

## Shear Creep Recovery Behavior of IUPAC Low-Density Polyethylenes

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### Synopsis

Shear creep and creep recovery measurements were carried out on three low-density polyethylenes that were the object of extended investigations of the International Union of Pure and Applied Chemistry Working Party on the Structure and Properties of Commercial Polymers. The measurements were carried out in torsion at 130° and 153°C using a frictionless apparatus with a magnetic levitation bearing. The three samples were found to be experimentally the same at short deformation times and at high shear rates. Larger nonlinear recoverable compliances were exhibited by one of the samples, which is suspected of containing a high molecular weight tail, possibly microgel, at long times and low creep stresses.

### INTRODUCTION

In 1967, the International Union of Pure and Applied Chemistry (IUPAC) Working Party on Structure and Properties of Commercial Polymers initiated studies on the rheological properties of three low-density polyethylene (LDPE) samples which were similar in their chemical characterization and in their melt-flow behavior but which exhibited differences in processing and end-use properties. The culmination of these cooperative studies is the Working Party report which was prepared by Dr. Joachim Meissner. He presented this extensive report<sup>1</sup> at the IUPAC International Symposium on Macromolecules, Madrid, September 15-20, 1974.

The samples studied are designated A, B, and C. The principal practical differences cited are critical film drawdown speeds and the optical properties of blown film. Samples B and C can be drawn almost twice as fast as A. B and C are also close to one another optically and exhibit less haze due to surface roughness than does A. Their gel permeation chromatography (GPC) curves are nearly identical, and their flow curves, i.e., viscosity-shear rate curves, are virtually identical. Number-average molecular weights  $M_n$  are reported to be the same ( $\sim 2 \times 10^4$ ), but light scattering results indicate that the weight-average molecular weight  $M_w$  of sample A ( $> 10^6$ ) is higher than that of B ( $6 \times 10^5$ ) and C ( $8-9 \times 10^5$ ). This difference is believed to be due to a small high molecular weight tail in A, probably microgel.

Viscosity, dynamic mechanical property, and stress relaxation measurements yielded results which differed very little. Among the most convincing differences

found in the characterization measurements were those seen in the extrusion viscometry end effects and extrudate swell, where sample A showed larger effects than B and C, which again were similar. Some results that showed differences between samples, such as the conditions for the onset of melt fracture, have to be questioned because of the contradictory trends reported by different participating laboratories.

It was noted that when differences were observed between the samples, they appeared consistently to be more exaggerated at lower rates of shear; see, for example, the tensile stress-strain curves presented for different rates of strain.

Having heard the Working Party Report, we expressed an interest in the materials, and we consequently were kindly supplied with samples by Dr. Meissner. We had previously become convinced that creep recovery in the terminal region of response was among the most sensitive material properties if not the most sensitive to variations of the molecular weight distribution. It, therefore, seemed reasonable that if small differences in the molecular weight distributions were responsible for the observed processing differences, then the recoverable creep compliances should also be significantly affected. The viscoelastic response of the three LDPEs had already been shown by various members of the Working Party to be indistinguishable at times out to about 100 sec. We obviously had to look at the response at substantially longer times.

## EXPERIMENTAL

Measurements of torsional creep and recovery on disc-shaped samples were carried out at 130° and 153°C in a frictionless creep apparatus<sup>2</sup> *in vacuo* (ca. 5 microns Hg). The three IUPAC samples A, B, and C are commercial-grade low-density (0.920 g/cm<sup>3</sup>) polyethylenes which were manufactured by BASF, Ludwigshafen am Rhein, Germany. In addition to measurements made on the IUPAC samples, we are reporting results obtained on a hydrogenated narrow-distribution anionically polymerized polybutadiene, HPB, which was kindly supplied to us by Professor William W. Graessley. Molecular weights obtained for this material, before and after hydrogenation, from intrinsic viscosities were both 33,000 (measurements made by Mr. Gregory Smith at Northwestern University). The heterogeneity indices,  $M_w/M_n$ , before and after hydrogenation were 1.05 (GPC, corrected for diffusion spreading) and 1.27 (GPC, not corrected), respectively. The melting point was found to be 111° ± 2°C, and the density (quenched from the melt) was 0.913 g/cm<sup>3</sup> at 25°C. The low density and melting point are due to the short-chain branching resulting from the vinyl content of the parent PBD (19 vinyl groups/1000 backbone carbon atoms). Residual unsaturation was less than one double bond per 1000 carbon atoms.

