TABLE I
COEFFICIENTS OF THE EQUATION $\Delta\epsilon/\epsilon = aE^2 + bE + c$ DETERMINED BY COMPUTER LEAST-SQUARES FIT OF THE EXPERIMENTAL DATA

Polymer	M_w	$a \times 10^{10}$	$b \times 10^6$	$c \times 10^3$	$\sigma^a \times 10^3$
1	51,000	1.11		0.800	3.94
2	73,000	1.23		1.60	1.67
3	133,000	1.20	0.879	−0.648	3.45
4	380,000	1.36	1.31	−1.33	3.76
5	1,700,000	1.24	0.970	−0.719	2.84

[a] σ is the standard deviation of the experimental data from the calculated curve.

by a least-squares computer fit of the data. Figure 1 shows a plot of dichroism data obtained for polymer 2. Polymers 1 and 2, with lower molecular weights, showed a purely quadratic dependence of $\Delta\epsilon/\epsilon$ on field strength. However, the data for polymers 3–5 could be better fitted by the addition of a linear term in E.

The deviation of the field strength from quadratic dependence arising from induced polarization effects is expected to take a form very similar to the directly related deviations from the quadratic electric birefringence.[2] On this basis using the dipole moment data for the 133,000 molecular weight sample from ref 11, and reasonable values for the optical anisotropy, the maximum derivation at field strengths of about 20 kV/cm would lead to a change in slope from the initial slope of the curve of $\Delta\epsilon/\epsilon$ *vs.* E^2 of about 20%. The observed deviation for this sample is 60 ± 5%, clearly outside the range of the deviation from E^2 dependence expected from the polarization phenomena alone. The same is true for the higher molecular weight samples. For the highest, $M_w = 1.7 \times 10^6$, the dichroism in fact is *less* than that observed with the sample of M_w = 380,000, despite the fact that the former has a dipole moment of about 4500 D and the latter a dipole moment of about 2120 D units.[11] There is no mechanism which has been proposed to account for this except a difference in structure such as that produced by flexibility.

The onset of flexibility, as evidenced by the appearance of a significant term linear in E, occurs at a molecular weight between 73,000 and 133,000. This result is consistent with indications from dielectric relaxation studies that PBIC begins to deviate from a rigid rod above 80,000 molecular weight.[11]

The value of the reduced dichroism at a particular field strength should be roughly proportional to the dipole moment of the molecule since this is a major force in its orientation in an electric field. However, Table I shows that polymer 5, with a molecular weight of 1,700,000, has approximately the same field strength dichroism dependence as polymers 3 and 4, which are much smaller. Thus this polymer must be not only flexible but considerably folded.

These experiments demonstrate the validity of the theoretically derived quadratic field strength dependence of electric dichroism for rigid polymer molecules. Furthermore, deviations from quadratic field strength behavior are shown to occur with hydrodynamically flexible polymers and this property may be very useful in determining the flexibility of rodlike polymers.

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The Molecular Weight Fractionation of Polypropylene

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Several studies[1-10] of the fractionation of polypropylene have been reported in the past. This paper also deals with the fractionation of the same polymer, but it differs from the previous studies in the following areas: (1) use of 1,2,4-trichlorobenzene (TCB)–dimethyl phthalate (DMP) as the solvent–nonsolvent system; (2) comparison of the results obtained by fractional precipitation and chromatographic techniques; and (3) treatment of fractionation data according to Weibull's (or Tung's) distribution function.

Experimental Section[11]

A polypropylene homopolymer of Diamond Shamrock Corp. was used in this work. This product had the following physical properties: state, fluff; melt flow rate, 12 g/10 min; intrinsic viscosity in TCB ($[\eta]_{\mathrm{TCB}}$), 1.230 dl/g; intrinsic viscosity in Decalin ($[\eta]_{\mathrm{DEC}}$), 1.738 dl/g; and isotactic content, 95%.

Fractionation of the polymer was carried out by fractional precipitation (FPF)[12] and chromatographic (CF)[13] methods. Thermal degradation was minimized by the addition of 0.3% Ionol–antioxidant to TCB and DMP, and also by maintaining a blanket of N_2 gas throughout the fractionation. Both $[\eta]_{\mathrm{TCB}}$ and $[\eta]_{\mathrm{DEC}}$ were measured at 135° in a Cannon–Fenske viscometer utilizing the classical expression

$$\lim_{c \to 0} (\eta_{\mathrm{sp}}/c) = [\eta]$$

Results and Discussion

The following correlation was established between $[\eta]$ in the two solvents used

$$\log [\eta]_{\mathrm{DEC}} = (0.15 \pm 0.05) + (0.95 \pm 0.11) \log [\eta]_{\mathrm{TCB}} \quad (1)$$

This relation should be found useful as it is easier to run $[\eta]_{\mathrm{TCB}}$ than $[\eta]_{\mathrm{DEC}}$ because of poor thermal stability of DEC.

