TABLE VI

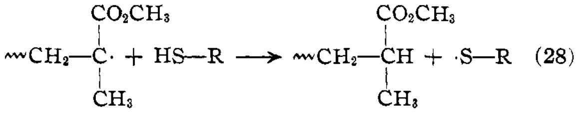
TRANSFER CONSTANTS OF THIOLS WITH MMA AT 60°

Thiol	C_s	Thiol	C_s
2-Naphthalenethiol	(3.1)[a]	2-Mercaptoethanol	0.62
Benzenethiol	2.7	2-Propanethiol	.38
1-Butanethiol	0.66	2-Methyl-2-propanethiol	.18
Ethyl mercaptoacetate	0.63		

[a] This value is relatively uncertain, for reasons discussed in the text.

benzenesulfenyl radical.[36] The increased stability of the radicals derived from the aromatic thiols is also reflected in their ability to produce a slight retardation of the polymerization rate. A related observation is the finding that benzenethiol is about four times more effective than benzyl mercaptan in promoting the degradation of rubber by the cold mastication process.[37] The mechanism postulated for this reaction involves chain transfer of the thiol with polymer radicals produced by the rupture of rubber molecules.[37]

The C_s values for 1-butanethiol (0.66), ethyl mercaptoacetate (0.63) and 2-mercaptoethanol (0.62) suggest that electron-withdrawing substituents may cause a slight *decrease* in the transfer activity of a primary thiol. However, the observed differences are so small that we cannot be certain they are real. In any event, it is clear that polar phenomena[13,35] play a very minor role in the reaction of a thiol with poly(MMA) radicals (equation 28).



$$\sim\!\!\sim CH_2-\overset{CO_2CH_3}{\underset{CH_3}{C\cdot}} + HS-R \longrightarrow \sim\!\!\sim CH_2-\overset{CO_2CH_3}{\underset{CH_3}{CH}} + \cdot S-R \quad (28)$$

In contrast, Gregg, Alderman and Mayo[11] reported that ethyl mercaptoacetate was approximately *three times more reactive* than a simple 1-alkanethiol toward polystyrene radicals. This result may perhaps be explained in terms of a facilitation of electron transfer from the polystyrene radical to the thiol in the transition state.[13]

The reported decrease in activity of a thiol toward polystyrene radicals which accompanies substitution of methyl groups on the α-carbon atom of the thiol[11] is paralleled here in the series: 1-butanethiol (0.66), 2-propanethiol (0.38), 2-methyl-2-propanethiol (0.18). This appears to be a straightforward example of steric hindrance. However, it is interesting to note that the approximately fourfold decrease in C_s in going from a primary to a tertiary thiol is slightly *less* than the corresponding (sixfold) decrease in the case of the monomer styrene. On the basis of steric considerations alone, a larger relative decrease for the "tertiary" poly(MMA) radical would be anticipated.[38] This result shows the difficulty encountered in attempts to correlate the reaction rates of polymer radicals on the basis of a single theoretical principle.

Acknowledgment.—The authors wish to thank Dr. J. F. Kincaid for his constant inspiration and Dr. T. G. Fox for many helpful suggestions. We are also indebted to Mr. H. Nields for assistance in the experimental work.

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[36] H. Z. Lecher, *Science*, **120**, 220 (1954).

[37] M. Pike and W. F. Watson, *J. Polymer Sci.*, **9**, 229 (1952).

[38] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 254–256.

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.' INC.]

Dissymmetry of Molecular Light Scattering in Polymethyl Methacrylates[1]

BY F. W. BILLMEYER, JR., AND C. B. DE THAN

RECEIVED MAY 2, 1955

A new angular dissymmetry light scattering instrument for molecular weight measurements was used in studying the molecular characteristics of polymethyl methacrylates of molecular weights between 35,000 and 10,000,000. Viscosity-molecular weight relations in butanone ($[\eta] = 6.8 \times 10^{-5} M^{0.72}$) and acetone ($[\eta] = 7.5 \times 10^{-5} M^{0.70}$) agreed within experimental error with those reported in the literature. Similar relations in chloroform and ethylene dichloride are not in good agreement with other results, primarily because shear rate corrections were omitted. Polymethyl methacrylates with high molecular weights and broad distributions showed curved Zimm plots associated with polydispersity. These plots could be analyzed to obtain $\bar{r}_z$, $\bar{r}_n$ (the z- and number-average molecular sizes), and $\bar{M}_w$, but not $\bar{M}_n$.

