THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

AN EXPERIMENT IN THE LIGHT-SCATTERING
OF A HIGH POLYMER SOLUTION

J. A. Manson

L. M. Hobbs

ACKNOWLEDGMENTS

TABLE OF CONTENTS

INTRODUCTION

During the last few years measurements of light-scattering
have provided much useful information about the properties and be-
haviour of high polymers in solution. The weight-average molecular
weight may be calculated from the intensity of scattering at a given
angle, the molecular extension in solution from the angular distribu-
of the intensity of scattering, and the osmotic second virial coeffi-
cient from the dependence of the scattering on concentration. Further-
more, the relationship between weight-average molecular weight and
intrinsic viscosity for a series of fractions is also valuable in the
characterization of a high polymer.

Now that excellent light-scattering photometers are avail-
able commercially, the routine use of scattering measurements for the
study of high polymers has gained widespread acceptance. When plans
were made for an intensive lecture and laboratory summer course in
the structure of high polymers at the University of Michigan in 1955,
it seemed, therefore, appropriate to include an experiment in light-
scattering in the experimental portion of the course. Accordingly,
an experiment was developed and integrated both with a series of
lectures on the characterization of a high polymer and with other
experiments. As well as light-scattering, such subjects as the fol-
lowing were discussed in lectures[2] and studied in laboratory classes:

---

[2] The lecturers in the course were Drs. F. Bueche, L. H. Cragg, S.
Krimm, R. Simha, and S. G. Weissberg.

---

osmotic pressure, viscosity, sedimentation and diffusion, and infrared
spectra.

Although the summer course was attended mainly by experienced scientists who wished either to learn new techniques or to review old ones, a similar experiment has been used successfully for two semesters in our laboratory course in high polymers for graduate and senior students. As we had hoped, the results obtained in the regular courses have been useful for research as well as instructional purposes. We have, therefore, described the basic experiment below in the hope that it may be useful to others interested in studying the properties of high polymers in dilute solution.

DESIGN OF THE EXPERIMENT

The basic theory of light-scattering has been presented and discussed adequately (1-6) in the literature. However, as with most new experimental methods, the reading of articles dealing with a diversity of research applications raises many questions regarding experimental technique and interpretation. Such problems as the clarification of solutions, the uncertainty of calibration of a so-called "absolute" method for determining molecular weights, and the effects of heterogeneity, become apparent to the reader; solutions to these problems are not, unfortunately, as apparent, and vary with the application and with the author concerned. To the reader interested in light-scattering mainly for routine measurements, an undesirable air of mystery may thus develop about this tricky but useful technique.

The experiment described below was intended to remove some of the mystery by making it possible for students to obtain results that are useful in themselves, not only for illustrating the possibilities inherent in light-scattering, but also for research. Once the base of experience provided by the experiment has been obtained, techniques can always be modified to suit other applications.

In order to make the experiment challenging and profitable, it was decided that the determination of the viscosity-molecular weight relationship -- one of the most basic properties of a solvent-polymer system -- would be attempted. In this experiment, viscosity data (that is, measurements of the intrinsic viscosity, $[\eta]$) were already available for solutions of the fractions used in benzene and butanone (7,8). In application of this experiment elsewhere, of course, the light-scattering measurements could readily be integrated with the preparation,

fractionation, and characterization by viscosity measurement, of a high polymer. Polystyrene was chosen as the polymer; benzene was chosen as the solvent instead of a more polar, and hence more difficult to clarify, liquid. Although other polymers and solvents can be used, this choice of polymer and solvent has been quite satisfactory.

As mentioned above, the basic principles of light-scattering were discussed in separate lectures. After a short preliminary introduction to the experiment at the beginning of the laboratory period, experimental details such as clarification, calibration, and determination of the refractive index increment were discussed during the experiment itself.

The class of twenty-two was divided into five groups, to each of which was assigned a 2.5-hour laboratory period. As long as certain preparations described below were made beforehand by the instructor, this period was adequate for each group to obtain enough data for the study of one fraction. Each student determined scattering ratios at 45, 90 and 135 degrees for one concentration of polymer; thus data for a given fraction were obtained at four or five concentrations. Calculations were made on a prepared record sheet while the experiment was in progress.