## RESULTS

Initial measurements of the recoverable shear compliance  $J_r(t)$ , cm<sup>2</sup>/dyne, were found to be nonreproducible at times greater than 100 sec. Since our measurements had to extend over lengthy periods of time, days instead of minutes, it was reasonable to be wary of thermal degradation. To decrease and hopefully eliminate degradation and its measurable effects, 0.1% by weight of

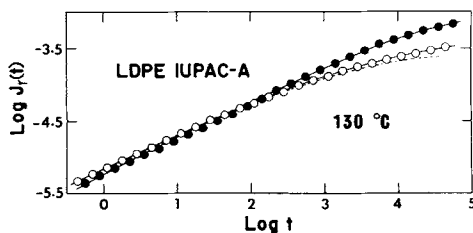


Fig. 1. Logarithmic plot of recoverable compliance  $J_r(t)$ ,  $\text{cm}^2/\text{dyne}$ , vs time, sec, for the IUPAC-A sample showing the effect of thermal degradation on the recovery of this sample. Open circles indicate the recovery after 4 hr of creep ( $\eta = 1.15 \times 10^6$  poises); filled circles represent the recovery after 65 hr of creep ( $\eta = 1.60 \times 10^6$  poises). Maximum stress in the sample in both cases is 285 dynes/cm<sup>2</sup>. Dashed curve is the estimated recovery curve at this stress level of the thermally stabilized sample.

Santonox antioxidant, 4,4-thiobis(6-*t*-butyl-*m*-cresol) (recommended and generously supplied to us by Dr. Robert Mendelson of Monsanto), was added to the samples in toluene solutions. The toluene was subsequently stripped off in a rotary vacuum evaporator. The resulting samples gave no indication of any degradation for periods as long as a week at temperatures between 130° and 150°C *in vacuo*. The onset of measurable degradation was not pursued further. Although thermal degradation was effectively eliminated the measurements of the recoverable strain per unit stress clearly indicated a remaining lack of uniqueness which was shown to reflect that the recovery response was strongly nonlinear at times greater than 100 sec at 130°C.

In the linear range of viscoelastic response, the ratio of the shear strain, which is monotonically increasing with the time after loading in creep, to the fixed applied stress is a unique characterizing curve, the shear creep compliance  $J(t)$ ,  $\text{cm}^2/\text{dyne}$ :

$$\frac{\gamma(t)}{\sigma_0} = J(t) = J_g + J_d \psi(t) + \frac{t}{\eta} \quad (1)$$

where  $J_g$  is the glassy recoverable contribution to the total deformation (ca.  $1 \times 10^{-10}$   $\text{cm}^2/\text{dyne}$ ) which is independent of time during the usual periods of measurement. The normalizing constant, the retarded steady-state recoverable compliance  $J_d$ , is often, as it is in this study, more than  $10^4 J_g$ . The recoverable creep compliance function  $\psi(t)$  ranges from 0 to 1 as  $t$ , the time, goes from 0 to infinity. The permanent strain per unit stress accumulates linearly in time with a coefficient which is the reciprocal of the limiting low rate of shear viscosity  $\eta$ . The usually referred to steady-state recoverable compliance  $J_e$  is equal to  $J_g + J_d$ . Recoverable compliance  $J_r(t)$  ( $= J(t) - t/\eta$ ) curves depicting the response of sample A, as received at 130°C, are shown logarithmically as a function of the logarithm of time (sec) in Figure 1. The compliance points represented by the open circles were obtained following a period of 4 hr of creep. A viscosity of  $1.2 \times 10^6$  poises was calculated from the creep terminal velocity. At the beginning of the recovery, the residence time of the sample at 130°C was 35 hr. Since recoverable deformation continued to accumulate at recovery times greater than that of the time of creep, it was apparent that steady-state creep deformation, defined by  $\psi(t) = 1$ , had not been attained.