Introduction

During the last decade light scattering has become an accepted and established method for measuring polymer molecular weights. Although several good commercial instruments for making light scattering measurements are available, no one of them, in our opinion, meets all the demands that might be made by workers in today's highly developed field of polymer science. One might ask, for example, for higher sensitivity, freedom from stray light, better angular resolution, more satisfactory optical geometry, easier operation, or more flexibility to meet unusual conditions such as high temperature operation.

This paper describes some studies made with a light scattering instrument which meets many of these demands. The performance of the instrument at room temperature was assessed by measuring the molecular weights and sizes of a series of polymethylmethacrylate samples.

Experimental

Angular Dissymmetry Instrument.—The detailed design of the instrument and its execution were carried out by F. J. Baum and W. H. Aughey[2] to performance specifications as proposed by J. B. Nichols and F. W. Billmeyer, Jr.

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[1] Presented at the 126th National Meeting of the American Chemical Society, New York, N. Y., September 17, 1954.

[2] Chemical Department of the du Pont Company.

The dissymmetry instrument differs in function and design from the angular-dependence unit described by Aughey and Baum[3] and by Sloan.[4] The angular-dependence instrument is intended for measurement of light scattered at very small angles with a high degree of angular resolution, whereas the angular dissymmetry unit is designed for measuring over the angular range of 20 to 160° from the primary light direction, with moderate resolution and high sensitivity. The former is used for characterization of particles above 0.1 μ in radius, the latter for molecular parameters.

The dissymmetry instrument has a mercury arc source operating from an autoreactive transformer fed from a voltage regulator. Light from this lamp passes through a condenser lens, a monochromatizing filter, a polarizer, and an optical system designed to obtain an intense beam of uniform cross section, substantially free from stray light, across the length of the scattering cell. The scattering cell is a right cylinder with a plane window for the entering beam and a black glass block to absorb the beam beyond the sample. The cell compartment is enclosed and equipped with a heating mantle. Temperature is controlled by a thermocouple in the cell and an electronic thermocouple controller. The instrument has operated successfully for long periods at temperatures as high as 150°.

Scattered light passing out of the cell and through a semicircular window in the cell compartment is focused by a lens upon a receiving slit in front of the photomultiplier tube. The slit is adjusted so that the receiver does not see past the edges of the light beam at any time. The angular resolution is about five degrees.

The phototube is driven in a circular arc around the cell by means of a synchronous motor. Angular position is indicated by a counter and by "pip" marks made on the recorder chart paper by a pen activated by micro-switches on the drive shaft.

Below the cell in the cell compartment is a diffusing block which acts as a working standard of light intensity. This block is placed in the optical path by raising the entire cell compartment by means of a handle on the front panel. Light from the block is received through a neutral filter by the phototube in the 90° position.

High voltage for the multiplier phototube is obtained from a regulated power supply. The phototube is a type IP21 selected for high sensitivity and low dark current. Its output signal is transmitted to a high impedance strip chart recorder.

Controls for the instrument are mounted below the optical train. Limit switches, shutters and other safety devices are provided.

The instrument was calibrated in two independent ways. (1) The turbidity of a standard polystyrene sample[5] was assumed to be 3.5×10^{-3} when dissolved in toluene at a concentration of 0.5 g./100 cc. and measured in mercury blue light. (2) The turbidities of a series of "Ludox" silica sols,[6] measured in a Beckman DU spectrophotometer, were used for the second calibration. The two calibrations were in excellent agreement.

