

Intrinsic Viscosity Studies of Linear Polyethylene Fractions in Good and Poor Solvents

INTRODUCTION

The purpose of this investigation was to measure the dilute-solution viscosity characteristics of relatively narrow fractions of linear polyethylene of low to moderately high molecular weight in a good and in a poor (θ) solvent and to compare the experimental data with existing correlations. Viscosity measurements were made rapidly under a helium atmosphere to avoid polymer degradation.

EXPERIMENTAL

Nine fractionated linear polyethylene samples of Marlex 6009, furnished by Gulf Oil Company, were used in this study. The samples were fractionated and characterized by U.S. Industrial Chemical Company. Characteristics of the samples are listed in Table I. The fractions, particularly those below 30,000, are quite narrow. Viscosity measurements were made using a technique similar to that described by Flory et al.¹ All of the experiments were carried out at initial relative viscosities of less than 2. Measurements were made at four or five concentrations based on equal volumes of added solvent. Elapsed time from preparation of the polymer solution to final viscosity measurement was always less than 2 hr.

Viscosity measurements were made in decahydronaphthalene at 135.0°C, a good solvent, and in diphenyl ether at 163.9°C, a poor (θ) solvent.

Linear least-squares fits of η_{sp}/c and $\ln(\eta_{rel})/c$ -versus- C data were used to obtain the intrinsic viscosities and values of k' and k'' . Flow time for decahydronaphthalene at 135.0°C was 192 sec, and that for diphenyl ether at 163.9°C was 153 sec so that kinetic energy corrections were negligible. Corrections for the effect of shear rate on intrinsic viscosity were also negligible. With the exception of sample 1, measurements were run on duplicate samples in order to determine the repeatability of the technique for obtaining intrinsic viscosities ($\pm 3\%$). The quantities of sample 1 available limited the number of measurements to one. Therefore, these data are less reliable than those for the other samples.

Several special experimental problems need to be taken into account in measuring the properties of linear polyethylene in solution at high temperature. The most serious of these are:

1. Polymer oxidation and degradation can occur after prolonged exposure to high temperature. This problem was minimized by the use of an antioxidant, an inert at-

TABLE I
Molecular Weights of Linear Polyethylene Fractions*

Fraction no.	$M_w \times 10^{-4}$	M_w/M_n
1	0.30	1.30
2	0.62	
3	1.16	to
4	1.95	
5	2.95	1.54
6	5.80	2.00
7	10.0	to
8	14.5	to
9	35.0	3.50

* All samples contain approximately 20 ethyl side chains per 1000 carbon atoms and contain less than one double bond per 1000 carbon atoms.

TABLE II
 Intrinsic Viscosities, Inherent Viscosities, and Huggins Constants of Polyethylene in Decalin at 135°C

Sample no.	$M_w \times 10^{-4}$	$[\eta]\theta$, dl/g	$(\eta_{sp}/c)_{c \rightarrow 0.1}$, dl/g	$100 \left\{ \frac{[\eta]}{[\eta]_0} - \frac{[\eta_{sp}/c]_{c \rightarrow 0.1}}{[\eta]_0} \right\} /$	k'	k''	$k' + k''$	$\frac{\{0.5 - (k' + k'')\}}{0.5} \times 100, \%$
1	0.30	0.148	0.140	5	0.24	0.23	0.47	6
2	0.62	0.194	0.194	0	0.37	0.15	0.52	4
3	1.16	0.321	0.306	5	0.31	0.17	0.48	4
4	1.95	0.462	0.450	3	0.39	0.13	0.52	4
5	2.95	0.603	0.612	2	0.35	0.15	0.50	0
6	5.80	1.269	1.260	1	0.34	0.16	0.50	0
7	10.0	1.930	1.880	3	0.34	0.16	0.50	0
8	14.5	2.571	2.470	4	0.32	0.17	0.49	2
9	35.0	4.858	4.588	6	0.40	0.14	0.54	8

mosphere, a closed system, high-purity solvents, and by making measurements quite rapidly.