The recoverable strain at recovery times approaching or greater than the time

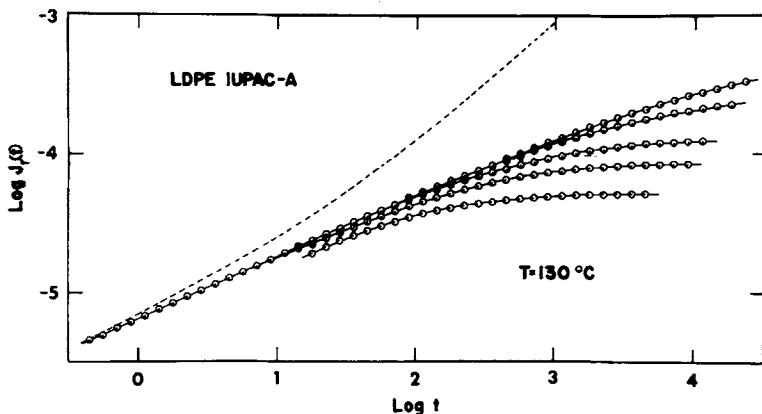


Fig. 2. Logarithmic plot of recoverable compliance  $J_r(t)$ ,  $\text{cm}^2/\text{dyne}$ , vs. time, sec, for the IUPAC-A sample at various stress levels:  $\circ - \sigma_{\max} = 60$  dynes/cm $^2$ ,  $\square - 187$  dynes/cm $^2$ ,  $\triangle - 1256$  dynes/cm $^2$ ;  $\diamond - 3602$  dynes/cm $^2$ ;  $\circ - 14691$  dynes/cm $^2$ . Dashed line is the creep curve at the lowest stress level. All curves at 130.0°C.

of creep must be less than that reflecting the characteristic recovery curve. For the curve in Figure 1, the stress at the cylindrical surface of the samples,  $\sigma_{\max}$ , was 285 dynes/cm $^2$ . In an attempt to reach steady state, a creep run extending for 65 hr was made. The ensuing recovery is depicted by the filled-in circles in Figure 1. The viscosity deduced just preceding the recovery (total residence time at 130°C  $\sim 110$  hr) was  $1.6 \times 10^6$  poises. A later determination (160 hr residence time) revealed a substantially higher viscosity of  $1.7 \times 10^7$  poises. The increasing viscosity reflects the thermal degradation that was occurring. The response of a stabilized sample is represented by the dashed line which shows that both  $J_r(t)$  curves for the unstabilized material were enhanced at long times by the thermal degradation. Crosslinking clearly dominated chain scission.

The results obtained at 130°C on stabilized IUPAC sample A are summarized in Figure 2 where recovery curves are shown which were obtained following creep curves that approached  $10^5$  sec in duration. The different curves represent recoveries where the  $\sigma_{\max}$  levels ranged from a low of 60 dynes/cm $^2$  (top curves, highest compliance at long times) to a high of 14,700 dynes/cm $^2$  (bottom curve, lowest compliance at long times).

The stress levels for the intermediate curves along with viscosity values are given in Table I. At the highest stress level, the speed of response of our recording system was being pushed. It is, therefore, reasonable to assume that the recovery starting point is in doubt and that all of the recovery curves are merged into one at times less than 10 sec. This fanning pattern is the most common form of nonlinear response of polymer melts encountered.<sup>3,4,5</sup> The characteristics appear to be threefold: (1) the departure from short-time linear behavior occurs at a critical strain level; (2) the compliance level decreases with increasing stress; (3) the time to attain steady state diminishes with increasing stress. Note that the  $J_r(t)$  curves for Sample A following the creep runs with the lowest stresses do not reach their long-time limiting levels. The dashed line represents the total creep compliance curve obtained at the lowest level of  $\sigma_{\max}$ .

