau_m^{\ 2}\right\}^{n/2}} \tag{12}$$

with approximations $[\eta]/[\eta]_0 = 1 - \dot\gamma^2\tau_m^{\ 2}$ at low $\dot\gamma$ and $[\eta]/[\eta]_0 = (n/2)^{n/2}\dot\gamma^{-n}\tau_m^{\ -n}$ at high $\dot\gamma$. This τ_m reduces to the characteristic relaxation time of eq 8 if $A_0 = 1$ and $r = 0$.

Effect of Polydispersity. It is assumed that for polydisperse polymers every fraction with a molecular weight between M and $M + \mathrm{d}M$ contributes proportionally to its volume (or weight) fraction $\phi(M)\mathrm{d}M$ to the intrinsic viscosity of the whole material:

$$[\eta]_{0p} = \int_0^\infty [\eta]_0\phi(M)\,\mathrm{d}M = \int_{-\infty}^{\infty}[\eta]_0\phi(M)M\,\mathrm{d}\ln M = \int_{-\infty}^{\infty}[\eta]_0\phi(\ln M)\,\mathrm{d}\ln M \tag{13}$$

In the following calculations we assume that we are dealing with a logarithmic normal distribution of molecular weights represented by

$$\phi(\ln M) = \frac{1}{\sqrt{\pi}\sigma\sqrt{2}}\exp-\left\{\left(\ln\frac{M}{M_0}\right)^2\Big/2\sigma^2\right\} \tag{14}$$

The maximum of this distribution is at M_0, and σ is a measure for the width of the distribution.

Assuming the Mark–Houwink equation (7) for the monodisperse polymer, we obtain for the intrinsic viscosity of polydisperse polymers

$$[\eta]_{0p} = \int_{-\infty}^{\infty}\frac{KM_0^{\ a}}{\sqrt{\pi}}e^{ax\sigma\sqrt{2}}e^{-x^2}\,\mathrm{d}x = KM_0^{\ a}\,e^{a^2\sigma^2/2} = KM_v^{\ a} \tag{15}$$

where use has been made of the substitution

$$x = \ln(M/M_0)/(\sigma\sqrt{2}) \tag{16}$$

and where M_v denotes the viscosity-averaged molecular weight.

Various averaged molecular weights can be defined for this type of distribution by $M_k = M_0e^{k\sigma^2/2}$. Then k has the values -1, $+1$, $+3$, and $+a$ for M_n, M_w, M_z, and M_v, respectively. The polydispersity P of the distribution can be characterized by

$$\frac{M_w}{M_n} = \frac{M_z}{M_w} = e^{\sigma^2} = P \tag{17}$$

It is also assumed that for polydisperse polymers the additivity of non-Newtonian intrinsic viscosities holds, so that

$$[\eta]_p = \int_{-\infty}^{+\infty}[\eta]\,\phi(\ln M)\,\mathrm{d}\ln M = \int_{-\infty}^{+\infty}\frac{[\eta]_0}{\left\{1 + \frac{2}{n}\dot\gamma^2\tau_m^{\ 2}\right\}^{n/2}} \times \phi(\ln M)\,\mathrm{d}\ln M \tag{18}$$

Applying relations 7 and 14–16, we get

$$\frac{[\eta]_p}{[\eta]_{0p}} = \int_{-\infty}^{+\infty}\frac{e^{-(x-a\sigma/\sqrt{2})^2}}{\left\{1 + \frac{2}{n}\dot\gamma^2\tau_0^{\ 2}e^{2x(a+1+r)\sigma\sqrt{2}}\right\}^{n/2}}\frac{\mathrm{d}x}{\sqrt{\pi}} \tag{19}$$

with

$$\tau_0 = KA_0\eta_s M_0^{\ a+1+r}/RT \tag{20}$$

which equals the shear-thinning relaxation time of molecules with molecular weight M_0.