2. Variations in solvent purity may have some effect on solution viscosities. From the refractive index results on the decahydronaphthalene used, it consisted of a mixture of trans (1.4828) and cis (1.4699) isomers or small amounts of even a third component, tetrahydronaphthalene (1.4614), which is difficult to separate from decahydronaphthalene. The effects of solvent purity were not investigated in this study, except that freshly distilled solvents were used in all cases.

RESULTS AND DISCUSSION

Intrinsic Viscosities and Huggins' Constants

For the nine fractionated linear polyethylene samples ($0.3 < M_w \times 10^{-4} < 35.0$) in decahydronaphthalene at 135°C, intrinsic viscosities ranged from 0.148 to 4.86 dl/g (Table II). The intrinsic viscosities of some of the same samples ($0.62 < M_w \times 10^{-4} < 5.80$) in diphenyl ether at 163.9°C are all lower than in decahydronaphthalene, ranging from 0.156 to 0.732 dl/g (Table III).

Measurements of inherent viscosities η_{sp}/c at concentrations of 0.1 g/dl were made to compare with $[\eta]$ values in decahydronaphthalene at 135°C (Table II). The differences did not exceed 6% for any sample, and the replacement of $[\eta]$ by $(\eta_{sp}/c)_{c=0.1}$ is not greatly in error. Thus, for many purposes, this more convenient determination can be used to approximate $[\eta]$.

Huggins' constants k' and k'' values are tabulated in Tables II and III; $k' + k''$ for all the samples in decahydronaphthalene at 135°C are between 0.47 and 0.54. Thus, all values deviate less than 8% from 0.50. The $k' + k''$ values for samples in diphenyl ether at 163.9°C are between 0.50 and 0.54.

Although a decrease in k' with increase in molecular weight has been predicted² and has been observed experimentally in polystyrene³⁻⁵ ($1.5 < M_w \times 10^4 < 177$) and in polyisobutylene^{6,7} ($1.27 < M_w \times 10^4 < 101$) solutions in good solvents, the good-solvent data reported in Table II show no consistent variation in k' with molecular weight from 6,200 to 350,000. The average value is 0.35. The 3000 molecular weight sample gave an unusually low value, i.e., 0.24. This was the only sample on which only a single determination was made, and the result may be in error. De La Cuesta and Billmeyer⁸ obtained a k' value of 0.44 for an unfractionated linear polyethylene sample in decahydronaphthalene at 135°C. Chiang obtained values of 0.39 to 0.41 in the same solvent for molecular weights ranging from 21,900 to 1,035,000.⁹ The lower average k' value

TABLE III
Intrinsic Viscosities and Huggins' Constants for Polyethylene
in Diphenyl Ether (163.9°C)^a

Sample no.	$M_w \times 10^{-4}$	$[\eta]_{\theta}$	k_{θ}'	k_{θ}''	$k_{\theta}' + k_{\theta}''$	$\frac{\{0.5 - (k_{\theta}' + k_{\theta}'')\}}{0.5} \times 100, \%$
2	0.62	0.156	0.41	0.09	0.50	0
3	1.16	0.275	0.44	0.10	0.54	8
4	1.95	0.353	0.53	0.00	0.53	6
5	2.95	0.467	0.53	0.00	0.53	6
6	5.80	0.732	0.54	0.00	0.54	8

^a Owing to the limited amounts of the polymers, only five samples could be measured in this solvent.

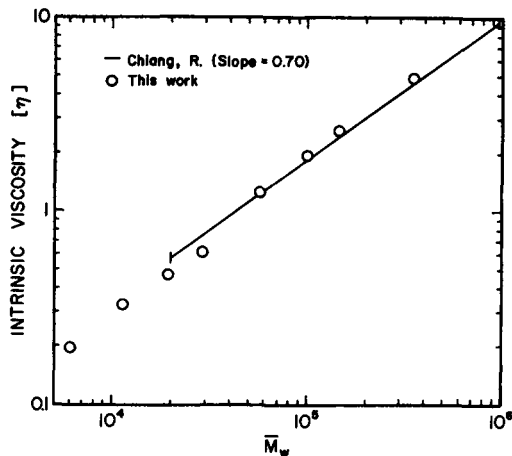


Fig. 1. Mark-Houwink plot for polyethylene in decahydronaphthalene at 135°C.

obtained in this investigation probably reflects the narrower fractions studied compared with those measured in references 8 and 9.