In Figure 3, the creep compliance of sample A at 130°C is compared with the

TABLE I  
Characterizing Parameters of the IUPAC Polyethylenes<sup>a</sup>

$\sigma_{\max}$	IUPAC-A			IUPAC-B		IUPAC-C	
	$\log \eta$	$\log J_e$	$\log J_r(10^4)$	$\log \eta$	$\log J_e$	$\log \eta$	$\log J_e$
60	6.114		-3.57	6.164	-3.79 <sup>b</sup>	6.140	-3.89
187	6.114		-3.685	6.164	-3.84	6.140	-3.90
1260	6.072	-3.900 <sup>b</sup>		6.146	-3.96	6.127	-3.98
3600	6.045	-4.065		6.107	-4.06	6.107	-4.12
14700	5.825	-4.290		5.865	-4.23	5.869	-4.27

<sup>a</sup> All measurements at  $T = 130^\circ\text{C}$ . Units:  $\sigma$ , dyne/cm<sup>2</sup>;  $\eta$ , poises;  $J_e$ , cm<sup>2</sup>dyne.

<sup>b</sup>  $J_e$  obtained by reasonable extrapolation. HPB data:  $\log \eta = 3.501$  ( $130^\circ\text{C}$ );  $\log \eta = 3.663$  ( $115^\circ\text{C}$ );  $\log J_e = -5.840$ .

response observed at  $153^\circ\text{C}$  ( $\sigma_{\max} = 60$  dynes/cm<sup>2</sup> for both). The dashed lines represent the permanent deformation  $t/\eta$  terms in eq. (1). The dotted line is  $t/\eta$  at  $130^\circ\text{C}$  and  $\sigma_{\max} = 14,700$  dynes/cm<sup>2</sup>. The change in level reflects a factor of 2 decrease in  $\eta$  as a function of  $\sigma_{\max}$ .

The corresponding  $J_r(t)$  curves for sample A at  $130^\circ$  and  $153^\circ\text{C}$  are shown in Figure 4, where the upper branch at each temperature was obtained at  $\sigma_{\max} = 60$  dynes/cm<sup>2</sup> and the lower branch at  $\sigma_{\max} = 1260$  dynes/cm<sup>2</sup>. Note that superposition, by a time-scale shift, of the  $J_r(t)$  curves measured at different temperatures and at the same stress level is indicated. This is in accord with similar results obtained on a polystyrene sample in the nonlinear range of response.<sup>3</sup> Since the viscosity in the experimental range of stresses does not show a large variation, the observation that  $J_e$  is independent of the temperature at a given stress level is compatible with the proposition that  $J_e$  is an intrinsic function of the rate of shear  $\dot{\gamma}$ .<sup>6</sup> The curves should more properly be identified as  $J(t, \dot{\gamma})$  to explicitly indicate the nonlinearity observed at long times at most of the stress levels.

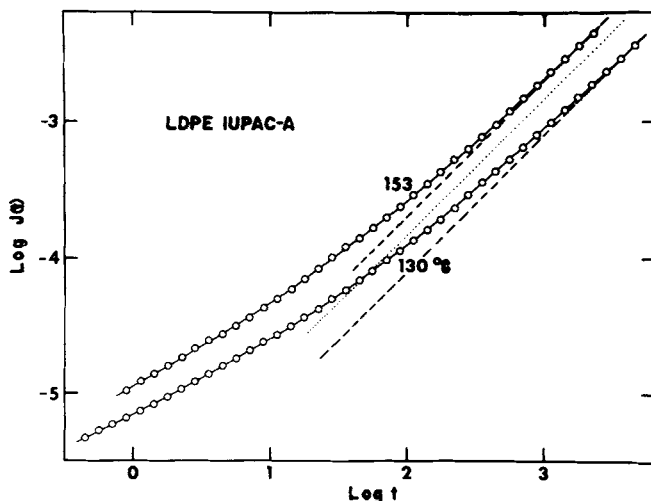


Fig. 3. Logarithmic plot of creep compliance vs. time at indicated temperatures. In both cases, the dash line is the viscous contribution to the creep compliance at the lowest stress level, 60 dynes/cm<sup>2</sup>. The dotted line is the viscous contribution to the creep at  $130^\circ\text{C}$  at the maximum stress level studied, which is 14,700 dynes/cm<sup>2</sup>.