At the end of the week, during a general summary lecture, the curve relating intrinsic viscosity to molecular weight was constructed and discussed.

EXPERIMENTAL

1. Advance Preparations

The following preparations were made before the laboratory periods:

1. The fractions of polystyrene used had been obtained previously (7, 8).

2. Before the laboratory periods, stock solutions of the polystyrene fractions in reagent-grade benzene were prepared. Although solutions were clarified by centrifuging for two hours at 25,000 g using a Servall high-speed angle centrifuge, Model SS-1a, satisfactory clarification could also be obtained by filtration through a fine or ultra-fine Corning sintered-glass filter. Concentrations of the stock solution were corrected for the loss of solvent during centrifuging by comparing the weights of the centrifuge tube and contents before and after centrifuging. Solutions were stored in bottles that had been rinsed six times with centrifuged solvent before use.

3. The value of the refractive index increment, dn/dc, was determined using a Hilger interference refractometer. For polystyrene in benzene, the value found was 0.106 for light (λ = 436 mμ) at 27°C.

4. Calibration of the light-scattering photometer, which was a Brice-Phoenix instrument, series 1000, was accomplished using dispersions of colloidal silica, "Ludox", the turbidities of which were determined independently by means of a Beckman model DU spectrophotometer equipped with 10-cm cells. Both scattering ratios and turbidities were corrected for the contribution due to the solvent.

From the slope of the linear curve relating the corrected observed scattering ratio to the corrected turbidity, τ, the calibration

constant was determined -- 0.131 in this case. Since the calibrating

medium used, water, has a refractive index different from that of

benzene, all instrument readings were multiplied by an appropriate

correction factor (10): $n_b(A' + Bn_b)/n_w(A + Bn_w)$, where n_b and n_w

are the refractive indices of benzene and water, respectively, A is

the distance from the cell wall to the center of the incident beam,

and B is the distance from the cell wall to the photomultiplier. For

our instrument, the value of this correction term was 1.33, so that

τ = 0.131 x 1.33 x S_{90}, where S_{90} is the scattering ratio for a polymer

solution, measured at 90 degrees and corrected for solvent scattering.

For solutions of polystyrene in benzene at 27°C, the following equa-

tion held for our instrument:

$$H \frac{c}{\tau} = 2.47 \times 10^{-5} \times \frac{c}{S_{90}}$$

where H is a constant for a given wavelength and polymer solution[3], and

---

---

c is the concentration in grams of polymer per milliliter of solution.

The calibration was checked using a sample of polystyrene distributed

by Professor Debye's laboratory. The turbidity, corrected for solvent,

of a 0.5 percent (0.5 g polymer/100 ml solvent) of this polymer in

toluene was found to be $3.56(\pm 0.03) \times 10^{-3}$ cm^{-1}. This result agrees

well with values determined elsewhere (see, for example, references 10

to 15, inclusive); the "best" average value is given by Notley and Debye (16) as 3.52×10^{-3} cm^{-1}.

2. Class Procedure

An hour before the laboratory period, the centrifuge, containing benzene, was started and the photometer turned on. At the beginning of the class, the centrifuged benzene was used first to rinse the scattering cell, in this case a cylindrical one, and then to fill the cell to a depth corresponding to a volume of about 30 ml of benzene -- this level being sufficient to clear the incident beam. A small hypodermic syringe was found to be convenient for transferring liquid from the centrifuge to the cell. The cell was then examined visually against a light source for the presence of motes; usually, very few motes were observed.

Then the solvent scattering ratio was determined at 45, 90, and 135 degrees. The value of the dissymmetry z, that is, the ratio of scattering observed at 45 degrees, S_{45}, to that observed at 135 degrees, S_{135}, was never greater than 1.05, and usually less.

