

Specific Refractive Index Increments of Polymer Solutions. Part II. Scope and Applications

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Synopsis

The data of Part I are examined in the light of accepted theories. The specific refractive index increment \bar{n} of most polymer solutions lies between -0.2 and $+0.2$ ml./g., although larger values can obtain in circumstances wherein the scattering unit is unusually large, e.g., solutions of partially neutralized polyacids the units of which contain the gegenions. \bar{n} depends on the indices of solvent n_1 and polymer n_2 . Among common solvents, water and 1-bromonaphthalene are capable of affording high positive and negative values, respectively, for n . The Gladstone-Dale rule applies rigorously to pure and mixed solvents, but the Lorenz-Lorentz expression is preferable for evaluating n_2 . Results of current theories applied to mixed solvents and copolymers are summarized. In the former, the true molecular weight M is determined by using \bar{n} and the variation of solvent index with composition. For a copolymer of monomers A and B, M as well as M_a and M_b are obtainable by using \bar{n} , \bar{n}_a , and \bar{n}_b . Dispersion is expressed as $(\bar{n})_\lambda = (\bar{n})_{436}[D' + D''/\lambda^2]$ at a wavelength λ , and dispersive constants D' and D'' are evaluated for some solutions. $\partial\bar{n}/\partial T$ is generally $3.2 (\pm 2.3) \times 10^{-4}$ ml./g./°C. and changes very little with λ . When \bar{n} increases with M , the limiting characteristic value is derived (at $1/M = 0$) from a plot of \bar{n} versus $1/M$. \bar{n} can be determined to a maximum accuracy of 1% by using n_2 calculated from the Lorenz-Lorentz equation and the experimental partial specific volume.

Introduction

In the preceding paper¹ the values of the specific refractive index increment, obtained under a variety of conditions, were collected for numerous polymer solutions. While the measurements were conducted primarily as a means to the evaluation of the weight-average molecular weight, several additional facets emerge, which are not inherently allied to this objective; these may be exemplified by the refractive index and density of a pure polymer and the polydispersity of a copolymer. Coupled with these aspects the dependence of dn/dc on experimental conditions will be examined and an attempt made to correlate the data with current theory. Much of the latter has been developed by the schools of Benoit, Debye, and Stockmayer, and their results are acknowledged at this point to obviate excessive future referencing. In general we review results rather than their derivation. As some workers omit reporting the temperature and wavelength, the available data cannot, unfortunately, be deployed to their

optimum potential. In order to simplify the notation the specific increment will henceforth be denoted by \tilde{n} , the units being milliliters per gram.

Specific Refractive Increment and Concentration

The variation of the refractive index of a solution n with the concentration of polymer c is adequately represented by

$$n - n_1 = a_1c + a_2c^2 \quad (1)$$

From eq. (1) it is seen that

$$(n - n_1)/c = \tilde{n} = a_1 + a_2c \quad (2)$$

and \tilde{n} is obtained as the slope of a plot of $n - n_1$ versus c . The coefficient a_2 has been shown to be zero for aqueous protein solutions up to 0.1 g./ml. in concentration² and is customarily assumed to be so for c below 0.03 g./ml. (Exceptionally³ n may be linearly related to c when the concentration is expressed in grams polymer per gram solution). The parabolic form of eq. (1) is not manifested until higher values of c are attained. It is important to realize, nevertheless, that the relationship does assume this form. Nils-son and Sundelöf⁴ have accordingly evaluated a_2 for polydimethylsiloxane (Part I, E-95) in toluene by plotting n versus c (0.005–0.05 g./ml.) and taking the true specific increment by extrapolating to zero concentration. Between 15° and 35°C., a_2 is temperature-independent, having values of 0.104 and 0.099 ml.²/g.² for $\lambda = 436$ and 546 m μ , respectively.