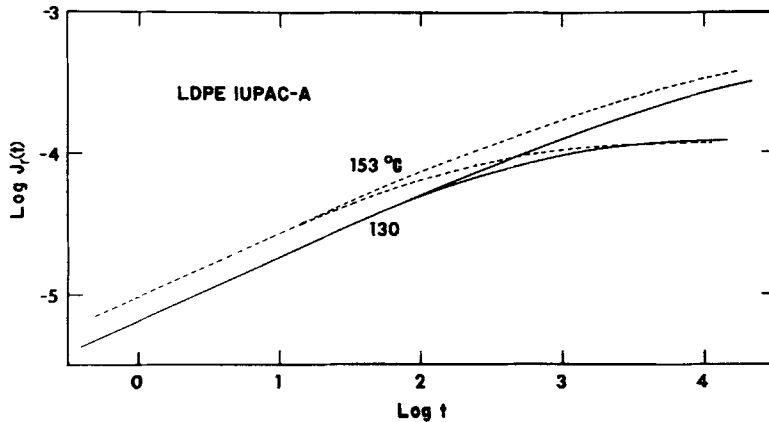


Fig. 4. Logarithmic plot of recoverable compliance vs time at 153°C (represented by dash lines) and at 130° represented by solid lines. In each case, top line corresponds  $\sigma_{max} = 60.0$  dynes/cm<sup>2</sup>, and the bottom line corresponds to  $\sigma_{max} = 1256$  dynes/cm<sup>2</sup>.

In addition, we have to qualify the presentation of our results by noting that the compliances have all been calculated as if they were in the linear range of response. The correction for the rate of shear dependence of the viscosity for our circular parallel plate geometry (twisting a right circular cylinder) is available.<sup>7</sup> This is analogous to the Weissenberg correction for tube flow.<sup>8</sup> However, the corresponding expressions for a viscoelastic deformation do not exist. Assuming that the corresponding corrections are of the same magnitude as those indicated by the viscosity correction expressions, our slight intrusion into the nonlinear range should result in errors that are of the same level of our usual experimental uncertainty, i.e., several per cent. The maximum possible correction indicated by the above cited expression<sup>7</sup> is 25%. This obtains when the viscosity is inversely proportional to the rate of shear. This dependence is strictly speaking approachable<sup>9,10</sup> but unachievable, since the rate of shear  $\dot{\gamma}$  would be independent of the shearing stress;  $\sigma = \eta(\dot{\gamma})\dot{\gamma} = (K/\dot{\gamma})\dot{\gamma} = K = \text{a constant}$ .

The recoverable compliance behavior of IUPAC sample C, low-density polyethylene at 130°C, is shown in Figure 5. The range of  $\sigma_{max}$  is the same as was applied to sample A. The values for  $J_r(t, \dot{\gamma})$  for samples A and C are the same within about 5% at short times and/or at high stress levels. At the lowest stresses

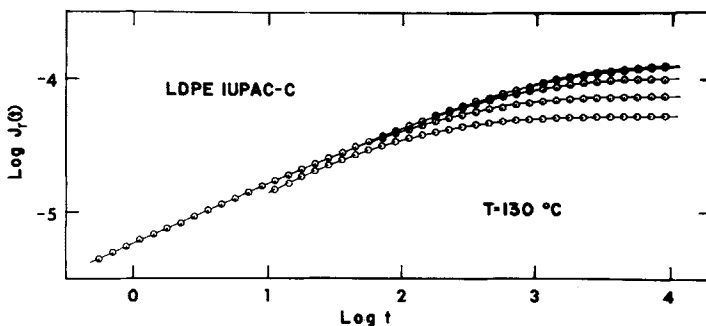


Fig. 5. Logarithmic plot of recoverable compliance vs. time for the IUPAC-C sample at 130°C. Pip directions correspond to applied creep stresses as indicated in Figure 2.

