is located. A_1 is partitioned as shown by the cross hatching and modified to produce the second base case A_2 of Figure 6. The cycle is now pseudo node a indicated in Figure 4.

Operations are continued up to A_2^4 when another cycle is located consisting of nodes 9, 10, 12, and pseudo node a. A_2 is partitioned and modified to produce the next base case matrix A_3 of Figure 7. The new cycle is now pseudo node b shown again in Figure 4.

Powers of A_3 are computed until with A_3^4 another cycle is found consisting of nodes 2, 3, 14, and pseudo node b. The matrix is changed again to produce A_4 of Figure 8.

As before, the matrix multiplications are carried out until the zero matrix A_4^3 appears. This indicates that there are no paths involving four or more modules left in the simplified scheme and, therefore, no possibility of additional cycles. This terminates the procedure.

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The Effect of Concentration on Diffusion Coefficient in Polymer Solutions

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A microinterferometric method was used to measure the diffusion coefficient as a function of concentration in the system dimethylformamide-polyacrylonitrile at 25°C. The diffusion coefficient increases with increasing polymer concentration up to the maximum employed, 17.72% by weight. The theoretical basis for this type of behavior is explained. The diffusion coefficient in the limit as the polymer concentration approaches zero was calculated from theory to be 0.30×10^{-6} sq.cm./sec. This value is consistent with the diffusion coefficients obtained experimentally.

Mass transfer operations involving polymer solutions are often controlled by molecular diffusion. However, values of the diffusion coefficient are usually lacking. Furthermore, since diffusion coefficients in polymeric systems are frequently very concentration dependent, it is important to include this dependence in mathematical representations of diffusional processes.

In a solution of flexible chain molecules so dilute that interactions between the macromolecules may be neglected, it has been shown that the diffusing polymer molecule may be represented by an equivalent hydrodynamic sphere. It has furthermore been established that the effective diameter of this sphere is proportional to the root-mean-square distance between chain ends for linear molecules. This model has permitted diffusion coefficients at infinite dilution to be calculated from the molecular weight of the polymer, the intrinsic viscosity of the polymer-solvent system, and the viscosity of the solvent (*11*).

A statistical treatment of dilute polymer solutions (*8*) has led to the development of an equation representing the concentration dependence of the diffusion coefficient when the domains of the polymer molecules do not overlap (*10*). As the volume in space occupied by a polymer molecule may be several hundred times its molecular volume (*7*), appreciable entanglement and overlapping can occur at polymer concentrations as low as a few tenths of 1%.

Since diffusion in polymer solutions exhibiting extensive overlapping of adjacent, mobile, polymer molecules has received very little attention, the present study was initiated.

EXPERIMENTAL METHOD, APPARATUS, AND PROCEDURE

Diffusion coefficients for the system dimethylformamide-polyacrylonitrile were determined at 25°C. by a microinterferometric method. The procedure was adapted from methods used for studying concentration profiles around growing crystals (*1*, *2*), for measurement of local viscosities (*13*), and for studies of diffusion (*5*, *14*, *16*). The experimental apparatus is shown in Figure 1. Light from a sodium lamp is passed through a collimating lens and a filter, which isolates the D line (589 mμ). The monochromatic light passes upward through the diffusion cell and into the objective lens of a microscope. The diffusion cell consists of two partially metallized, plate glass microscope slides separated by a spacer at one end to form a wedge. The slides ($3 \times 1 \times \frac{1}{8}$ in.) were coated on one side with aluminum by vacuum evaporation so that they were partly transmitting and partly reflecting to light. The light passing through the wedge produces interference fringes that may be viewed through the eyepiece of the microscope.

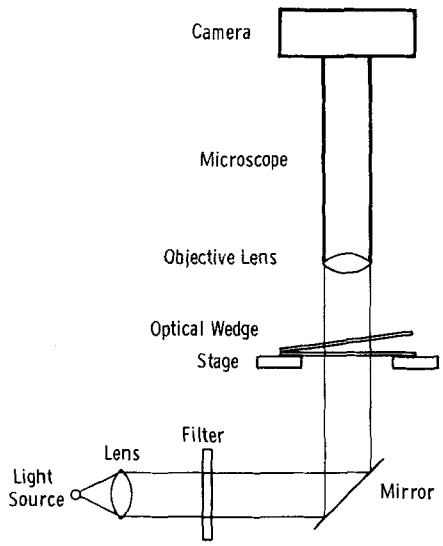
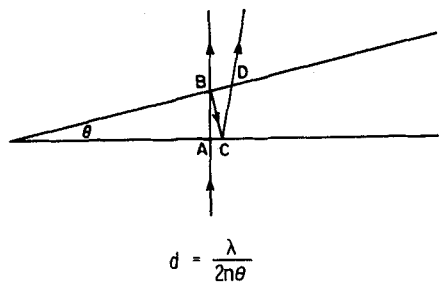


Fig. 1. Experimental apparatus.

