A Rapid Molecular Weight Determination for Linear Polyethylene

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Introduction

The molecular weight of high-density–high-molecular-weight polyethylenes is usually calculated by use of the Tung[1] or Francis et al.[2] equations from viscosity data obtained by dissolving of the polyethylene in hot solvents (e.g., decalin at 135°C., tetralin 130°C.). The solutions are stabilized by addition of antioxidants like phenyl-β-naphthylamine.

In this work an attempt is made to find some very simple viscoelastic measurement which would correlate with the molecular weight. It was hoped to devise an empirical measurement of the molecular weight of high density polyethylene which would be much easier to carry out than the measurement of intrinsic viscosity.

Samples

In order to make this study as general as possible samples of high-density–high-molecular-weight polyethylene were used. These samples were prepared by different processes based on heterogeneous catalysis and kindly supplied by the Allied Chemical Corp. (samples A-2-58, A-2-61, and A-2-52); Koppers Co., Inc. (samples K-6, K-5, K-4, and K-3); and Phillips Petroleum Co. (samples P-38494, P-38493, P-38492, P-38491, P-28490, and P-38489). W. R. Grace provided some fractionated samples.

The samples were prepared with large amounts of powerful antioxidants.

Experimental

1. Intrinsic viscosity measurements were carried out by the laboratories who supplied the samples using methods described in the literature.[1,2]

2. By use of a relaxation balance described previously[3] the stress-relaxation tensile modulus $Er(t)$ of different polyethylene samples was measured at 141.7°C., and the results of the experiments are given in Figure 1.

3. The 10-sec. shear modulus G(10) as a function of temperature was measured by use of the Gehman apparatus,[4] and the results of the experiments in the region above the melting point of linear polyethylene (about 135°C.) up to about 155°C. are shown in Figure 2.
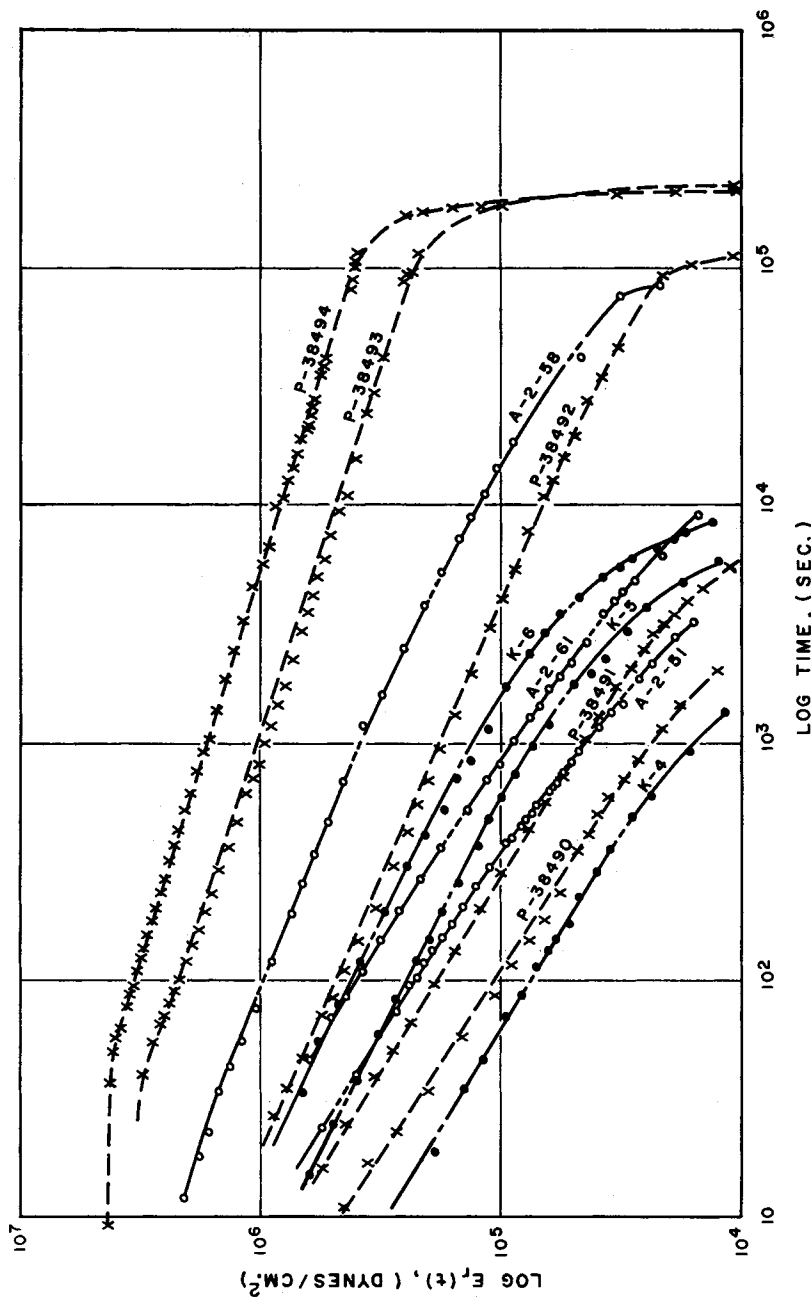
Fig. 1. Stress-relaxation tensile modulus of different polyethylene samples measured at 141.7°C. Samples: (○) Allied Chemical Corp., (●) Koppers Co., and (✕) Phillips Petroleum Co.