At low $\dot\gamma$ a proper approximation is

$$[\eta]_p = [\eta]_{0p}\{1 - \dot\gamma^2\tau_{p1}^{\ 2}\} \tag{21}$$

with

$$\tau_{p1} = KA_0\eta_s[M_0e^{\sigma^2(2a+1+r)}]^{a+1+r}/RT \tag{22}$$

showing that a high moment of the molecular weight distribution, viz. with $k = 2(2a + 1 + r) \approx 4.9$ if $r = 0$ and $a = 0.725$, hence about M_{z+1}, defines the first deviation from Newtonian behavior at low $\dot\gamma$.

At high shear rates we obtain

$$[\eta]_p = [\eta]_{0p}\left(\frac{n}{2}\right)^{n/2}\dot\gamma^{-n}\tau_{p2}^{\ -n} \tag{23}$$

with

$$\tau_{p2} = KA_0\eta_s[M_0e^{\sigma^2(2a-na-n-nr)/2}]^{a+1+r}/RT \tag{24}$$

Hence at high $\dot\gamma$ a lower moment of the molecular weight distribution plays a part, viz., with $k = 2a - na - n - nr$

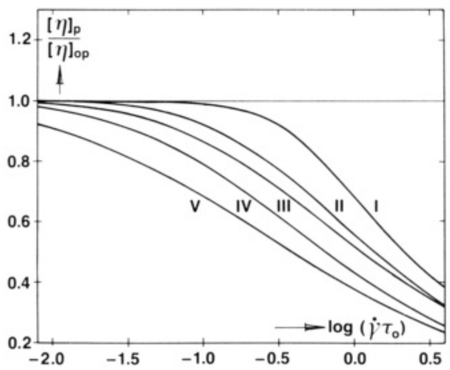

Figure 4. $[\eta]_p/[\eta]_{0p}$ vs log $\dot{\gamma}\tau_0$, calculated by means of eq 19 with $a = 0.725$, $n = 0.42$, and $M_w/M_n = 1$ (I); $M_w/M_n = 2$, $r = -0.5$ (II); $M_w/M_n = 2$, $r = 0$ (III); $M_w/M_n = 5$, $r = -0.5$ (IV); and $M_w/M_n = 5$, $r = 0$ (V).

$= 0.88$ or 0.59, if $r = 0$ and $n = {}^1/_3$ or ${}^1/_2$, respectively, i.e. about M_v.

This analysis demonstrates that also for solutions of polydisperse polymers the first deviation from Newtonian behavior is proportional to $\dot{\gamma}^2$ and that at high shear rates the intrinsic viscosity decreases proportionally to $\dot{\gamma}^{-n}$. It can be deduced directly from eq 19 that at constant $\dot{\gamma}\tau_0$ the quotient $[\eta]_p/[\eta]_{0p}$ is smaller the broader the distribution and the better the solvent, so the greater σ, a, and n are. The effect of the polydispersity is shown in Figure 4, together with influence of the parameter r, always for the combination $a = 0.725$, $n = 0.42$. The effect of r is very similar to the effect of σ. The effects we find of the parameters σ and a are qualitatively very well in agreement with those Suzuki et al.[14] calculated numerically for Schulz–Zimm distributions of the molecular weight.

Experimental Section

Viscometry. For this investigation we designed a new multiple-bulb viscometer shown in Figure 5. It consists of three capillaries, all with an internal diameter of 0.50 mm. A glass capillary of 15 cm in length is placed vertically, with on top of it four bulbs of which the centers vary in height with respect to the lower end of the capillary from 16.0 to 34.0 cm. The volumes of the bulbs lie between 3.3 and 7.9 cm^3. The times required for these volumes of pure decalin to flow through the capillary at 135 °C are longer than 144 s. The second glass capillary, with a length of 127 cm, is positioned horizontally. Above it six bulbs are placed varying in height from 2.38 to 38.3 cm and in volume from 0.10 to 2.3 cm^3. For this combination the blank flow times are longer than 230 s. The third capillary is made of stainless steel and is 1010 cm long. It is placed horizontally and joined by means of stainless steel couplings with graphite ferrules to the vertical glass parts containing six bulbs at heights between 2.76 and 25.4 cm and of volumes between 0.01 and 0.1 cm^3. The blank flow times of this system are longer than 145 s.