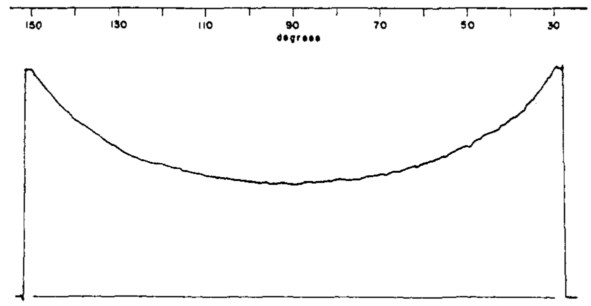

Fig. 1.—Typical recorder chart for calibration with fluorescein.

Figure 1 shows a typical recorder trace for a slightly basic solution of fluorescein in water. After the geometrical correction factor[7] proportional to the sine of the angle of observation was applied, the observed intensities were constant within 1% over the angular range 30 to 150°. In a test at a considerably lower light level, the turbidity of well filtered butanone was found to be constant within 2% over the same angular range.

Figure 2 shows a typical recorder trace for a polymer solution showing considerable angular dissymmetry. The break in the trace at low angles is due to a change in range of the recorder. A trace from the calibrating block is superimposed on the polymer record. The time to traverse the total angular range is 10 minutes.

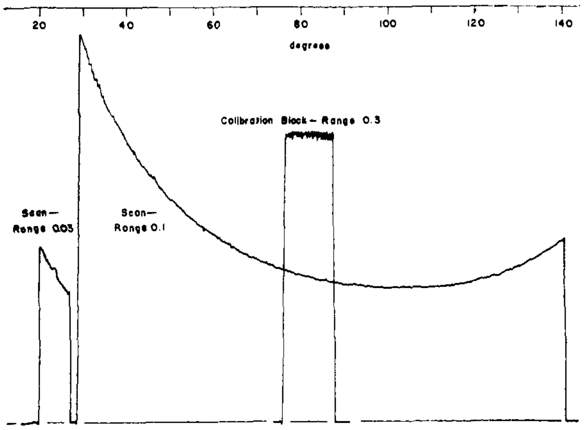

Fig. 2.—Typical recorder chart for polymer solution showing dissymmetry.

As a final example of the performance of the instrument, Table I shows some molecular parameters of one of the standard polystyrene fractions studied by the International Union of Pure and Applied Chemistry,[8] and by Outer, Carr and Zimm.[9] Some of the minor differences shown here may have been caused by factors such as solvent purity rather than instrument performance.

Table I

Molecular Parameters of Polystyrene Fraction (2–1–1949)-2; or III

Quantity	This work	International Union[8]	Outer, Carr and Zimm[9]
$\bar{M}$w	1,030,000	960,000–1,010,000	980,000
$A_2 \times 10^4$	1.29	1.15–1.20	1.05
z_{45} (c = 0)	1.44	1.37–1.45	1.36
$\bar{r}_z$, Å.	1120		920
μ	0.4871		0.4895

Samples.—Samples 1–4 were relatively broad fractions from a polymethyl methacrylate made by a suspension polymerization technique. The fractions were prepared by B. M. Marks of this Laboratory by precipitation with hexane from acetone solution. Sample 3 is the material designated M by Billmeyer and Stockmayer.[10] The fractions covered the molecular weight range from 35,000 to 300,000. Samples 5–10 were relatively heterogeneous experimental cast whole polymers which had weight-average molecular weights between 600,000 and 10,000,000.

Light Scattering Measurements.—The light scattering measurements were made at room temperature with butanone as the solvent. Mercury green light (5461 Å.) was used. The refractive index gradient dn/dc was measured

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(3) W. H. Aughey and F. J. Baum, *J. Opt. Soc. Am.*, **44**, 833 (1954).

(4) "Angular-Dependence Light Scattering," a series of papers by C. K. Sloan, C. H. Arrington and C. J. Wortz, presented at the 125th National Meeting of the American Chemical Society, Kansas City, Missouri, April 1, 1954.