Integral molecular weight distribution curves were

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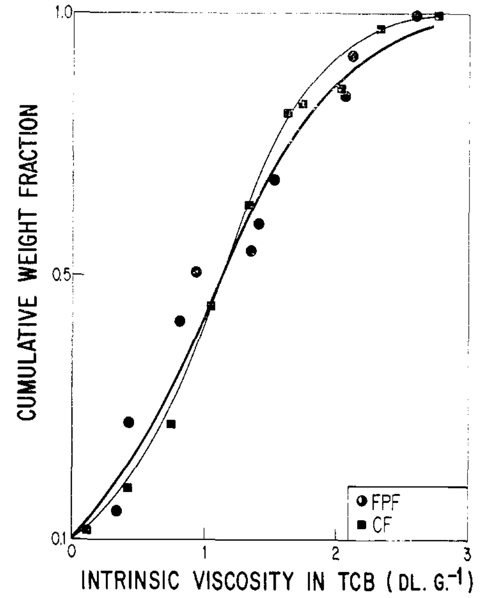

Figure 1. Integral molecular weight distribution curve, $C(M)$ *vs.* $[\eta]_{\mathrm{TCB}}$.

constructed for both FPF and CF data (Figure 1) using eq 2.[14] Notice that these curves follow an S-shaped pattern.

$$C(M_i) = W_i/2 + \sum_{j=1}^{i-1} W_j \qquad (2)$$

No molecular weight backlash behavior was observed. The data did not fit Wesslau (or log normal) distribution; it was treated according to Weibull's (or Tung's) distribution function. Weibull distribution in linearized form was written as eq 3.[15]

$$\log\log\frac{1}{1 - C(M)} = A + B\log([\eta] - k) \qquad (3)$$

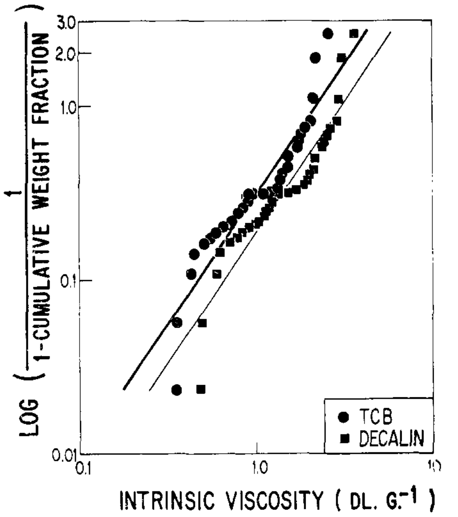

Figure 2. Weibull distribution function fit for FPF data.

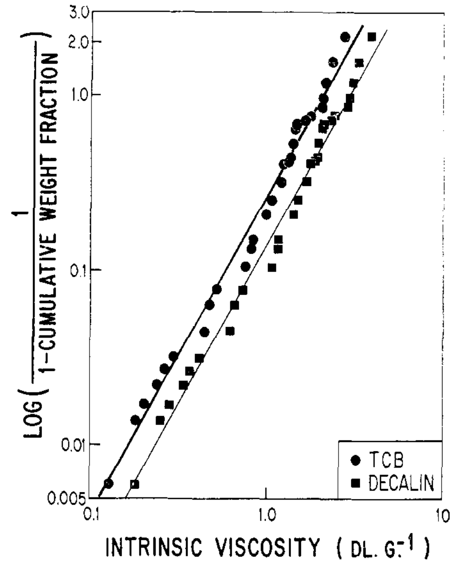

Figure 3. Weibull distribution function fit for CF data.

Equation 3 was reduced to eq 4, the Weibull curve fit equation, by putting $k = 0$. Equation 4 was related to

$$\log\log\frac{1}{1 - C(M)} = A + B\log[\eta] \qquad (4)$$

Tung's distribution equation (5)[16] by correlating A and B to Y and Z. Substitution of $[\eta]$ for M in eq 5 should not invalidate results because $\log[\eta]$ and $\log M$ are linearly related. Results plotted according to

$$\log\log\frac{1}{1 - C(M)} = \log\frac{Y}{2.303} + Z\log[\eta] \qquad (5)$$

eq 4 are shown in Figures 2 and 3. Note that CF data show a better fit to this function than do FPF data.

Weibull distribution for statistical purposes was written as eq 6. Rewriting of (6) in linearized curve

$$C(M) = 1 - \exp\left[-\left(\frac{[\eta] - k}{b}\right)^c\right] \qquad (6)$$

fitting form resulted in eq 7. When eq 4, 5, and 7 were

$$\log\log\frac{1}{1 - C(M)} = [-c\log b - \log 2.303] + c\log[\eta] \qquad (7)$$

compared, the following equivalences were found

$$Z = B = c$$
$$Y = 2.303 \times 10^A = \left(\frac{1}{b}\right)^c \qquad (8)$$

Weibull's and Tung's distribution parameters are summarized in Table I. The fitting of fractionation data according to Weibull analytical function suggested that this polymer exhibited an asymmetric molecular weight distribution with tailing in the high molecular weight region. This result, certainly, is in contradiction with the belief that Zeigler catalyzed systems show Wesslau distribution.[4]