The results in Table III show that k' tends to increase with molecular weight (6,200 to 58,000) in a poor solvent. This reversal of the expected trend is probably due to increased aggregation as the precipitation temperature is approached at high molecular weights. This reversal has been observed previously in poor-solvent solutions of polystyrene, poly(methyl methacrylate), and copolymers of the two,⁴ and of polyisobutylene.^{6,7}

In good solvents, polymers have expanded conformations, and the resulting k' values are lower than in poor solvents. The k' values measured here (Tables II and III) are significantly lower for the good solvent (decahydronaphthalene at 135°C) than the k' values of the same samples in a poor solvent (diphenyl ether at 163.9°C). Simha and Zakin,⁴ Berry et al.,¹ Chou,⁷ and Luh⁵ found that, except for low molecular weights, k' values for linear polymers in good solvents are below 0.5, while for linear polymers in poor solvents they are near 0.5 or above. The data reported here are consistent with these observations.

Chiang⁹ obtained the relationship $[\eta] = 6.20 \times 10^{-4} M_w^{0.70}$ for polyethylene in decahydronaphthalene at 135°C, using samples ranging in molecular weight from 2×10^4 to 1×10^6 . A careful examination of the present data (Fig. 1) indicates that the data from 58,000 to 350,000 fit Chiang's equation quite well, while the lower molecular weight samples, 6,200 to 29,500, appear to fit a parallel straight line lying below an extension of Chiang's line, i.e., lower value of K . Tompa¹¹ shows that the value of K depends on the molecular weight distribution and the Mark-Houwink exponent a , with narrow distributions having lower values of K . The M_w/M_n ratios of these four lowest molecular weight samples are 1.30 to 1.54 (Table I) and are lower than those of the four highest molecular weight samples (M_w/M_n from 2.00 to 3.50). The latter may be similar to the samples used by Chiang. This would explain the deviations observed for the low molecular weight samples and the good agreement of the high molecular weight samples.

An averaged value of $K_\theta = 27.1 \times 10^{-4}$ for samples 3 to 6 in diphenyl ether at 163.9°C was obtained from a Stockmayer-Fixman plot, $[\eta]/M^{0.50}$ versus $M^{0.50}$ of the data. This is close to $K_\theta = 29.5 \times 10^{-4}$ reported by Chiang⁹ for polyethylene in diphenyl ether at 161.4°C and $K_\theta = 30.9 \times 10^{-4}$ reported by Nakajima and Hamada¹² for the same system at 163.9°C. However, the same four low molecular weight samples tend to lie below an extension of Chiang's equation (see Fig. 2). The explanation for this behavior is prob-

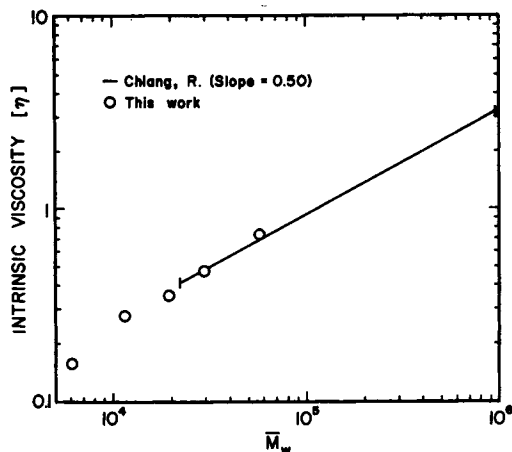


Fig. 2. Mark-Houwink plot for polyethylene in diphenyl ether at 163.9°C.

ably the same as that for the deviations in decahydronaphthalene at 135°C, i.e., the narrower molecular weight distributions of these four samples. The deviation is less pronounced in the poor solvent. Maximum deviation was obtained with the 6200 molecular weight sample which is below 10^4 , the minimum molecular weight of polyethylene for which Nakajima and Hamada¹² claimed a statistical treatment is valid.

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J. S. CHIANG
J. L. ZAKIN
K. G. MAYHAN

Department of Chemical Engineering and
Graduate Center for Materials Research
University of Missouri-Rolla
Rolla, Missouri 65401

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