(5) B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950).

(6) W. F. H. M. Mommaerts, *J. Colloid Sci.*, **7**, 71 (1952).

(7) J. J. Hermans and S. Levinson, *J. Opt. Soc. Am.*, **41**, 460 (1951).

(8) International Union of Pure and Applied Chemistry, *J. Polymer Sci.*, **10**, 129 (1953).

(9) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 850 (1950).

(10) F. W. Billmeyer, Jr., and W. H. Stockmayer, *J. Polymer Sci.*, **5**, 121 (1950).

on a differential refractometer as 0.112 cm.^{3}/g., in good agreement with the value of 0.111 cm.^{3}/g. reported by Desreux.[11] The light scattering constant $H = 1.46 \times 10^{-6}$.

Selas FD54 porous porcelain filter candles (Selas Corp. of America) of grade 03 (0.6 μ rated maximum pore radius) were used to clarify all of the polymer solutions. Polymer concentrations were determined by evaporating the contents of the light scattering cell to dryness at the end of each run.

Intrinsic Viscosity Measurements.—Intrinsic viscosities were measured in butanone, acetone, chloroform and ethylene dichloride. The measurements were made in Ubbelohde suspended level viscometers modified to allow successive dilutions to be made in the viscometer, or in Ostwald–Fenske viscometers. Shear corrections were made only for ethylene dichloride solutions of polymers with $\bar{M}_w > 10^6$. Intrinsic viscosities are expressed in deciliters per gram.

Results

Table II lists the weight-average molecular weights, second virial coefficients and z-average root-mean-square end-to-end distances $\bar{r}_z$ obtained from the light scattering of polymethyl methacrylate samples in butanone.

TABLE II

MOLECULAR PARAMETERS OF POLYMETHYL METHACRYLATES IN BUTANONE

Sample	$\bar{M}_w$	$A_2 \times 10^4$	$\bar{r}_z$, Å.
1	34,000	2.78	..
2	56,000	2.88	..
3	167,000	2.55	..
4	306,000	1.95	..
5	620,000	2.19	960
6	715,000	1.74	915
7	2,000,000	1.54	1710
8	2,800,000	1.54	2140
9	4,600,000	0.99	3040
10	9,800,000	1.46	4700

Virial Coefficients.—The second virial coefficients A_2 in butanone ranged from 1 to 3 $\times 10^{-4}$, corresponding to μ values of 0.46 to 0.49. They are in fair agreement with a value of 3.22×10^{-4} at $\bar{M}_w$ = 760,000 quoted by Bischoff and Desreux[11] and in good agreement with a value of 2.39×10^{-4} at $\bar{M}_w$ = 136,000 quoted by Casassa.[12] A_2 decreased with increasing molecular weight, roughly as the 0.15 power of the molecular weight. Flory's lattice theory[13] of the virial coefficient predicts that the quantity $A_2M/[\eta]$ should be almost independent of M. Our data scatter somewhat but group around the value of 130 which has been found for several other polymers in good solvents.

Molecular Size.—The z-average end-to-end distances $\bar{r}_z$ were calculated from the initial slopes of Zimm plots of the light scattering data for the whole polymer samples, numbers 5–10. The dissymmetry of the light scattering from the fractionated samples 1–4 was too small to allow reliable estimates of $\bar{r}_z$. Values of $\bar{r}_z$ are proportional to $\bar{M}_w^{0.60}$ (Fig. 3). They are about 1.3 times the sizes for fractions reported by Bischoff and Desreux[14] (also shown in Fig. 3).