The theory of the optical wedge has been treated in detail by Searle (*17*). For the present purpose, however, Figure 2 illustrates the principle on which the experimental measurements are based. A ray of monochromatic light *AB*, which enters the wedge, is partly transmitted and partly reflected. The reflected ray travels along the path *BCD*. When the difference in optical path between the reflected and transmitted rays is an integral number of wave lengths, reinforcement occurs, and a bright fringe is observed. Between the bright fringes, destructive interference occurs where the paths of the two rays differ by an odd number of half wave lengths, and a dark fringe is observed. With a material of constant refractive index in the wedge, the fringes are parallel and are spaced at a distance $d = \lambda/2n\theta$ apart, provided the wedge angle is not too large. The wedge angle shown in Figure 2 is greatly exaggerated to show the light paths clearly. The experimental measurements were made with a wedge angle of about 40 min. of arc.

Polymer solution, of known concentration and refractive index, is placed on the lower slide, which rests on the microscope stage. The upper slide is then rotated down to contact the polymer solution and form the wedge. Both metallized surfaces contact the polymer solution. The interface between the polymer solution and the surrounding air is then scanned through the microscope to find a region where the interface is perpendicular to the interference fringes. If such a region cannot be found, a new slide is placed on the stage and the procedure is repeated. In practice it is advisable to apply the polymer solution to the lower slide in the form of an elongated strip, approximately parallel to the long dimension of the slide.



$$d = \frac{\lambda}{2n\theta}$$

d = Distance between adjacent bright fringes
n = Refractive index of medium in wedge
λ = Wavelength of light
θ = Wedge angle

Fig. 2. The optical wedge.

In most cases, the first or second attempt will yield a suitable interface.

The selected portion of the interface is carefully brought into focus, and a drop of solvent is placed in contact with the side of the wedge. The drop is drawn in immediately by surface tension forces, comes in contact with the polymer solution, and diffusion begins. At time zero, when the solvent and solution contact each other, the interference pattern appears through the microscope as shown in Figure 3*a*. At some later time *t*, the fringes are curved and produce a pattern like that shown in Figure 3*b*. At large values of time, the material in the wedge approaches a uniform concentration, and the fringes become straight and uniformly spaced, as in Figure 3*c*.

It is possible to derive the concentration-distance profile at a known time *t*, after the start of diffusion, by photographing the interference pattern at that time.

Figure 4 shows the experimental interference pattern obtained 60 sec. after the start of diffusion for dimethylformamide diffusing into a 17.72 wt. % solution of polyacrylonitrile in dimethylformamide at 25°C. The pure solvent is at the top of the figure. The apparatus was in a room maintained at 25.0° ± 0.5°C.

The interference pattern of Figure 4 has two important characteristics on which the experimental method depends:

1. Along any line drawn parallel to the original interface, the distance between any two adjacent fringes is constant; and
2. Along any line drawn perpendicular to the original interface, the change is refractive index between any two adjacent fringes is constant.

It is apparent from Figure 4 that the concentrations of the initial materials have not yet been affected by diffusion