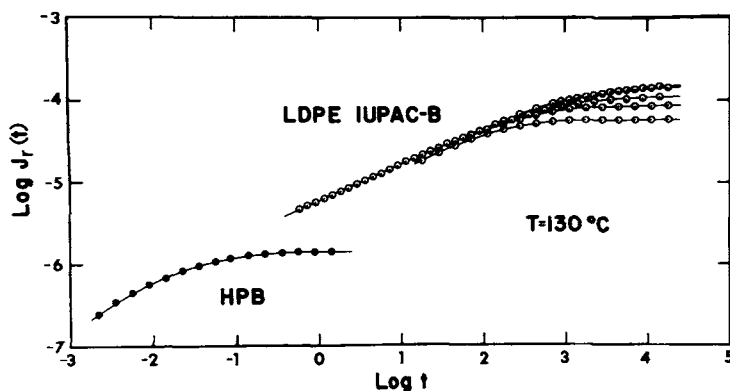


Fig. 6. Logarithmic plot of recoverable compliance vs. time of IUPAC-B and the hydrogenated polybutadiene (HPB) sample. Pip directions correspond to the stress levels indicated in Figure 2.

at long times,  $J_r(t, \dot{\gamma})$  of A is more than twice as big as that of C. The qualitative difference that should be noted is that steady state was attained at all stress levels for C and that for  $\sigma_{\max} < 200$  dynes/cm<sup>2</sup>, the  $J_r(t, \dot{\gamma})$  values for C are the same indicating that the response was linear at all times.

The results for sample B, shown in Figure 6, for all intents and purposes are the same as those for C. All the curves for B are within about 10% of the corresponding curves for C at long times and within about 3% at short times. The recoverable compliance of the hydrogenated polybutadiene, HPB, is also shown in Figure 6. Its response was found to be linear over the entire accessible range of creep shear stresses, which ranged up to  $\sigma_{\max} = 59,000$  dynes/cm<sup>2</sup>. The persistent linear response, the level of  $J_e$ , and the relatively short time to reach steady-state behavior are all indicative of a very narrow molecular weight distribution. To obtain the limited amount of transient response displayed before steady state was reached, a special detector system was employed. The position of a light lever which was reflected off of a mirror on the creep instrument rotor was detected with a Schottky barrier photocell Model PIN-LSC/2 (United Detector Technology, Santa Monica, California), and the output, which was a measure of the angular deformation, was displayed and photographed on a storage oscilloscope Model 564 B (Tektronix, Beaverton, Oregon 97005).

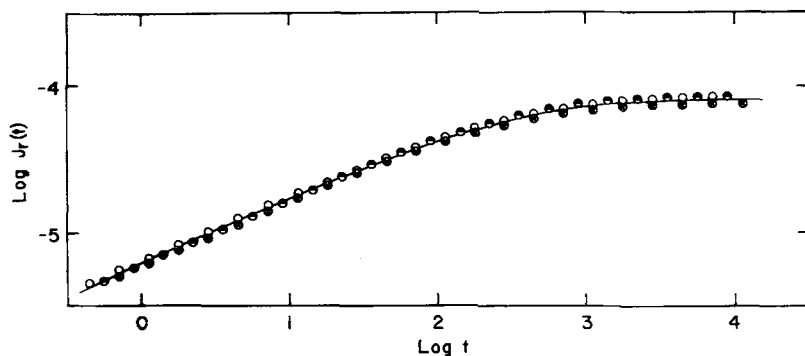


Fig. 7. Logarithmic plot of recoverable compliances for (○) IUPAC-A, (●) B, and (⊗) C as a function of time;  $\sigma_{\max} = 3600$  dynes/cm<sup>2</sup>.