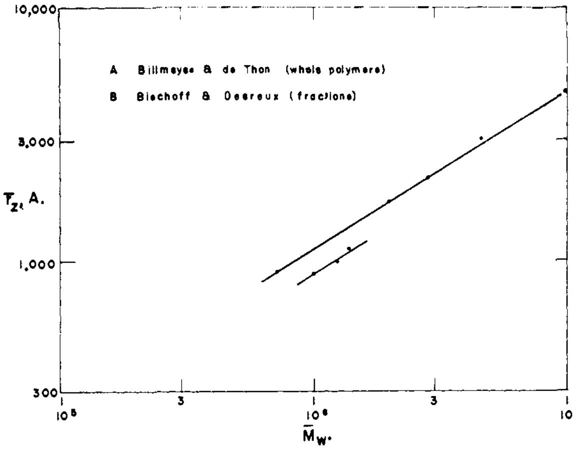

Fig. 3.—Molecular size of polymethyl methacrylates in butanone.

Viscosity–Molecular Weight Relations.—The logarithms of the intrinsic viscosities of the polymethyl methacrylates in acetone, butanone, chloroform and ethylene dichloride are plotted against the logarithms of their molecular weights in Fig. 4.

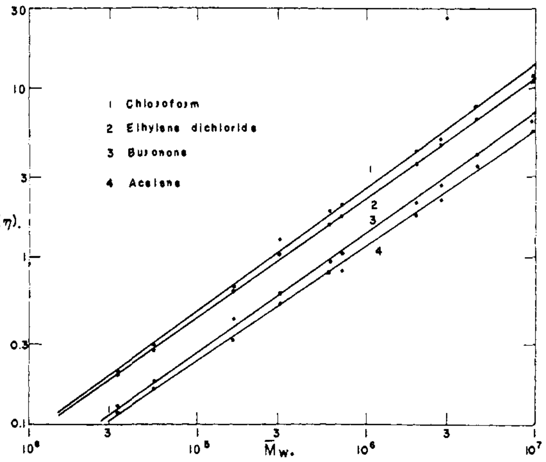

Fig. 4.—Viscosity–molecular weight relations for polymethyl methacrylates.

In the cases of acetone and butanone, the lines are those of Bischoff and Desreux.[11] Our points agree within experimental error. The corresponding equations are

$$[\eta] = 6.8 \times 10^{-5}\ \bar{M}_w^{0.72}\ \text{(butanone, 25°)}$$

$$[\eta] = 7.5 \times 10^{-5}\ \bar{M}_w^{0.70}\ \text{(acetone, 25°)}$$

In the case of acetone solutions, Fox[15] and Cantow and Schulz[16] give similar equations based on light scattering experiments, but Meyerhoff and Schulz' ultracentrifuge results[17] are slightly different.

Our viscosity results in the chlorinated solvents are not in good agreement with those of other researches. We believe that this derives in part at least from the fact that corrections for shear rate were not applied. In the case of chloroform, Bischoff and Desreux,[11] Meyerhoff and Schulz,[17] Can-

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[11] J. Bischoff and V. Desreux, *Bull. soc. chim. Belges*, **61**, 10 (1952).

[12] E. F. Casassa, Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1953.

[13] P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

[14] J. Bischoff and V. Desreux, *J. Polymer Sci.*, **10**, 437 (1953).

[15] T. G. Fox, Jr., private communication.

[16] H.-J. Cantow and G. V. Schulz, *Z. physik. Chem. N. F.*, **2**, 117 (1954).

[17] C. Meyerhoff and G. V. Schulz, *Makromol. Chem.*, **7**, 294 (1952).

tow and Schulz,[18] and Baxendale, Bywater and Evans[19] all give equations approximating

$$[\eta] = 4.8 \times 10^{-5}\, \bar{M}_w{}^{0.80} \text{ (chloroform, 25°).}$$

For ethylene dichloride, our preferred relation is

$$[\eta] = 1.7 \times 10^{-4}\, \bar{M}_w{}^{0.68} \text{ (ethylene dichloride, 25°).}$$

Flory–Fox Parameters.—The Flory–Fox[20] theory of intrinsic viscosity should strictly be applied only to fractionated polymers. Since our fractions were too low in molecular weight to show appreciable angular dissymmetry we made no attempt to evaluate Flory's constant ϕ. Other constants of of the theory, K, C and α, defined by the equations

$$[\eta] = KM^{1/2}\alpha^3$$
$$\alpha^5 - \alpha^3 = CM^{1/2}$$

were evaluated from plots of $[\eta]^{2/3}/M^{1/2}$ *vs.* $M/[\eta]$. As shown in Table III, the values of K we obtained were not far from that of 1.0×10^{-3} found for many other polymers. The parameter α represents the ratio by which the polymer coil is expanded in solution over its size in the absence of the excluded volume effect. We did not make any experiments in a θ-solvent in which $\alpha = 1$.