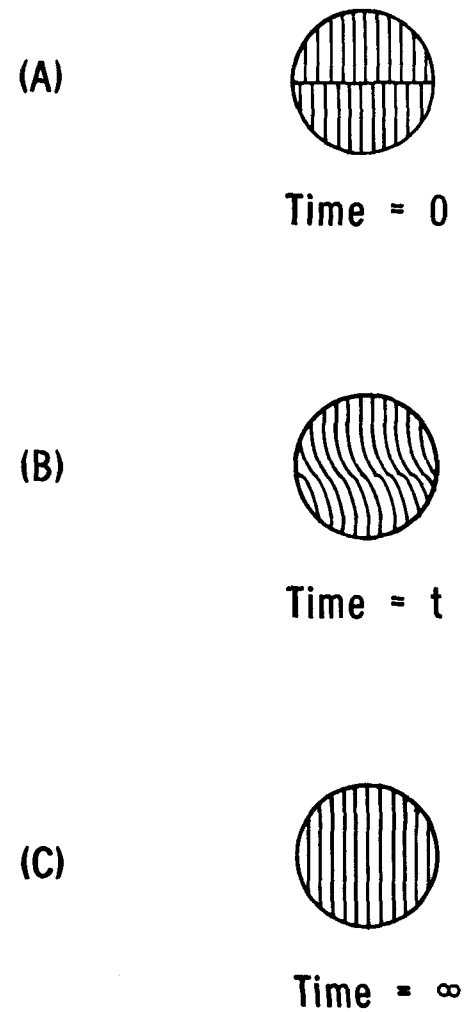


Fig. 3. Light-interference patterns observed during a diffusion experiment.

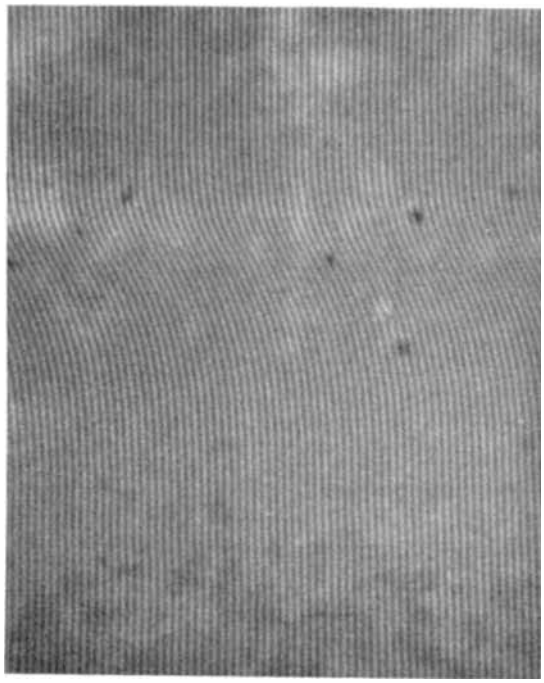


Fig. 4. Photograph of the experimental interference pattern obtained at $t = 60$ sec.

in the regions remote from the original interface. Since the difference in refractive index between the initial polymer solution and the pure solvent is known by refractometer measurements, the refractive index change between any two adjacent fringes in the direction of diffusion is also known. From the distance scale, which is easily determined by photographing a ruled microscale through the microscope, it is possible to obtain the refractive index-distance curve. Since the refractive index-concentration relationship can be obtained by making measurements on a series of polymer solutions with a refractometer, the concentration-distance curve is also known.

The polyacrylonitrile used for the experimental measurements had an intrinsic viscosity in dimethylformamide of 1.50 at 25°C. The polymer was unfractionated. It had a number-average molecular weight of 50,600 as determined by osmometry and a weight-average molecular weight of 122,200 as determined by light scattering. The refractive indices of solutions of the polymer in dimethylformamide were determined. The resulting refractive index-concentration relationship at 25.0°C. for the sodium D line is given by the equation.

$$n = 1.4269 - 0.0815c \tag{1}$$

with a maximum deviation of 0.0001 in refractive index for ten samples over the concentration range 0 to 20 wt. % polyacrylonitrile at 25.0°C. The polymer solutions were made up by weight, and the weight fractions were converted to grams per cubic centimeter by multiplying by the corresponding solution densities. It was found by experimental determination that the density was linear in the weight fraction of polymer. The data were represented by the equation

$$\rho = 0.942 + 0.203w \tag{2}$$

with an average deviation of 0.001 g./cc. and a maximum deviation of 0.003 g./cc for ten samples over the concentration range 0 to 20 wt. % polyacrylonitrile at 25°C.

Since the refractive index-concentration relationship is linear within experimental error, the change in concentration (as well as in refractive index) between any two adjacent fringes along a line perpendicular to the original interface is a constant. The experimental concentration-distance profile is shown in Figure 5. From this curve the relationship between the diffusion coefficient and concentration can be determined.