The ranges of the shear rate at the wall of the solvent obtainable with these capillaries can be calculated from[19]

$$\dot{\gamma}_0 = \frac{rhg}{2\nu l} = 1752\,\frac{h}{l} \qquad (25)$$

where h is the mean height of the liquid column (cm), l is the length of the capillary (cm), r is the radius of the capillary (0.025 cm), g is the gravitational constant (981 cm/s^2), and ν is the kinematic viscosity of decalin at 135 °C (0.0070 cm^2/s).

The shear rates in the different capillaries range from 3970 to 1870, from 530 to 33, and from 44 to 4.8 s^{-1}, respectively, so that with this equipment 16 measurements can be performed over a shear rate range of nearly three decades. The usual multiple bulb capillary viscometers reach shear rates from 100 to 2000 s^{-1}.[20] For very low shear rates of about 1 s^{-1} special rotational-type viscometers have been developed.[20,21] Intrinsic viscosities at very high shear rates, up to more than 10^4 s^{-1}, can be obtained with a double-capillary viscometer with external hydrostatic pressure.[22] When different kinds of viscometers were used, a shear rate range of almost five decades has been covered,[16] but the disadvantage is that the measurements in the various instruments have to be made on different solutions. With our viscometer measurements of high precision can be made in one run on the same solution, providing optimal comparable viscosity values over a wide range of shear rates.

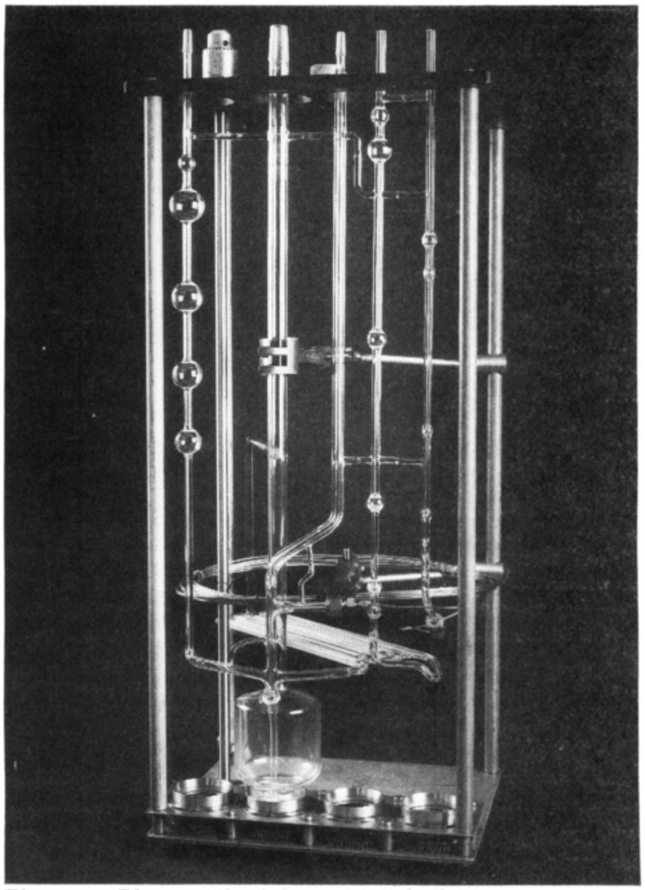

Figure 5. Photograph of the multiple-bulb viscometer.

The polyethylene solutions were prepared in an erlenmeyer set in a dissolution box purged with nitrogen. The polymer was dissolved in decalin stabilized with 2 g/L di-*tert*-butyl-*p*-cresol (DBPC) at 135 °C in 10 h with mild continuous stirring. From this solution three dilutions were made with concentrations of 0.6, 0.43, and 0.33 times the original concentration. These four solutions were kept at room temperature.

Stabilized decalin was brought into the store vessel, provided with a stirrer, of the dry multiple-bulb viscometer which was placed in a 70-L oil thermostat set to 135 ± 0.05 °C. The solvent was transported by means of nitrogen pressure through a G$_0$ glass filter and all three capillaries, so going simultaneously to the various bulbs. Then the blank flow times of the different bulb volumes of solvent were determined accurate to 0.2 s with stopwatches. Next the viscometer was sucked empty and blown dry.