TABLE III

FLORY–FOX PARAMETERS FOR POLYMETHYL METHACRYLATE

Solvent	$K \times 10^3$	$C \times 10^3$	α at $M = 10^6$
Ethylene dichloride	0.66	4.1	1.5
Chloroform	.48	9.7	1.8
Butanone	.60	1.5	1.3
Acetone	.54	1.4	1.3
Av.	0.57		

Discussion

Recently Benoit, Holzer and Doty[21] investigated the asymptotic behavior of the function $P(\theta)$ which describes the angular distribution of scattered light for a monodisperse system of randomly coiling molecules. It is well known that the initial intercept and slope of this function, averaged over all molecular species present in a heterogeneous mixture, correspond to the inverse weight-average molecular weight and the z-average molecular size, respectively. Benoit, Holzer and Doty show that the function approaches an asymptote at high angles also, and that the asymptotic intercept and slope correspond to the inverse of twice the number-average molecular weight and to the number-average molecular size, respectively.

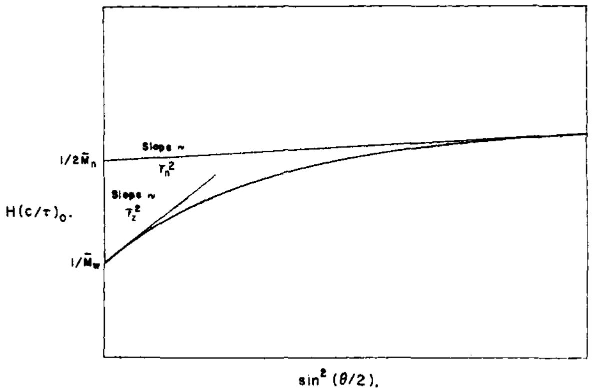

Fig. 5.—Asymptotic behavior of Zimm plot (after Holzer, Benoit and Doty[21]).

Thus, as illustrated in Fig. 5, one should be able to obtain $\bar{M}_n$, $\bar{M}_w$, $\bar{r}_n$ and $\bar{r}_z$ from a single light scattering experiment, provided that the polymer is large enough that both the limiting tangents can be obtained in the available angular range.

Stockmayer and Schultz[22] have analyzed the problem in more detail. As shown in Fig. 6, they find that it is likely that the correct slope of the high angle asymptote will be approached much sooner than the correct intercept, so that in practice $\bar{r}_n$, $\bar{r}_w$ and $\bar{M}_w$, but not $\bar{M}_n$, may be estimated for some high molecular weight samples.

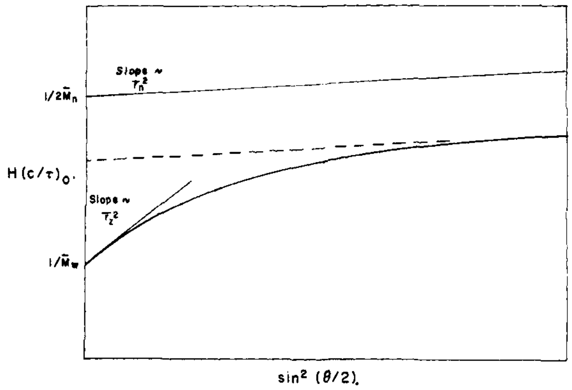

Fig. 6.—Asymptotic behavior of Zimm plot (after Stockmayer and Schultz[22]).