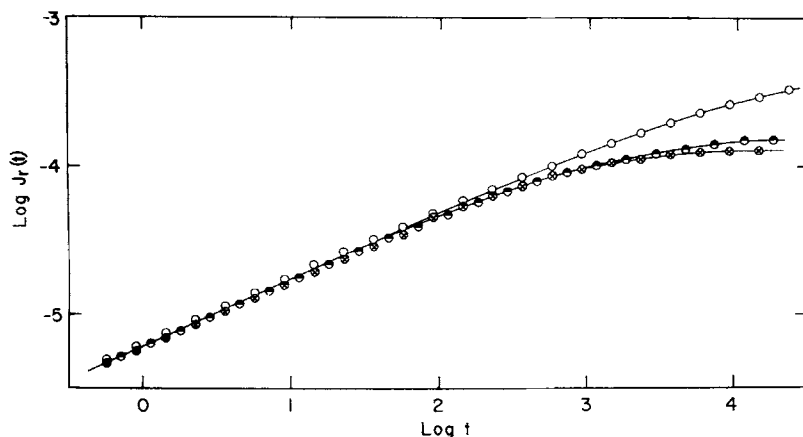


Fig. 8. Logarithmic plot of recoverable compliances for IUPAC-A, B, and C. Symbols as indicated in Figure 7;  $\sigma_{\max} = 60$  dynes/cm<sup>2</sup>.

Use of the fast-responding photocell and the oscilloscope made it possible to obtain recovery measurements at times as short as 2 msec. The limiting factor was the moment of inertia of the instrument rotor and not the detection system.

The HPB sample clearly reached steady-state deformation in less than a second at 130°C. It is interesting to note that the  $J_e$  value obtained for this special narrow molecular weight distribution linear polyethylene,  $1.45 \times 10^{-6}$  cm<sup>2</sup>/dyne, is quantitatively close to the high molecular weight limiting values obtained on all the polymers measured with the exception of polybutadiene.<sup>11</sup> Values for poly(dimethylsiloxane), poly(vinyl acetate), poly( $\alpha$ -methylstyrene), *cis*-1,4-polyisoprene, compiled by Graessley,<sup>11</sup> and polystyrene<sup>3</sup> and polyisobutylene<sup>12</sup> are all within 25% of  $1.25 \times 10^{-6}$  cm<sup>2</sup>/dyne. At present, there is no known reason for such a universality.

In Figures 7 and 8, the recoverable creep compliances of the IUPAC polyethylenes are compared. In Figure 7, the  $J_r(t)$  curves obtained, where  $\sigma_{\max} = 3600$  dynes/cm<sup>2</sup>, for three materials are presented. At this relatively high shearing stress, no significant differences in the response curves can be seen. At the lowest stress level,  $\sigma_{\max} = 60$  dynes/cm<sup>2</sup>, however, it can be seen in Figure 8 that beyond 100 sec, IUPAC polyethylenes B and C approach steady-state response (attained in approximately 4 hr), while A diverges from the common curve toward ever increasing values. It looks as if  $J_e$  ( $\sigma_{\max} = 60$  dynes/cm<sup>2</sup>) for A might be about  $2 \times 10^{-3}$  cm<sup>2</sup>/dyne, which would make it three to four times higher than the values for B and C. At still lower stress levels or strain rates, the trend indicates even larger differences.

These differences can clearly be seen in terms of the steady-state response as a function of the maximum rate of shear present in the specimens,  $\dot{\gamma}_{\max}$ . Figure 9 includes logarithmic plots of  $J_e(\dot{\gamma})$  as a function of  $\log \dot{\gamma}_{\max}$ . The filled-in circles represent the recoverable compliance values for A attained at 10<sup>4</sup> sec. Since steady state was not achieved for sample A, these values constitute minimum limits. The values shown for sample B were decreased 12% to emphasize the similarity of the steady-state behavior of B and C.

The viscosity values obtained on A and C are also presented logarithmically in Figure 9 as a function of  $\log \dot{\gamma}_{\max}$ . They illustrate another characteristic