Second-order transition temperatures for solutions of polyacrylonitrile in dimethylformamide were reported as a function of concentration by Krigbaum and Tokita (9). Their results show that all measurements in the present work were made well above the second-order transition temperature.

It is estimated that the method employed has a probable error of from ± 5 to ± 10%. It is evident that the method is dependent upon the existence of a sufficiently large refractive index difference between the solutions initially contacted. The minimum refractive index difference required depends on several factors. However, as an approximate rule, a difference of 0.01 is usually sufficient. The method may sometimes be affected by the volatility of the solvent, but this was not an important factor in this study.

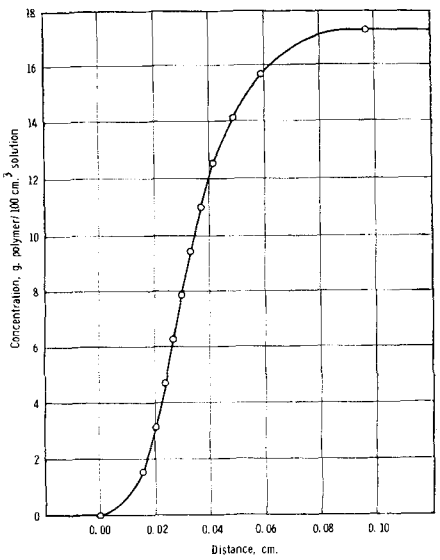


Fig. 5. Experimental concentration profile at $t = 60$ sec.

COMPUTATIONS

The differential equation describing the diffusion process is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{3}$$

The boundary conditions are

$$c = 0, t = 0, x < 0 \tag{4}$$

$$c = c_o, t = 0, x > 0 \tag{5}$$

By introducing the substitution $y = x/2\sqrt{t}$, the following result is obtained (4):

$$D = \frac{-\int_o^c x dc}{2t\left(\frac{dc}{dx}\right)} \tag{6}$$

The c axis (locus of $x = 0$) is defined by the requirement that

$$-\int_o^c x dc = \int_o^{c_o} x dc \tag{7}$$

which demands equal areas under the concentration-distance curve above and below the c axis.

The integral in Equation (6) was evaluated by graphical integration of the experimental concentration-distance curve.

The derivative (dc/dx) was obtained by fitting an empirical equation, designed to represent S-shaped curves (6), to the data and differentiating the equation. The relationship between concentration gradient and distance obtained in this way is shown in Figure 6.

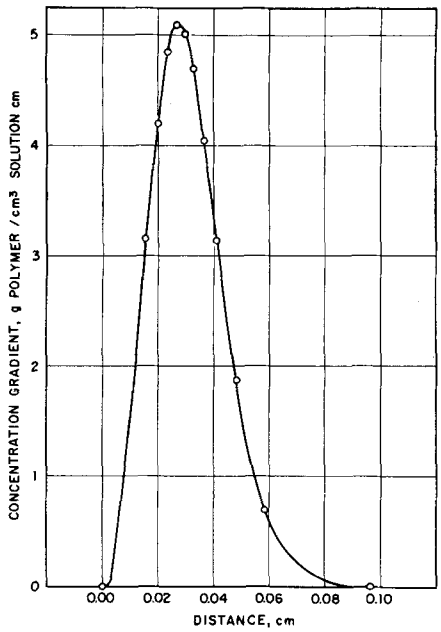


Fig. 6. Experimental concentration gradient as a function of distance at $t = 60$ sec.

RESULTS

The results obtained by making the appropriate substitutions in Equation (6) are shown in Figure 7. The diffusion coefficient for the system studied is seen to increase with increasing polymer concentration. Qualitatively, this effect has been observed for other polymer-solvent systems (*10, 19*). It is expected that eventually the diffusion coefficient would reach a maximum and then decrease if the polymer concentration were increased further. This is a consequence of the expected increase in diffusion coefficient with solvent concentration at the polymer rich end of the concentration range.