As shown in Fig. 7, the Zimm plot for our highest molecular weight sample shows clearly the curvature associated with polydispersity at high molecular weights. The data taken at the low and high angle ends of the plot tend to confirm Stockmayer and Schultz's conclusions. The value of $\bar{r}_z$ = 4700 Å. is consistent with our data for lower molecular weight samples. The value of $\bar{r}_n$ = 3650 Å. is very close to that obtained by extrapolating Bischoff and Desreux' sizes for fractions to higher molecular weights with a slope equal to that of our own z-average data. The value of r calculated from Flory's ϕ is 3100 Å.

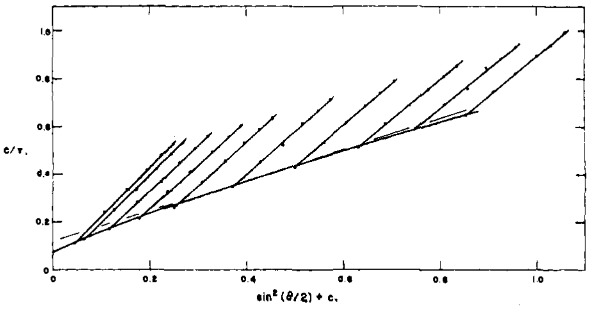

Fig. 7.—Zimm plot of polymethyl methacrylate sample 10; $\bar{M}_w$ = 9,800,000.

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(18) H.-J. Cantow and G. V. Schulz, ref. 16, see also H.-J. Cantow, T. Pouyet and C. Wippler, *Makromol. Chem.*, **14**, 110 (1954).

(19) J. H. Baxendale, S. Bywater and M. G. Evans, *J. Polymer Sci.*, **1**, 244 (1946).

(20) P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

(21) H. Benoit, A. M. Holzer and P. Doty, *J. Phys. Chem.*, **58**, 635 (1954).

(22) W. H. Stockmayer and A. R. Schultz, private communication.

The number-average molecular weight of this sample was not measured, but we expect a value not much over 1,000,000, since the polymer was made under conditions where the chain termination was diffusion controlled.[23] We have shown before[10] that such polymers have broad molecular weight distributions. The intercept of the high angle asymptote of sample 10 corresponds to a number-average molecular weight of nearly 3,000,000, however.

A more severely curved Zimm plot (Fig. 8) was obtained from a sample with a very broad molecular weight distribution made by mixing 1 part of sample 10 and 10 parts of sample 3. The observed weight-average molecular weight of the mixture agrees well with the calculated value of just over 1,000,000.

The number-average molecular weight of the mixture is essentially the same as that of sample 3, or about 130,000. The high angle asymptote gives $\bar{M}_n$ = 170,000.

The value of $\bar{r}_n$ for this sample, from the high angle slope, is 935 Å., identical with the size found by Bischoff and Desreux for a fraction with a molecular weight of 1,000,000.

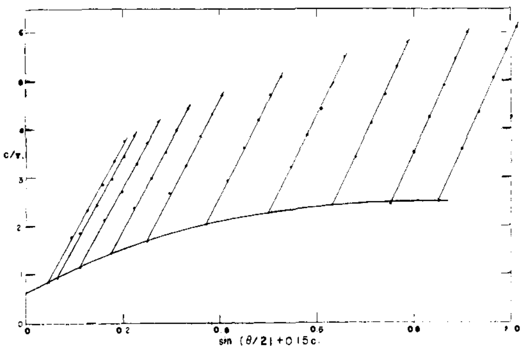

Fig. 8.—Zimm plot of a mixture of polymethyl methacrylate samples 10 (1 part) and 3 (10 parts).

The value of $\bar{r}_z$ = 3400 Å. for this sample appears too low, as it should correspond to that found for one of our whole polymers with the same z-average molecular weight as the mixture. We estimate this size to be well over 5,000 Å.

WILMINGTON, DEL.