High fractionation efficiency was obtained with about 99% of the polymer being recovered as fractions, and degradation based on $[\eta]$ data amounted to 5–9%. No change in the tactic content of the polymer during

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TABLE I
WEIBULL'S AND TUNG'S DISTRIBUTION EQUATIONS PARAMETERS

Solvent	Fractionation method	Weibull's *K*	Weibull's *A*	Weibull's *B*	Tung's *Y*	Tung's *Z*
TCB	FPF	0	−0.51 ± 0.05	1.50 ± 0.20	0.71 ± 0.05	1.50 ± 0.20
DEC		0	−0.73 ± 0.06	1.50 ± 0.20	0.43 ± 0.06	1.50 ± 0.20
TCB	CF	0	−0.58 ± 0.03	1.82 ± 0.08	0.60 ± 0.03	1.82 ± 0.08
DEC		0	−0.85 ± 0.03	1.82 ± 0.08	0.32 ± 0.03	1.82 ± 0.08

fractionation was noted. $[\eta]_{\text{TCB}}$ of the fractions varied from 0.348 to 2.608 dl/g for FPF, and 0.130 to 2.780 dl/g for CF. $\overline{M}_w/\overline{M}_n$, an index of polydispersity of the whole polymer was 7.0 and that of some of the fractions 1.1 as shown by initial gel permeation chromatographic (gpc) analyses. Gpc results and conditions of analysis will be presented elsewhere when complete.

In conclusion, TCB–DMP was found to be a useful solvent–nonsolvent system for the fractionation of polypropylene.

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Molecular Weight Dependence of Surface Tension and Refractive Index for Some Poly(ethylene oxide) Derivatives

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The surface tension and density of liquid poly(ethylene glycols)—*i.e.*, hydroxyl-terminated poly(ethylene oxides)—show little dependence on molecular weight.[1,2] On the other hand, the refractive indices of these compounds increase appreciably with chain length[3,4] and this variation has been proposed as a basis for molecular weight determination.[5] It has long been known, however, that the densities of other polymers increase with increasing molecular weight.[6,7] We have also recently noted that the surface tensions of several series of polymer liquids exhibit similar behavior, the variation in this case appearing proportional to $M^{-2/3}$.[8] Both of these effects have been discussed in terms of free volume concepts.

We have now examined the surface tension and refractive index of some methoxy- and acetoxy-terminated poly(ethylene oxides). In these series, there is an appreciable variation of both properties with molecular weight. The functional form of the dependence is the same as that previously noted, *i.e.*, the refractive index is linear in M^{-1}, and the surface tension is linear in $M^{-2/3}$. Furthermore, the values of both properties extrapolated to infinite molecular weight agree closely with similar extrapolated values for the poly(ethylene glycols).

Experimental Section

Low molecular weight compounds were commercial materials. Ethylene glycol diacetate, ethylene glycol dimethyl ether ("dimethyl Cellosolve"), and diethylene glycol dimethyl ether ("dimethyl Carbitol") were distilled before use. Other samples were from freshly opened bottles of Eastman reagents.

The high molecular weight poly(ethylene glycol) diacetates were prepared by acetylation of Carbowax 4000 and 1540 (Union Carbide). A 100% excess of acetic anhydride was added to a 5% solution of the Carbowax in pyridine and the mixture was refluxed for 5–8 hr. Approximately 75% of the solvent was removed by evaporation and the product was isolated by precipitation in diethyl ether cooled to −35°. After drying the polymer under vacuum, a 5% solution in CCl_4 was stirred with 0.75 g of activated alumina per gram of polymer for 30 min. This procedure was repeated twice, filtering the solution after each treatment. The polymer was finally precipitated in hexane at 0°. The products were white solids which gave no indication of hydroxyl groups in either infrared or nmr spectra. Molecular weights were determined by vapor pressure osmometry in CCl_4; the two samples had $\overline{M}_n$ = 1537 and 2393.

Surface tension was measured at 55.6 ± 0.1° by the pendent drop technique; the ring method was used for measurements at 24 ± 1°. The refractive indices were measured with a Zeiss Abbe-type refractometer. Densities were determined pycnometrically.

Results and Discussion

Figures 1–4 show the results of the surface tension and refractive index measurements. On each plot, the solid points represent the polymer samples and open points refer to the lower molecular weight homologues. The corresponding values for the poly(ethylene

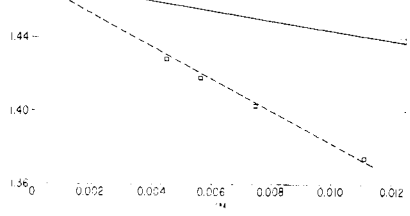

Figure 1. Refractive indices *vs.* $1/M$. Poly(ethylene oxide) dimethyl ethers at 29.5°.

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