Although the experimental measurements extend only as far down as 0.0158 g. polymer/cc. solution, it is instructive, for comparison, to calculate the diffusion coefficient at infinite dilution. Based on the theory for the configuration of real polymer chains, Mandelkern and Flory (*11*) derived the following equation for the diffusion coefficient at infinite dilution:

$$D_o = \frac{RTP^{-1}\,\Phi^{1/3}}{N\eta_o\,(M[\eta])^{1/3}} \tag{8}$$

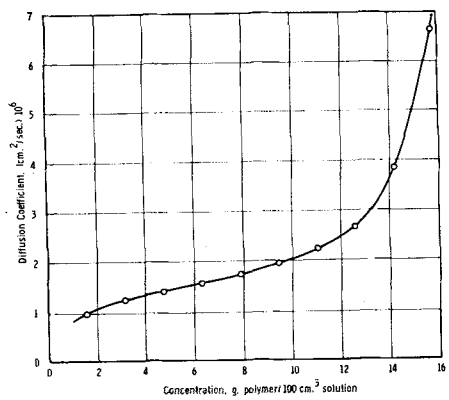


Fig. 7. Effect of concentration on the diffusion coefficient for solutions of polyacrylonitrile in dimethylformamide at 25°C.

where $(P^{-1}\,\Phi^{1/3})$ is a universal constant for flexible chain molecules, independent of the nature of the polymer and solvent. From experimentally determined sedimentation data for several polymer-solvent systems (*11, 12*), is was shown that within ± 10% $(P^{-1}\,\Phi^{1/3}) = 2.5 \times 10^{6}$ in the units stated in the Notation. Taking the viscosity of dimethylformamide as 0.798 centipoise at 25°C. and using the number-average molecular weight in Equation (8), one finds that $D_o = 0.30 \times 10^{-6}$ sq. cm./sec. Since the diffusion coefficient decreases with decreasing polymer concentration, the experimental results plotted in Figure 7 are compatible with the calculated value of D_o.

A comparison can also be made with the experimental results of Bisschops (*3*) on the polyacrylonitrile-dimethylformamide system, although those results extend up to a concentration of only 0.0084 g. polymer/cc. solution. At that concentration, for a polymer having an intrinsic viscosity of 1.08 at 25°C., the diffusion coefficient was found to be 0.48×10^{-6} sq. cm./sec. Inasmuch as a different polymer sample having a different molecular weight distribution was used, there is reasonable consistency between Bisschops' result and the values found in the present work. Bisschops also found that the diffusion coefficient increased with increasing polymer concentration.

Since a theory for the dependence of the diffusion coefficient on concentration in very dilute polymer solutions has been formulated, it is instructive to investigate the theoretical predictions for the system studied here. Based on statistical mechanics, the theory yields the following expression for the ratio of the diffusion coefficient to its value at infinite dilution (*8, 10*):

$$\frac{D}{D_o} = \frac{(1 + 2\Gamma_2 C + 3\Gamma_3 C^2)}{(1 + k_1 C)} \tag{9}$$

provided $\Gamma_2 C \leq 1$. For the polyacrylonitrile-dimethylformamide system, Bisschops (*3*) found $\Gamma_2 = 1.35 \times 10^{2}$ cc./g. and in general that $k_1 = 1.6\,[\eta]$, which in the present study gives $k_1 = 2.4 \times 10^{2}$ cc./g. Substituting into Equation (9) one gets

$$\frac{D}{D_o} = \frac{(1 + 2.70\,C + 3\Gamma_3 C^2)}{1 + 2.4\,C} \tag{10}$$

Using approximate models for the intermolecular potential energy, Stockmayer and Casassa (*18*) found that

$$\frac{5}{8} \leq \frac{\Gamma_3}{\Gamma_2^2} \leq 0 \tag{11}$$

Equation (10) then becomes

$$\frac{D}{D_o} = \frac{(1 + 2.70\,C + \alpha C^2)}{(1 + 2.4\,C)} \tag{12}$$

where

$$3.42 \leq \alpha \leq 0 \tag{13}$$

For any value of α in this range, D increases with increasing polymer concentration. The restriction $\Gamma_2 C \leq 1$ corresponds to $C \leq 0.74$ g./100 cc. for the present study. Since the data of the present work extend down only as far as 1.58 g./100 cc., there can be no direct comparison of experiment with theory. However, there are no evident inconsistencies between the two. The direction of the change of the diffusion coefficient with concentration found experimentally is the same as that predicted by the theory.

At higher polymer concentrations, the polymer molecules are forced to overlap extensively and the chain segments approach a statistically uniform (random) distribution throughout the solution volume. It is apparent that a gradual transition must occur from a state in which

the dissolved polymer molecules are separated from one another to a state in which a random distribution of chain segments occurs. Such a transition must be reflected in the diffusion coefficient-concentration relationship.