Next a portion of stock solution was added to the scattering cell using the syringe, and mixed with the solvent by drawing liquid up and down in the syringe several times. The concentration of the resulting solution was determined from the weights of the added solution and the solvent. When mixing was complete, one member of the class determined scattering ratios for the solution at 45, 90, and 135 degrees; agreement to within ± 1 percent was taken to be satisfactory. Then another portion of stock solution was added, another member of the class determined scattering ratios for the new concentration, and so on.

After data had been obtained in this fashion for four or

five concentrations of polymer, values of $H \frac{c}{\tau}$ were calculated and

plotted against concentration according to the familiar equation

relating scattering to molecular weight and dissymmetry:

$$H \frac{c}{\tau} = \frac{1}{\overline{M}_w \cdot P_{90}} + 2 A_2 c$$

$\overline{M}_w$ is the weight-average molecular weight, P_{90} is the particle scat-

tering factor that allows for the dissymmetry of scattering resulting

from the intraparticle interference of scattered light, A_2 is the second

osmotic virial coefficient, a measure of the deviation in behavior

from Raoult's Law, and the other symbols are as before. At the same

time values of the dissymmetry, z, were plotted against concentration.

Values of $H \frac{c}{\tau}$ for a given fraction were extrapolated to zero

concentration; the value of $\frac{1}{\overline{M}_w P_{90}}$ was determined from the intercept,

and A_2 from the slope of the curve obtained (see Fig. 1). From the

limiting dissymmetry at zero concentration, [z], $1/P_{90}$ and $n_0 R_z$ (R_z

being the z-average root-mean-square end-to-end distance of a random

coil, and n_0 the refractive index of benzene) were determined with the

aid of tables given by Doty and Steiner (14) or by Cashin (17). Finally,

values of $\overline{M}_w$ and R_z were calculated. For the sake of convenience, two

corrections were discussed rather than made: the depolarization cor-

rection (2), which was small (less than 2 percent), and the correction

for secondary scattering due to reflection of the incident beam (18).

RESULTS AND DISCUSSION

In Table I (taken from references 8 and 9), light-scattering
data are given for five fractions studied by the summer class, and
also for two fractions examined separately by one of us (J. A. M.) as
a check on the accuracy of the class data. The viscosity data had
been obtained prior to the summer course (8, 9). The following equa-
tions relating intrinsic viscosities in two solvents to molecular
weights were obtained:

$$\text{Butanone:} \quad [\eta] = 1.8 \times 10^{-4} \, M^{0.66}$$
$$\text{Benzene:} \quad [\eta] = 3.5 \times 10^{-4} \, M^{0.71}$$

The relationship for intrinsic viscosities in butanone is close to
the one obtained by Doty, Affens, and Zimm (19) -- namely, 1.6×15^{4}
$M^{0.66}$; the relationship for benzene is similar to one obtained by
Gregg and Mayo (20) -- namely, $1.7 \times 10^{-4} \, M^{0.72}$

As may be seen from the sets of duplicate data for fractions
Q2B2 and RP-3-2, the precision of measurement is satisfactory. A check
on the accuracy of the data is given by the determination of the Flory
constant, Φ, relating the intrinsic viscosity of a linear polymer in
a given solvent to the size in the same solvent and the molecular
weight:

$$[\eta] = \Phi \, \frac{R^3}{M}$$

The average value for solutions in benzene, 2.2×10^{21} mole^{-1}, clearly
agrees well with the range $(1.9 - 2.3) \times 10^{21}$ mole^{-1} suggested by
Flory (3, 16). This agreement confirms the adequacy of the experimental
procedures.

It was gratifying to find results of high quality; indeed, the results were suitable for use in a research problem that required a comparison of branched and linear polystyrene (8, 9). We believe that this integration of teaching with research-quality results is beneficial and satisfying to both the student and the instructor. Certainly this approach seems preferable to the all-too-common practice of having students perform instrumental manipulations with the idea that the demonstration of technique, not the result, is the most important purpose of the experiment.