Matsumoto and Ohyanagi⁵ report somewhat anomalous behavior for aqueous solutions of poly(vinyl alcohol) differing in degree of polymerization (DP); $(\tilde{n})_{436}^{20} = 0.168$ ml./g. is obtained from a graph of $n - n_1$ versus c , which is linear and independent of DP for all samples below concentrations of about 0.005 g./ml. Above certain critical concentrations c_{crit} (varying for each sample), different parallel linear plots obtain, revealing that the distance $\Delta(n - n_1)$ between lines above and below the abnormal range increases with increase in DP. A graph of $\log c_{\text{crit}}$ versus $\log \text{DP}$ is found to be linear with a slope of -0.5 . The empirical formula $c_{\text{crit}}(\text{DP})^{1/2} = \text{constant}$ ($= 0.039$) thus adduced is interpreted as the result of two possible effects: (1) the destruction of the structure of water or, as appears more likely on account of the absence of this behavior in other aqueous polymer solutions, (2) the close packing of swollen poly(vinyl alcohol) molecules.

Specific Refractive Increment and Solvent

The concept of specific refractivity r_t , first introduced by Gladstone and Dale, has been reviewed chronologically^{6,7} and is defined as

$$r_t = (n_t - 1)/d_t \quad (3)$$

where d_t (in grams per milliliter) is the density of the substance at the temperature to which the value of n_t applies. In the form of expression (3), thermal changes in n_t and d_t are self-canceling, and r_t is independent of

temperature for light of a definite wavelength. It is also found to be independent of the state of aggregation. The Gladstone-Dale rule is simply an assertion of the additivity of r_i for a mixture. Thus, considering r_i as a partial quantity in the thermodynamic sense, the specific refractivity of a binary mixture r may be written

$$r = w_1 r_1 + w_2 r_2 \quad (4)$$

Here the relative contributions of solvent (1) and solute (2) are affected by their weight fractions w_i . Denoting $w_2 d$ by the concentration c and, on the assumption of additivity of volumes, writing

$$1/d = w_1/d_1 + w_2/d_2 \quad (5)$$

eq. (4) becomes

$$\tilde{n} = (n_2 - n_1)/d_2 \quad (6)$$

Outer, Carr, and Zimm⁸ consider eq. (6) in its entirely equivalent form:

$$\tilde{n} = r_2 - (d_1/d_2)r_1 \quad (7)$$

and compare calculated (and experimental) values of $(\tilde{n})_{546}^{20}$ for polystyrene in toluene, dichloroethane, and butanone (E-119, Part I). They obtain, respectively, 0.108 (0.104), 0.158 (0.161), and 0.221 (0.214) ml./g. by utilizing $r_2 = 0.581$ ml./g. as calculated from the refractive index and density of the pure polymer at 20°C. In the light of more recent⁹ work the agreement is probably better than this.

Equation (6) may be arranged as

$$\tilde{n} = n_2/d_2 - (1/d_2)n_1 \quad (8)$$

and hence a plot of \tilde{n} against n_1 should be linear with negative slope. Rather than calculate r_2 it is thus simpler to read \tilde{n} for any solvent of known n_1 directly from the graph once the form of the latter has been established with a few solvents. Examples are provided by Altgelt and Schulz^{10,11} for rubber (E-139, Part I), and by Elias and Schumacher¹² for nylon 66 (E-85, Part I). Solutions of this polyamide in nine solvents, excepted only by dichloroacetic acid, all complied with the equation

$$\tilde{n} = 1.418 - (1/1.074)n_1$$

In Figure 1 we have used the data of E-111 (Part I) for poly(methyl methacrylate) to plot $(\tilde{n})_{546}^{20}$ against n_1 for twenty-four sets of results corresponding to nineteen distinct solvent systems. The refractive indices of the solvents were obtained from the appropriate papers and from standard tables.²⁰ n_2 can be calculated from the product of the reciprocal slope and the intercept at zero n_1 . To avoid such an inaccurate extrapolation from $n_1 = 1.3$ to 0 it is preferable to obtain n_2 from the intercept at zero \tilde{n} . In these circumstances $n_2 = n_1 = 1.500$ compared with the literature value²¹ of $(n_2)_{546}^{20} = 1.493$. The density of poly(methyl methacrylate) obtained from the slope of the line is 1.13 g./ml. thus differing by 4% from the value