DISCUSSION

Fick's law is usually written as

$$\vec{J} = c\vec{v} = -D\nabla c \qquad (14)$$

in which D may be concentration dependent. Onsager and Fuoss (*15*) have investigated the nature of this concentration dependence for two-component diffusion by rewriting Fick's law in the form

$$\vec{J} = c\vec{v} = -\Omega\nabla\mu \qquad (15)$$

Combining Equations (14) and (15) one gets

$$D = \Omega\left(\frac{\partial\mu}{\partial c}\right) \qquad (16)$$

From Equation (15), Ω/c is the velocity imparted to a polymer molecule by unit driving force, which is merely the reciprocal of f, the frictional coefficient commonly employed in polymer studies. Accordingly

$$D = \frac{c}{f}\left(\frac{\partial\mu}{\partial c}\right) = \frac{RT}{f}\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right) \qquad (17)$$

If both $(\partial\mu/\partial c)$ and f could be evaluated as functions of concentration, then the diffusion coefficient would be known as a function of concentration. It will be noted that $(1 + \partial \ln\gamma/\partial \ln c)$ is a thermodynamic quantity, dependent upon intermolecular forces under equilibrium conditions, while f is a hydrodynamic quantity, dependent upon the viscous resistance of the medium to motion of the polymer molecules. On this basis, the results of Figure 7 indicate that the thermodynamic term increases more rapidly with polymer concentration than the hydrodynamic term, resulting in an increase in the diffusion coefficient with increasing polymer concentration. Diffusion coefficients that increase with increasing polymer concentration have been observed for several other polymer-solvent systems (*10, 19*) and appear to be quite common.

CONCLUSIONS

The microinterferometric method described is a useful, rapid technique for determining concentration-dependent diffusion coefficients in polymer solutions. The experimental results for the dimethylformamide-polyacrylonitrile system at 25°C. indicate that the diffusion coefficient increases with polymer concentration up to the limit of the study, 17.72 wt. % polymer. Calculated diffusion coefficients for very dilute solutions of polyacrylonitrile in dimethylformamide are consistent with the data obtained at higher concentrations.

NOTATION

c = concentration of polymer, g./cc.
C = concentration of polymer, g./100 cc.
c_o = initial concentration of polymer solution, g./cc.
d = distance between adjacent fringes, cm.
D = diffusion coefficient, sq. cm./sec.
D_o = diffusion coefficient at infinite dilution, sq. cm./sec.
f = frictional coefficient, (dyne) (sec.)/(cm.) (g.-mole)
$\vec{J}$ = rate of diffusion, g./(sq. cm) (sec.)
k_1 = constant in Equation (9), 100 cc./g.
M = molecular weight, g./g.-mole
n = refractive index
n_o = refractive index of pure solvent
N = Avogadro's number = 6.023×10^{23} molecules/g.-mole
P = universal constant for all polymers, independent of molecular weight, temperature, and solvent, (g.)/(cm.) (sec.) (poise) (molecule)
R = gas constant, 83.15×10^6 (g.) (sq.cm.)/(g.-mole) (sec.^{2}) (°K.)
t = time, sec.
T = absolute temperature, °K.
$\vec{v}$ = velocity of polymer molecules, cm./sec.
w = weight fraction polymer
x = distance in the direction of diffusion, cm.
y = $x/2\sqrt{t}$, cm./sec.$^{1/2}$

Greek Letters

α = constant in Equation (12)
γ = activity coefficient of polymer
Γ_2 = second virial coefficient in the osmotic pressure-concentration relationship, 100 cc./g.
Γ_3 = third virial coefficient in the osmotic pressure-concentration relationship, (100 cc./g.)^2
η_o = viscosity of solvent, poises
$[\eta]$ = intrinsic viscosity, 100 cc./g.
θ = wedge angle, rad.
λ = wavelength of light, cm.
μ = chemical potential of polymer, (dyne) (cm.)/g.-mole
ρ = density of solution, g./cc.
Φ = universal constant for all polymers, independent of molecular weight, temperature, and solvent, 100 cc./(g.-mole) (cc.)
Ω = proportionality constant in Equation (15), (g.-mole) (sec.)/cc.

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