In conclusion, this experiment, or a similar experiment using other polymers and solvents, has been found useful at the graduate or senior undergraduate level at this university over a period of two years. The experiment is flexible enough to permit modification or expansion in scope to meet the particular needs; for example, two students have just completed a study of molecular weight distribution using Zimm plots (21), which involve the extrapolation of scattering data to zero angle as well as to zero concentration, as part of a small research problem. Now that many research laboratories have satisfactory light-scattering photometers, it is hoped that this experiment might serve as a basis for an introduction to light-scattering in other laboratories.
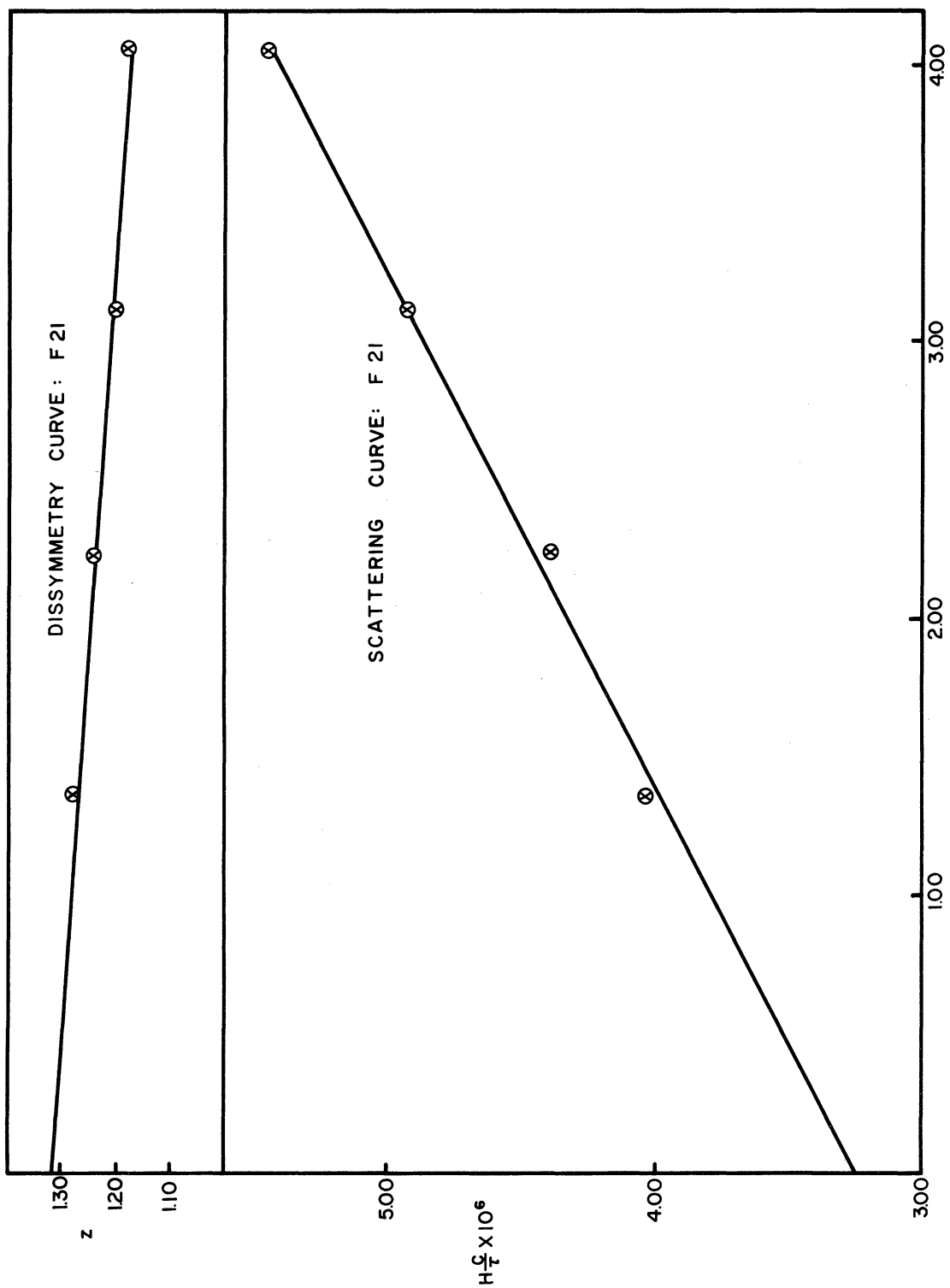
DISSYMMETRY CURVE: F 21