After heating again in the dissolution box for 1 h at 135 °C, a solution was brought into the store vessel of the viscometer via a preheated funnel and stirred for another 30 min to reach the right temperature. The capillaries and bulbs were first washed twice with the solution, after which the actual measurement of the flow times took place, at least in duplicate. The total procedure of measurement of one blank plus one solution took a whole day. Then the viscometer was cleared out and filled with decalin. Usually the lowest concentration of a polyethylene sample was measured first, followed by the other solutions in order of increasing concentration. In most cases the viscometer was polluted after such a series and had to be cleaned.

Polymer Samples. Samples of eight specially prepared, experimental high-density polyethylenes were used, all of rather high molecular weight. The molecular characterization of these samples was made as complete as possible by means of wide-

Table I
Polyethylene Samples Used, Listed with Their Molecular Weights M_0, Polydispersity Parameters σ, and Fitted Values of Intrinsic Viscosity $[\eta]_{0p}$

sample	log M_0	σ	$[\eta]_{0p}$, dL/g
PEP750	6.44[a]	0.76	27.20 ± 0.09
PEP751	6.08[b]/6.30[a]	0.72/0.76/0.74	21.92 ± 0.07
PEP749	5.91[b]/5.85[a]	0.95/0.76/0.70	9.84 ± 0.03
HS2	6.16[c]	1.12/1.30/1.40	31.84 ± 0.13
HS5	5.80[c]	1.15/1.30/1.35	16.89 ± 0.06
HS15	5.67[c]	1.30/1.40/1.51	13.72 ± 0.05
HS9	5.54[c]	1.04/1.26/1.46	7.89 ± 0.03
HS16	5.34[c]	1.34/1.34/1.30	5.25 ± 0.02

[a] From WALS. [b] From SEC-LALLS. [c] From SEC-RI. For further details see text.

angle light scattering (WALS), intrinsic viscosity, and size exclusion chromatography (SEC) with refractive index (RI) as well as low-angle laser light scattering (LALLS) detection. Judging by the results of these analyses and taking into account the way of synthesis, all samples are believed to consist of linear polyethylene molecules.

For this investigation the characterization of the polydispersity of the samples is crucial. Cumulative molecular weight distributions were obtained of two PEP samples by SEC in trichlorobenzene at 140 °C by using a Waters 150 C instrument in-line with a Chromatix KMX6 LALLS detector. The value of M_w measured by off-line WALS on the sample PEP 749 was 15% lower than the one obtained by SEC-LALLS, but for sample PEP 751 the SEC-LALLS value was only about 60% of the WALS value. This difference is most likely due to chain fracture in the SEC. This phenomenon was even more pronounced in sample PEP 750, so that for this sample only the WALS results were used. On the basis of the similarity of the Zimm plots this sample was given the same value of the polydispersity parameter σ as the other two PEP samples.

The three PEP samples, together with lower molecular weight samples, were used to calibrate the SEC. Then the HS samples with wider molecular weight distributions were characterized only by SEC-RI. Transfer of the cumulative distributions to probability paper revealed that for all samples a logarithmic normal distribution is a reasonable approximation for the bulk of the material. The molecular weight M_0 of the top of the distribution and the polydispersity parameter σ of the samples are represented in Table I. The inaccuracy of the value of M_0 is less than 15%, i.e., 0.06 in log M_0. The values of σ were calculated from the slope of the best lines through the data, mostly of several measurements, between log M_{10} and log M_{50}, log M_{20} and log M_{80}, and log M_{50} and log M_{90}, respectively, where M_x indicates the value of M at a cumulative fraction of x% ($M_{50} = M_0$). In SEC-LALLS the low molecular part between 10 and 50% is the least accurate, in SEC-RI the high molecular part. The polydispersities of the HS samples are rather similar, with an average value $\sigma = 1.32$, i.e., $P = 5.7$.