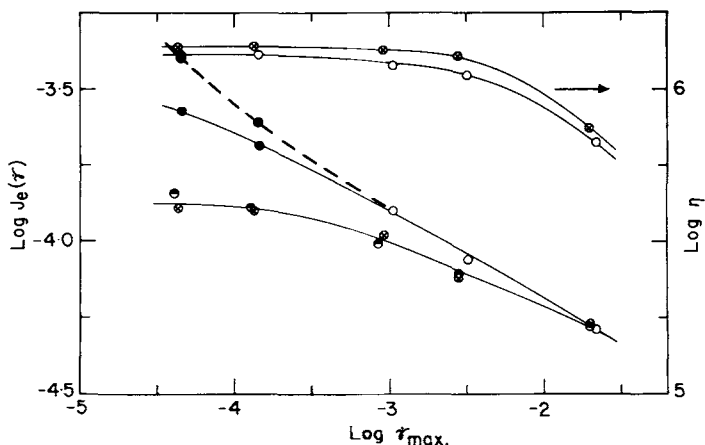


Fig. 9. Logarithmic plots of steady-state recoverable compliances of IUPAC A, B, and C as a function of the maximum strain rate in the samples. Viscosities of A and C also presented. Symbols as in Figure 7, except for the lower filled points (solid line) which represent  $J_r$ ,  $10^4$  sec, for IUPAC-A and therefore are minimum limits for  $J_e$ . The upper filled points (dashed line) are extrapolated estimates of the true steady-state levels.

feature which has been observed previously,<sup>3,13</sup> and that is: severe nonlinear behavior of  $J_r(t, \dot{\gamma})$  can be encountered at shear rates that are several decades slower than those at which the initial departure of the viscosity from its limiting low rate of shear value can be seen.

## DISCUSSION AND CONCLUSIONS

The three IUPAC low-density polyethylenes A, B, and C have been found to display the same viscoelastic response within experimental uncertainty at short times (low strains) and high stresses. Sample A, which is suspected of containing a microgel component, deviates from a common recoverable compliance curve toward higher compliances at relative long times ( $>100$  sec at  $130^\circ\text{C}$ ) and low creep stresses. At the lowest creep stresses,  $\sigma_{\max} = 60$  dynes/cm<sup>2</sup>, linear steady-state deformation was achieved with samples B and C, but A remained nonlinear at long times and did not reach a steady-state deformation in  $10^5$  sec of creep.

These results, although in agreement with the elongational deformation results shown in Meissner's report, contradict conventional wisdom which, over the past several decades, has maintained that linear viscoelastic behavior, measured at low stresses and at long times, is not pertinent to the processing of commercial polymers where nonlinear responses at short times and high stresses are believed to be the appropriate descriptors. In part, we now realize that at *low strains*, linear behavior usually obtains at all ordinary stress levels and that nonlinear response appears to enter with the passage of time when a critical strain is achieved.<sup>3,4,14</sup> Apparently, in the case of sample A, the microgel particles interact with one another to a far lesser degree when the strain and the strain rate are sufficiently high and their contribution to the support of applied tractions diminishes. In the same way, the effect of molecular weight heterogeneity is diminished at long times of deformation at high rates of shear.<sup>3,13</sup> The rate of disentangling of high molecular weight species must be enhanced relative to the rate of entangling by the shearing field.

In noting that the effects seen in the elongational measurements are paralleled by the phenomena we have observed in shear, we wish to claim that there exists no evidence to indicate that there are any rheological phenomena that occur in elongation (save that which is uniquely caused or related to dilation arising from the tension) that are not paralleled in shear. Until such evidence is obtained, it seems to be unnecessary to resort to the far more difficult and less accurate elongational measurements. Varied claims have been made for the strain rate dependence of the elongational viscosity: increases, decreases, and no change are all reported. While we assume that the viscosity being referred is the steady-state parameter that is a measure of permanent deformation, there appears to be an increasing number of investigators that report what is being called the "stressing viscosity," which is defined as the time-dependent stress divided by the imposed constant rate of strain. This certainly is a legitimate definition just so long as it is recognized that this parameter is a viscoelastic function and that the long-time limiting value is the commonly referred to viscosity. Limiting values of viscoelastic functions are often elusive and difficult to establish; for example, we have found that constancy only has meaning on a logarithmic time scale. If a measured strain is "constant" for an hour after a day of creep, the constancy must persist for two or three days before it can be considered effectively constant.

Many high polymers at the temperatures of interest take hours, days, or even weeks to reach steady-state deformation. When appraising results obtained in elongation, we ask ourselves the question: Can a polymer filament be extended at a high strain rate for hours, days, or weeks? If the time to reach steady state in shear, where the duration of the deformation process is usually no problem, is established, confidence in the achievement of steady-state deformation in elongation could be enhanced. Comparison of existing data on similar materials made in both modes, shear and elongation, indicate that the terminal relaxation times are close to one another.

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