SCATTERING CURVE: F 21

CONCENTRATION X 10^3 , G./G. SOLUTION

Fig. 1 Light-Scattering Curves for Fraction F21

z

$\frac{c}{\tau}$ H X10^6

TABLE I

VISCOSITY AND LIGHT-SCATTERING DATA FOR FRACTIONS OF LINEAR POLYSTYRENE

Fraction	Intrinsic viscosity, [η],[4] dl/g		R_z(A° × 10^{-3})	$\bar{M}_w$(× 10^{-6})	Φ(× 10^{-21}) for benzene, mole^{-1}	A_2(× 10^4)
	benzene	butanone				
F21	1.48	0.73	0.637	0.334	2.50	4.3
F7B3	2.10	1.03	0.995	0.524	1.45	3.5
F5A2	4.05	1.82	1.50	1.33	2.12	3.0
F3A2	4.37	2.05	1.65	1.76	2.22	2.6
Q2B2[5]	5.82	2.06	1.91	2.20	2.38	4.2
Q2B2	5.82	2.60	1.90	2.29	2.52	3.2
T8[5]	6.75	3.00	2.11	2.76	2.55	4.4
RP-3-2[5]	4.53	2.00	1.63	1.50	2.73	5.4
RP-3-2	4.53	2.00	1.62	1.43	2.67	3.7

Average Φ (benzene) = 2.2 × 10^{21} mole^{-1}.

Average Φ expected (4, p. 616) = 2.1 × 10^{21} mole^{-1}.

4 These data were available before this experiment was developed (8, 9).
5 These results were obtained outside the class as a check on the accuracy of the class data.

REFERENCES

1. Bender, M., J. Chem. Educ. 29, 15 (1952).

2. Doty, P. M., and Edsall, J. T., Advances in Protein Chemistry 6, 35 (1951).

3. Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

4. Frith, E. M., and Tuckett, R. F., Linear Polymers, Longmans, Green, and Co., London, 1951.

5. Stacey, K. A., Light-Scattering in Physical Chemistry, Academic Press, Inc., New York, 1956.

6. Zimm, B. H., Stein, R. S., and Doty, P., Polymer Bull. 1, 90 (1954).

7. Manson, J. A., and Cragg, L. H., Can. J. Chem. 30, 482 (1952).

8. Manson, J. A., Ph.D. Thesis, McMaster University, Hamilton, Ontario, September, 1956.

9. Manson, J. A., and Cragg, L. H., Manuscript submitted to J. Polymer. Sci.

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

11. Brice, B. S., Halwer, M. L., and Speiser, R., J. Opt. Soc. Am. 40, 768 (1950).

12. Carpenter, D. K., and Krigbaum, W. R., J. Chem. Phys. 18, 1616 (1950).

13. Carr, C. I., and Zimm, B. H., J. Chem. Phys. 18, 1616 (1950).

14. Doty, P. M., and Steiner, R. S., J. Chem. Phys. 18, 1211 (1950).

15. Kronman, M. J., and Stern, M. D., J. Phys. Chem. 59, 969 (1955).

16. Notley, N. T., and Debye, P., J. Polymer Sci. 17, 99 (1955).

17. Cashin, W. M., Technical Report to the Reconstruction Finance Corporation, Office of Rubber Reserve, Sept. 12, 1950.

18. Sheffer, H., and Hyde J. C., Can. J. Chem. 30, 817 (1952).

19. Doty, P. M., Affens, W. A., and Zimm, B. H., Trans. Faraday Soc. 42, 66 (1946).

20. Gregg, R. H., and Mayo, F. R., J. Am. Chem. Soc. 70, 2373 (1948).

21. Zimm, B. H., J. Phys. and Colloid Chem. 52, 260 (1948); also
    J. Chem. Phys. 16, 1093, 1099 (1948).