Results and Discussion

The eight different polymers were normally measured at four concentrations and at 12–15 shear rates. The actual values of the shear rates depend on the viscosities of the solutions and therefore on the concentrations of the solutions. The shear rates of the solvent decalin at 135 °C are indicated by $\dot{\gamma}_0$ and the viscosity of the solvent by η_s. The viscosity of the solution is represented by η, and the specific viscosity is defined by $\eta_{sp} = (\eta - \eta_s)/\eta_s$. When the values of η_{sp}/c obtained at constant h/l are plotted against the concentration c, the four points are found to be reasonably collinear in all cases, as is demonstrated in Figure 6. This line yields $[\eta]_p$ at $\dot{\gamma}_0$ and the constant k_H, in agreement with the Huggins relation

$$\eta_{sp}/c = [\eta]_p + k_H[\eta]_p^2 c \qquad (26)$$

It soon became clear in the preliminary analysis of the large amount of data that for all samples at all shear rates

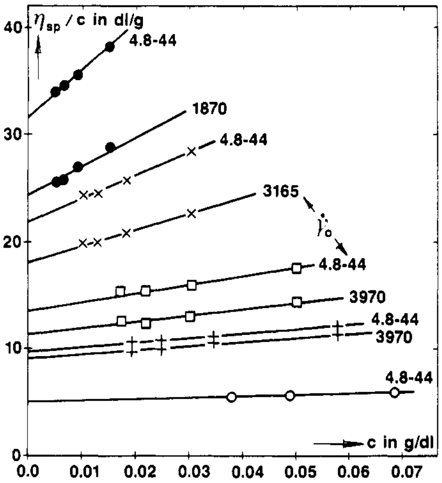

Figure 6. Measured values of η_{sp}/c vs c at various shear rates $\dot{\gamma}_0$ for the polyethylene samples HS 2 (●), PEP 751 (×), HS 15 (□), PEP 749 (+), and HS 16 (○). All straight lines satisfy eq 26 with $k_H = 0.45$.

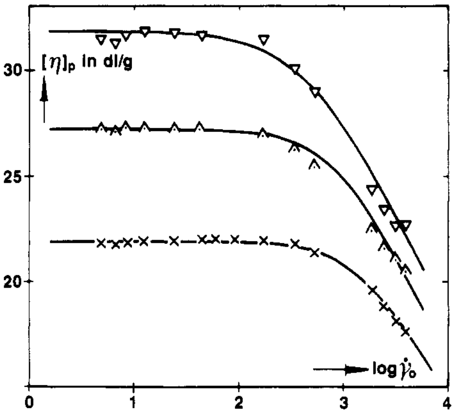

Figure 7. Shear rate dependence of $[\eta]_p$ for the polyethylene samples HS 2 (▽), PEP 750 (△), and PEP 751 (×). Symbols, experimental data; curves, calculated by means of eq 19 with $a = 0.725$, $n = 0.25$, $r = -0.7$, and $[\eta]_{0p}$, log M_0, and σ given in Table I.

a value $k_H = 0.45$ very well satisfies. This independence of k_H on molecular weight, molecular weight distribution, and shear rate is also demonstrated in Figure 6, where measured data of η_{sp}/c are plotted vs c for a number of different samples and values of $\dot{\gamma}_0$. All drawn lines have been calculated by eq 26 with $k_H = 0.45$. This figure also shows that the maximum concentration used was taken smaller for samples with higher $[\eta]_p$, so that always $c[\eta]_p < 0.6$. In this way at each value of $\dot{\gamma}_0$ the value of $[\eta]_p$ has been determined four times for all samples. The averaged results are represented in Figures 7 and 8. It is evident that the deviation from Newtonian behavior is better detectable for samples of higher molecular weight and is more gradual the wider the molecular weight distribution. All samples show a constant value of the intrinsic viscosity at low shear rates which can be taken to be $[\eta]_{0p}$.