All samples were conditioned for about 1 hr. at 141.7°C. to allow shrinkage before any measurements were made.

The Gehman apparatus used was slightly modified with a spring adjustment for keeping the sample under constant very slight tension during the measurements. Temperature control was maintained in a silicone oil bath.

Discussion

The results of the experiments described above are shown in Table I and in Figures 1–4. Table I shows the intrinsic viscosity of the samples and the viscosity-average molecular weight computed from the equation of Tung.[1] The plots of log $E_r(t)$ versus log t in Figure 1 show a very definite
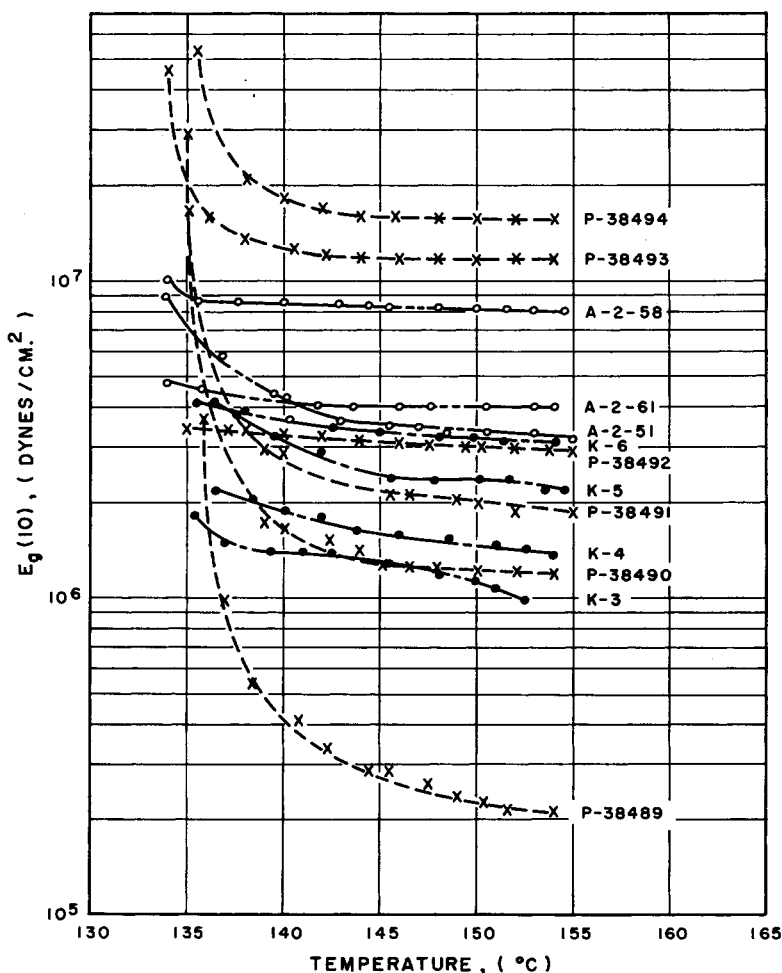

Fig. 2. Results of measurements by use of the Gehman apparatus. Samples: (O) Allied Chemical Corp., (●) Koppers Co., and (×) Phillips Petroleum Co.

