

## Some Light Scattering Experiments with High Polymer Solutions

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mation<sup>1,2</sup>), an exact analysis can be given which illustrates these points clearly, as the accompanying graphs show. In Fig. 1 the distribution of total substrate among growing radicals, stable polymer, and unreacted monomer is shown as a function of time for several values of  $k_3/k_2$ , and in Fig. 2 the instantaneous apparent order (defined as  $d \ln v_2/d \ln m$ ) of the rate of monomer consumption is sketched as a function of the percentage of reacted monomer. As can be seen from Eq. (3), the steady-state approximation gives a first-order law.

The curves of Fig. 1 were obtained from the expressions:

$$m = m_0 \exp(-\varphi/\nu), \quad (\text{unreacted monomer}) \quad (6)$$

$$\Sigma nr_n = (m - m_0 e^{-\varphi})/(\nu - 1), \quad (\text{monomer in radicals})$$

where  $\varphi = \ln \cosh(t/\tau)$ ,  $\nu = k_3/k_2$ , and  $m_0$  is the initial monomer concentration. The amount of stable polymer is found by difference. The apparent order is found to be

$$\frac{d \ln v_2}{d \ln m} = 1 - \frac{\nu}{(m_0/m)^{2\nu} - 1}. \quad (7)$$

Recently Mark and his co-workers<sup>1</sup> have estimated frequency factors of  $10^6$  and  $10^4$  liter/mole/sec. for  $k_2$  and  $k_3$ , respectively, in the case of styrene, and have assigned to each rate an activation energy of 5 kcal./mole. Not only do these figures disobey Eq. (5), but the low frequency factors are difficult to explain. Since only the ratio  $k_2/k_3$  can be obtained with any accuracy from experimental data, and since the estimated activation energies are not far from lower limits, a revision which satisfies both the experimental data and the dictates of Eq. (5) will necessarily give higher, more normal frequency factors for  $k_2$  and  $k_3$ .

\* Contribution No. 507 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

<sup>1</sup> See, for example, J. Abere, G. Goldfinger, H. Mark, and H. Naidus, *Ann. N. Y. Acad. Sci.* **44**, 267 (1943).

<sup>2</sup> C. C. Price, *Ann. N. Y. Acad. Sci.* **44**, 351 (1943).

<sup>3</sup> R. Ginell and R. Simha, *J. Am. Chem. Soc.* **65**, 706 (1943).

### Some Light Scattering Experiments with High Polymer Solutions\*

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DEBYE<sup>1</sup> has recently pointed out that light scattering in solutions of high polymers permits the determination of the slope of the osmotic pressure curve of such solutions and the molecular weight (weight average) of the solute.

Einstein,<sup>2</sup> Von Smoluchowski,<sup>3</sup> Gans,<sup>4</sup> and Raman and Ramanathan<sup>5</sup> give essentially the following equation for the turbidity of a colorless binary mixture due to fluctuations in density and concentration.

$$\tau = \frac{8\pi^3}{3\lambda^4 N_0} \left\{ RT\beta \left[ \rho \frac{\partial \epsilon}{\partial \rho} \right]^2 + \frac{M_1 c_2}{\rho \left( -\frac{\partial \ln f_1}{\partial c_2} \right)} \left( \frac{\partial \epsilon}{\partial c_2} \right)^2 \right\}, \quad (1)$$

where  $\tau$  = turbidity (extinction coefficient) units  $\text{cm}^{-1}$ ,  $f_1$  = fugacity of solvent, of molecular wt.  $M_1$ ,  $c_2$  = weight fraction of solute,  $N_0 = 6.02 \times 10^{23}$ ,  $\lambda$  = wave-length of light in cm.

