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. $[\eta]_{\mathrm{TCB}}$ 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

G. W. Bender, D. G. LeGrand, and G. L. Gaines, Jr.

General Electric Research and Development Center, Schenectady, New York. *Received July 2, 1969*

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

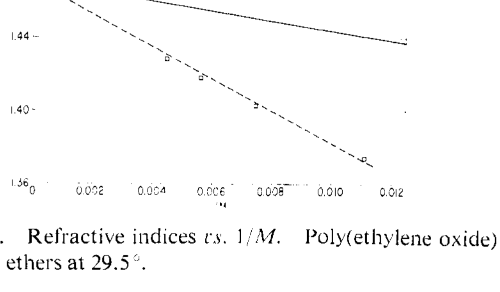

Figure 1. Refractive indices *vs.* $1/M$. Poly(ethylene oxide) dimethyl ethers at 29.5°.

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(1) A. F. Gallaugher and H. Hibbert, *J. Amer. Chem. Soc.*, **59**, 2514 (1937).
(2) "Carbowax" polyethylene glycols, Union Carbide Corp.
(3) A. F. Gallaugher and H. Hibbert, *J. Amer. Chem. Soc.*, **58**, 813 (1936).
(4) A. Weissler, J. W. Fitzgerald, and I. Resnick, *J. Appl. Phys.*, **18**, 434 (1947).
(5) J. D. Ingham and D. D. Lawson, *J. Polym. Sci., Part A*, **3**, 2707 (1965).
(6) P. J. Flory, *J. Amer. Chem. Soc.*, **62**, 1057 (1940).
(7) T. G Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).
(8) D. G. LeGrand and G. L. Gaines, Jr., *J. Colloid Interface Sci.*, in press; see preprints, 43rd National Colloid Symposium.

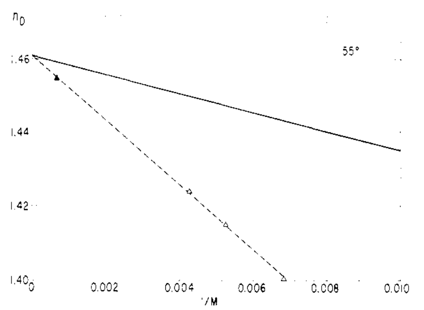

Figure 2. Refractive indices *vs.* $1/M$. Poly(ethylene oxide) diacetates at 55.5°. In Figures 1 and 2, solid lines represent poly(ethylene glycols) at the corresponding temperature, from data of Ingham and Lawson.[5]

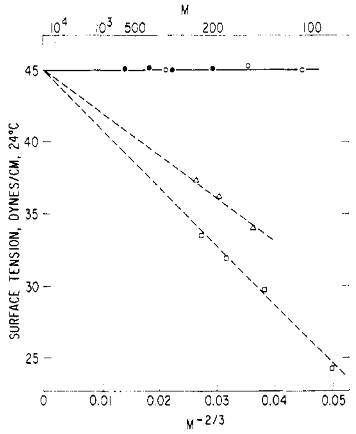

Figure 3. Surface tension of poly(ethylene oxide) derivatives at 24°: ○, ●, poly(ethylene glycols) (data of Gallaugher and Hibbert[1] and ring measurements in this laboratory); △, poly(ethylene oxide) diacetates; ☐, poly(ethylene oxide) dimethyl ethers (data of Gallaugher and Hibbert[1] and A. I. Vogel, [*J. Chem. Soc.*, 616 (1948)] for di- and tetraethylene oxide dimethyl ethers, respectively).

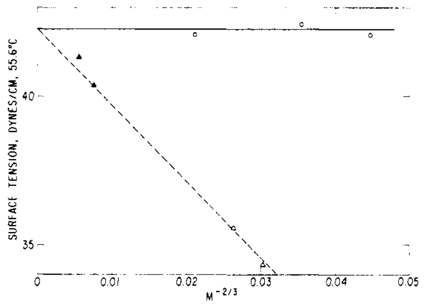

Figure 4. Surface tension of poly(ethylene oxide) diacetates at 55.6° (△, ▲). Data for poly(ethylene glycols) at 55.6° (○) from data of Gallaugher and Hibbert[1] included for comparison.

glycols) are also indicated. The dashed straight lines, drawn in each case to intercept the infinite molecular weight axis at the extrapolated poly(ethylene glycol) value, appear to represent the data adequately.

Some comment is needed concerning the first member of each series. The refractive indices of these materials appear to fit the molecular weight correlation shown in Figures 1 and 2. Their surface tensions, however, are anomalous. Ethylene glycol has a higher surface tension than the higher glycols over the temperature range 20–150°.[1] Ethylene glycol diacetate, which fits the $M^{-2/3}$ correlation at room temperature, has a lower surface tension at 55.6° than would be predicted. A cursory examination over the temperature range 6–70° shows $d\gamma/dT = -0.125$ dyn/cm/deg, about twice the value for the higher diacetates. The fit at room temperature, therefore, appears to be accidental. Consideration of the structure of ethylene glycol and its diacetate shows that they differ from the higher homologues in that they contain no $-CH_2OCH_2-$ segments and suggests that they should not be considered members of these homologous series.

We have already noted the relevance of free volume concepts to the molecular weight dependence of these properties. The coincidence of the extrapolated infinite molecular weight values indicated in the figures would appear to lend further credence to this (admittedly vague) interpretation. Measurements of glass transition temperatures for these derivatives would permit comparison with our earlier attempt[8] to provide a quantitative connection to free volume theory. Unfortunately, our attempts (by differential scanning calorimetry) to obtain such measurements on the poly(ethylene oxide) diacetates have not yielded meaningful results because of the strong tendency of the samples to crystallize. Hence we prefer not to attempt a more detailed discussion at the present time.

Thermoelastic Behavior of Some Acrylic Polymers

M. Shen,[1] E. H. Cirlin, and H. M. Gebhard

Science Center, North American Rockwell Corporation,
Thousand Oaks, California 91360.

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In previous publications from this laboratory, we have proposed a new equation for the calculation of the relative energy contribution to the elasticity of polymers in the rubbery state[2]

$$f_e/f = 1 - \frac{d \ln G}{d \ln T} - \beta_L{}^0 T \qquad (1)$$

where f is the total force, f_e is the energetic component of the elastic force, T is absolute temperature, $\beta_L{}^0$ is the linear thermal expansion coefficient of unstrained rubber, and G is the shear modulus. The latter is defined by the equation of state for rubber elasticity

$$f = GA_0(\lambda - V/V_0\lambda^2) \qquad (2a)$$

and

$$G = (NRT/V_0)(\overline{r_i^2}/\overline{r_f^2}) \qquad (2b)$$

In eq 2, λ is the extension ratio, L/L_0; L_0, A_0, and V_0 are the length, cross-sectional area, and volume of the rubber at zero pressure, zero force; and L and V are the length and volume at force f, and pressure P; N is the number of moles of network chains in the sample; R is the gas constant; $\overline{r_i^2}$ is the mean square

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[1] Address correspondence to this author at the Department of Chemical Engineering, University of California, Berkeley, California 94720.

(2)(a) M. Shen and P. J. Blatz, *J. Appl. Phys.*, 39, 4937 (1968); (b) M. Shen, *Macromolecules*, 2, 358 (1969).