TABLE I

Sample	$[\eta]^a$	$\bar{M}_v{}^b$	3G(10) at 150°C., dynes × cm.$^{-2c}$	$E_r(100)$ at 141.7°C., dynes × cm.$^{-2\ d}$
P-38494	16.77	17.3 × 10⁵	1.57 × 10⁷	3.4 × 10⁶
A-2-58	12.3	11.1	8.16 × 10⁶	9.7 × 10⁵
P-38493	11.17	9.8	1.17 × 10⁷	2.4 × 10⁶
A-2-61	6.66	4.84	4.00 × 10⁶	4.0 × 10⁵
A-2-51	5.57	3.71	3.34	2.25
P-38492	5.51	3.6	2.98	4.9
K-6	5.29	3.43	3.20	4.2
P-38491	4.47	2.8	2.00	1.83
K-5	4.19	2.45	2.38	2.45
P-38490	3.81	2.2	1.22	1.07
K-4	3.25	1.78	1.50	7.5 × 10⁴
K-3	2.74	1.40	1.16	
P-38489	2.65	1.37	2.31 × 10⁵	

ᵃ $[\eta]$ was obtained by measurement in decalin with addition of 0.1% phenyl-β naphthylamine at 135°C. (courtesy of Mr. E. K. Walsh).

ᵇ Calculated from Tung's (see ref. 1) relationship: $[\eta] = 5.10 \times 10^{-4} \bar{M}_n{}^{0.725}$.

ᶜ Rubbery plateau 10 sec. modulus measured at 150°C. by use of modified Gehman apparatus.

ᵈ The 100-sec. modulus from stress relaxation measurements at 141.7°C. The stress relaxation of the samples K-3 and P-38489 was not measured because of the very rapid flow of those samples above the melting point.
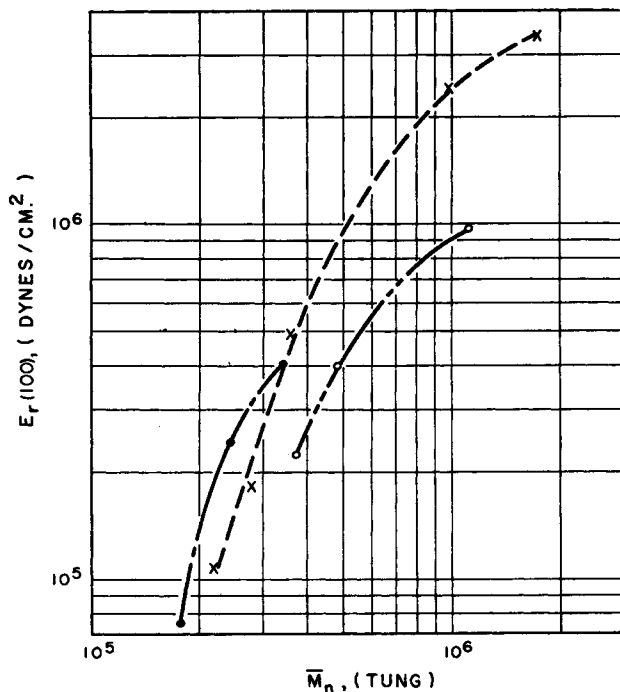

Fig. 3. Plot of log $E_r(100)$ versus $\bar{M}_v$ for samples: (O) Allied Chemical Corp., (●) Koppers Co., and (×) Phillips Petroleum Co.