The model eq 19 is used to fit the whole set of 112 data points of $[\eta]_p$ at different values of $\dot{\gamma}_0$ for the eight samples simultaneously. If we introduce instead of eq 20 the relation $\tau_0 = CM_0^{a+1+r}$, then four general parameters, i.e., a, r, n, and C, have to be determined and eight sample specific values of $[\eta]_{0p}$. The parameter estimation was performed with the DSM Research PAREST package[23] on an IBM 3090 mainframe computer. This package is based on the method of Britt and Luecke.[24] The values of M_0 and σ, given in Table I, together with their estimated inaccuracies were introduced, as well as for every data

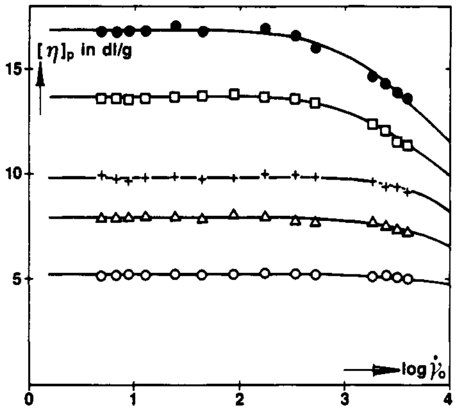

Figure 8. Shear rate dependence of $[\eta]_p$ for the polyethylene samples HS 5 (●), HS 15 (□), PEP 749 (+), HS 9 (△), and HS 16 (○). Symbols, experimental data; curves, calculated by means of eq 19 with $a = 0.725$, $n = 0.25$, $r = -0.7$, and $[\eta]_{0p}$, $\log M_0$, and σ given in Table I.

point the value of $[\eta]_p$, with a calculated error of 1% based on an estimation of the experimental errors in η_{sp} and in c and on the distribution of the points on the curves in Figure 6, and the value of $\dot{\gamma}_0$ with an inaccuracy of less than 3%. The program yielded values for all parameters with their standard deviations, the optimal shifts of the position of all data points, the sum of the squares of all relative shifts, and the normalized variance covariance matrix. The first calculation gave for a the value 0.79 ± 0.16. In view of the narrow range of M_0 values of the investigated samples, this estimate is surprisingly close to the right value $a = 0.725$. In a second calculation the value of a was fixed at 0.725 and all other parameters were computed. The result was $n = 0.25 \pm 0.03$, $r = -0.69 \pm 0.11$, and $\log C = -10.43 \pm 0.72$, and for $[\eta]_{0p}$ the values listed in Table I were found.

The fit is very good, witness the fact that the sum of the least-squares is small, and no systematic error trends are observed. The standard deviations on n and on the $[\eta]_{0p}$'s are very small, but those on r and $\log C$ are substantial, while moreover r and $\log C$ are strongly correlated (with a correlation coefficient of −0.997!), which can be readily understood from the form of eq 19. It would be obvious to eliminate one of these parameters, e.g., by stating that $\log C$ is proportional to r, but then the physical meaning is lost. The fit can also be assessed by comparing the calculated curves in Figures 7 and 8 with the experimental data, for samples with narrow as well as wide molecular weight distributions.

This result means that the exponent n is rather small, smaller than the values usually found from high-frequency dynamic viscosity data. Moreover, the shear-thinning monodisperse relaxation time τ_0 appears to be proportional to $M_0^{a+0.3}$. This deviates significantly from the relation that τ is proportional to M_0^{a+1}, which is normally found theoretically and which we have shown to hold for PS in Θ conditions in Figure 3. Our finding indicates that for monodisperse polymers in Θ solvents $\tau_{\dot{\gamma}}$ would be proportional to $[\eta]_0^{1.6}$. It is certainly not possible to draw a line with a slope of 1.6 through the values of $\tau_{\dot{\gamma}}$ vs $[\eta]_0$ in Figure 3. Hence, the shear-thinning relaxation time of PE samples in decalin is much less molecular weight dependent than this time is for PS samples in a Θ solvent.

Concluding, we can state that for the investigated PE samples a good description of the effects of molecular weight and polydispersity on the shear rate dependence of the intrinsic viscosity can be obtained with the help of eq 19. This equation expresses that at equal $[\eta]_{0p}$ UHMPE's with narrowly distributed molecular weights will show higher values of intrinsic viscosity at high $\dot{\gamma}$ than samples with wide distributions, which effect can also be deduced from the data given by Wagner and Dillon.[25] A less favorable consequence of this result is that it is not possible to predict by means of a simple relation the zero shear rate viscosity from the viscosity measured on only one high shear rate in a capillary viscometer.

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