Assuming that  $\beta$ , the isothermal compressibility, is independent of concentration, the first term represents the turbidity due to fluctuations of the density  $\rho$  of the solvent. Thus if the turbidity of the solvent is subtracted from the measured turbidity of the solution, the remainder  $\tau_2$  will be, replacing  $\epsilon$  by  $n^2$ , where  $n$  is the refractive index,

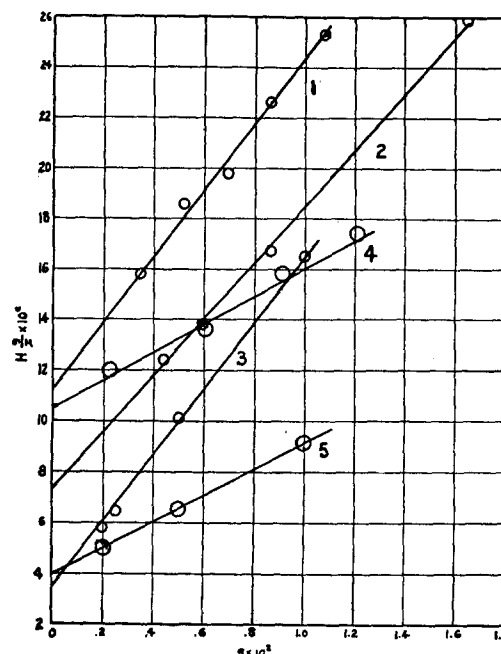


FIG. 1. Plot of  $H(g_2/l)$  against  $g_2$  for various samples of polystyrene in toluene and methylethyl ketone (see Table I).

$$\tau_2 = \frac{32\pi^3 M_1 c_2 n^2 \left( \frac{\partial n}{\partial c_2} \right)^2}{3\lambda^4 N_0 \rho \left( -\frac{\partial \ln f_1}{\partial c_2} \right)}. \quad (2)$$

Recalling the relation

$$-\frac{\partial \ln f_1}{\partial c_2} = \frac{\bar{V}_1}{RT} \frac{\partial \pi}{\partial c_2}, \quad (3)$$

where  $\pi$  is the osmotic pressure,  $\bar{V}_1$  the partial molal volume of solvent, and introducing  $g_2$  (grams/cm<sup>3</sup>) =  $\rho c_2$ , Eq. (2) becomes

$$\tau_2 = \frac{32\pi^3 g_2 n^2 \left( \frac{\partial n}{\partial g_2} \right)^2}{3\lambda^4 N_0 \frac{1}{RT} \frac{\partial \pi}{\partial g_2}} \quad (4)$$

assuming  $\bar{V}_1 = V_1 = M_1/\rho$ .

TABLE I.

Graph No.	Os. Mol. Wt.	Turb. Mol. Wt.	Solvent
1	100,000	88,500	toluene
2	127,000	137,000	toluene
3	200,000	285,000	toluene
4	100,000	95,000	methylethyl ketone
5	200,000	250,000	methylethyl ketone

It has been found<sup>6,7</sup> that even for very low concentrations of high polymer solutions, it is necessary to use for the osmotic pressure:

$$\pi = RT \left( \frac{g_2}{M_2} + b g_2^2 + \dots \right).$$

Equation (4) now becomes, with rearrangement,

$$\frac{g_2}{\tau_2} = \frac{3\lambda^4 N_0}{32\pi^3 n_1^2} \left( \frac{\partial n}{\partial g_2} \right)^2 \left[ \frac{1}{M_2} + \frac{2b_2}{RT} g_2 + \dots \right] \\ = \frac{1}{H} \left[ \frac{1}{M_2} + \frac{2b_2}{RT} g_2 + \dots \right]. \quad (5)$$

Hence a plot of  $H(g_2/\tau_2)$  versus  $g_2$  should give at low concentrations a straight line whose intercept is  $1/M_2$ .

We have made preliminary measurements of the turbidity of polystyrene fractions of known osmotic molecular weight<sup>8</sup> in two solvents. Our results, plotted in Fig. 1, show the expected linear relationship. The molecular

weights obtained from the intercept are compared with the osmotic molecular weights in Table I.

Because of present experimental uncertainties, we attach no significance to the differences between the two methods of measurement. The slopes of the lines for the measurements in toluene agree within experimental error (30 percent) with the slopes calculated from the osmotic data<sup>7</sup> (samples 120° and 180°). Our measurements of refractive index ( $\pm 0.00001$ ) have shown that  $n$  varies linearly with  $g_2$  over the concentration range used, and thus  $(\partial n / \partial g_2)$  is considered a constant having a value 0.213 for polystyrene-methylethyl ketone and 0.102 for polystyrene-toluene (Na-D line).

In the above, we have not considered the scattering due to orientation fluctuation.<sup>1,4,9</sup> However, measurements of the depolarization showed that this contribution is small enough to neglect in this preliminary work.

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