and expected progression with molecular weight. Samples P-38494, P-38493, A-2-59, and P-38492 show a very sharp drop of $E_r(t)$ at the long time region, due to the complete exhaustion of the antioxidant and consequent oxidative scission of the polymer. For quite prolonged periods of time there appears to be no oxidative scission. The stress relaxation curves were essentially independent of the preheating time for periods of
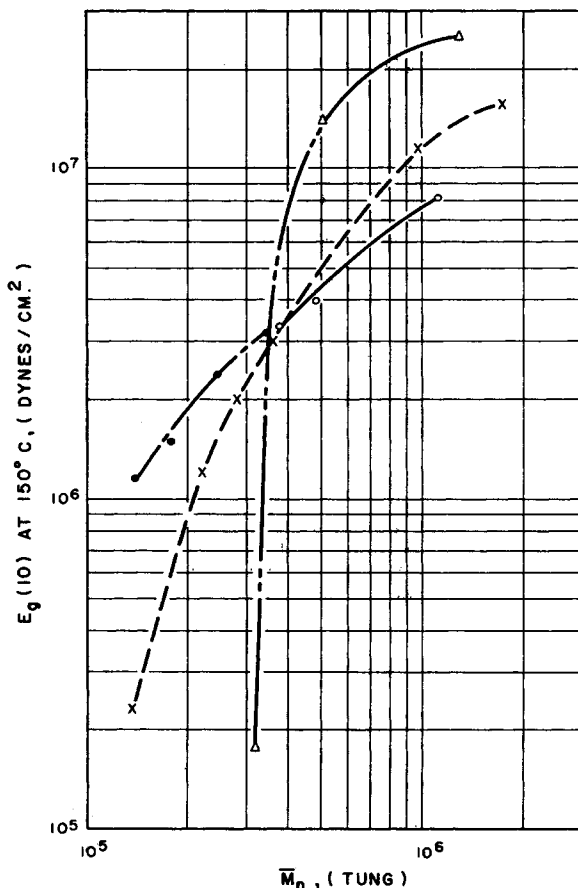

Fig. 4. Plot of log 3G(10) measured in the plateau region versus log $\bar{M}_v$. (O) Allied Chemical Corp., (●) Koppers Co., (×) Phillips Petroleum Co., and (△) W. R. Grace.

time between 40 min and 2 hr. However, the long time region of most of the stress relaxation curves appear to be affected both by crosslinking and scission.

The stress relaxation modulus after 100 sec. is defined as $E_r(100)$. A plot of log $E_r(100)$ versus $\bar{M}_v$ for all of the samples is shown in Figure 3. There appears to be a monotonic relation between these quantities which is slightly different for the samples prepared by the three different suppliers. It is presumed that this is due to different molecular weight distributions.

Figure 4 shows a plot of log 3G(10) measured in the plateau region (at 150°C.) versus log $\bar{M}_v$ (Tung[1]). There clearly is a monotonic relation between the plateau Gehman modulus and the molecular weight. In this case the samples from the different suppliers were not as distinguishable as in Figure 3.

Inasmuch as the Gehman test is a very simple one to carry out, it is proposed that for molecular weights above 150,000 Figure 4 be used as a calibrating relation between the Gehman plateau modulus at 150°C. and $\bar{M}_v$. The effect of molecular weight distribution is not resolved at the present, so that a plot against another type of average molecular weight might be even more satisfactory. For comparison the results on some fractionated polyethylene samples supplied by Dr. Horowitz of W. R. Grace are also shown on the figure.

References

1. Tung, L. H., *J. Polymer Sci.*, **24**, 333 (1957).
2. Francis, P. S., R. C. Cooke, Jr., and J. H. Elliott, *J. Polymer Sci.*, **31**, 453 (1958).
3. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960, p. 143.
4. ASTM Standards on Rubber Products, 550, Designation 3 1053-58T, 1958.

Synopsis

For linear polyethylene in the molecular weight range above 100,000 it is proposed that a measurement of the 10-sec. Gehman modulus at 150°C. can be used as a nonabsolute but very rapid and convenient measurement of the molecular weight.

Résumé

On a proposé l'emploi du module de 10 secondes de Gehman à 150°C comme mesure non-absolue mais aisée et très rapide des poids moléculaires supérieure à 100.000 pour le polyéthylène linéaire.

Zusammenfassung

Als nicht-absolute, aber sehr rasche Molekulargewichtsbestimmung für lineares Polyäthylen im Molekulargewichtsbereich über 100.000 wird die Messung des 10-Sekunden-Gehman-Moduls bei 150°C vorgeschlagen.