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[23] E. Trommsdorff, H. Kohle and P. Lagally, *Makromol. Chem.*, **1**, 69 (1947); G. V. Schulz and G. Harborth, *ibid.*, **1**, 104 (1947).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEXAS TECHNOLOGICAL COLLEGE]

Electric Moments of Some Alkyl Phosphates and Thiophosphates

BY GEORGE K. ESTOK AND WESLEY W. WENDLANDT

RECEIVED FEBRUARY 28, 1955

Electric moments at 25° in benzene solution have been determined for triethyl- and tri-*n*-butyl phosphate, and triethyl- and tri-*n*-butyl thiophosphate. The respective values are 3.08, 3.07, 2.82 and 2.84. From this, and other work, the values of 3.3 ± 0.1 and 3.0 ± 0.1 have been assigned as the most probable bond moments for the $P \rightarrow O$ and $P \rightarrow S$ semi-polar bonds, respectively. Dielectric constants were also determined for liquid tri-*n*-butyl phosphate (8.05 ± 0.05) and tri-*n*-butyl thiophosphate (6.82 ± 0.03), and the respective moments calculated by Onsager's equation are 3.35 and 3.02.

Disagreements have been noted in the literature relative to assigned values for the bond moments of the semi-polar $P \rightarrow S$ and $P \rightarrow O$ bonds in certain compounds. From electric moment determinations of thiophosphoryl chloride ($PSCl_3$) and phosphorus oxychloride ($POCl_3$),[1] and triphenyl thiophosphate and triphenyl phosphate,[2] Smyth and co-workers arrived at values of 2.5 and 3.2 *D*, respectively, for the $P \rightarrow S$ bond moments in $PSCl_3$ and triphenyl thiophosphate, and 3.5 *D* for the $P \rightarrow O$ bond moments in both the oxychloride and the phosphate. The low value of 2.5 for the $P \rightarrow S$ moment in $PSCl_3$ is reasonably attributed to the easy polarization of the sulfur atom by the highly electronegative chlorine atoms. Arbuzov and Shavsha[3] worked with alkyl thiophosphates which led them to assign what seems an abnormally high value of 3.55 *D* for the $P \rightarrow S$ bond moment. Arbuzov and Rakov[4] worked with alkyl phosphates, and in this case were in agreement with Smyth by assigning 3.5 for the $P \rightarrow O$ moment.

Svirbely and Lander,[5] from a moment determination on triethyl phosphate chose a value of 2.8 for the $P \rightarrow O$ moment, a value also suggested by Lister and Sutton[6] on the basis of unpublished work by a colleague (J. S. Hunter). Recalculations[7] on the method of Svirbely and Lander (hereinafter called Method II) indicate that 2.7 would derive from their treatment instead of 2.8 as published. If 1.2 for the P–O covalent link moment (from work of Lewis and Smyth, hereinafter called Method I) is used, instead of 1.4, then the semipolar $P \rightarrow O$ moment calculates to be 2.5 by Method II. Thus, depending on method and assumptions used, values ranging from 2.5 to 3.5 have been calculated for the $P \rightarrow O$ bond moment.

The experimental work and analysis reported here were undertaken to help clarify the above mentioned situation, particularly in view of the fact that the moments previously reported[3] for certain alkyl thiophosphates appeared anomalous.

Experimental

Triethyl phosphate, an Eastman Kodak Co. yellow label product, was carefully fractionated at reduced pressure

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[1] C. P. Smyth, G. L. Lewis, A. J. Grossman and F. B. Jennings, THIS JOURNAL, **62**, 1219 (1940).

[2] G. L. Lewis and C. P. Smyth, *ibid.*, **62**, 1529 (1940).

[3] B. A. Arbuzov and T. G. Shavsha, *C. A.*, **46**, 3817d (1952).

[4] A. E. Arbuzov and P. I. Rakov, *ibid.*, **44**, 8713g (1950).

[5] W. J. Svirbely and J. J. Lander, THIS JOURNAL, **70**, 4121 (1948).

[6] M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939).

[7] Dr. Svirbely advises by private communication that errors in calculation occurred in connection with use of his equations 7, 6, and 1, in reference 5.