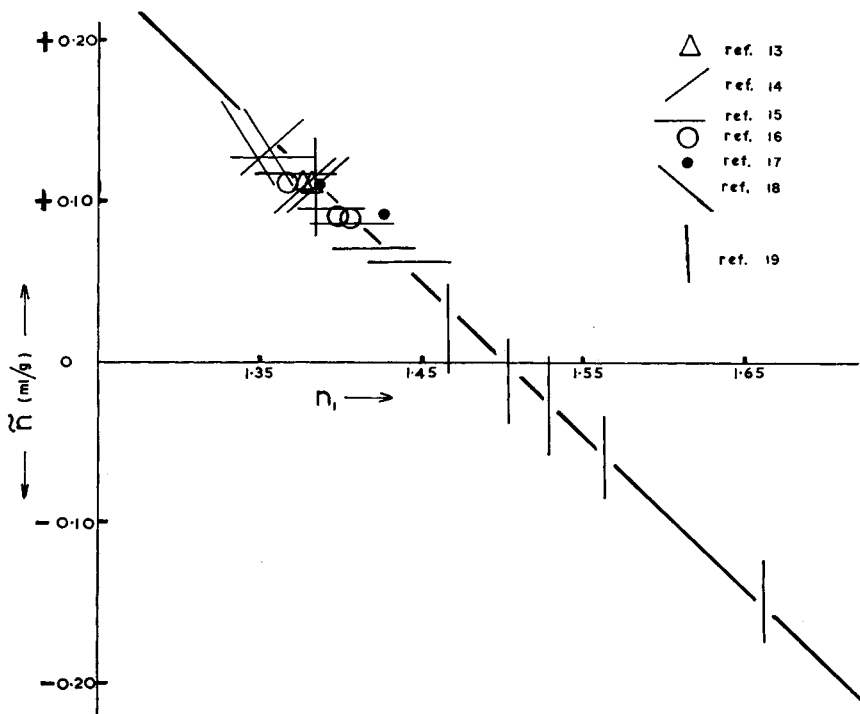


Fig. 1. Dependence of specific refractive index increment on refractive index of solvent for solutions of poly(methyl methacrylate) at 25°C. and 546 μ .

of 1.18 g./ml. quoted.²¹ Part of this discrepancy (ca. 1%) can be accounted for by the use of reciprocal density in place of partial, specific volume \bar{V}_2 in eq. (8). Although d_2 is a constant at a particular temperature, \bar{V}_2 depends to some extent on the nature of the solvent. For example, the partial specific volumes²² of polystyrene in MEK and cyclohexane at 25°C. are 0.9076 and 0.9291 ml./g. respectively, whence r_2 is 0.5607 and 0.5650 ml./g., respectively, at $\lambda = 546 \mu$. In Figure 1, 1/1.13 ml./g. should be regarded as an average of the partial specific volumes in the nineteen solvents.

Lorenz and Lorentz proposed an alternative formulation R_i for specific refraction with a sounder theoretical basis than the Gladstone-Dale expression.

$$R_i = (1/d_i) [(n_i^2 - 1)/(n_i^2 + 2)] \quad (9)$$

For a binary system

$$\frac{1}{d} \left(\frac{n^2 - 1}{n^2 + 2} \right) = \frac{w_1}{d_1} \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) + \frac{w_2}{d_2} \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right)$$

which is readily converted to

$$\frac{n^2 - 1}{n^2 + 2} = \frac{c}{d_2} \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) + \left(1 - \frac{c}{d_2} \right) \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \quad (10)$$

If the function $(n_i^2 - 1)/(n_i^2 + 2)$ is replaced for brevity by Z_i , then eq. (10) becomes

$$Z = Z_1 + (c/d_2)(Z_2 - Z_1) \quad (11)$$

Equations (10) and (11) represent straightforward forms of the Lorenz-Lorentz expression. With the purpose of determining n_2 very accurately for proteins, Putzeys and Brosteaux (see also Rupp and Mommaerts²⁴) compared the values of n_2 obtained via the Gladstone-Dale rule (6), the normal Lorenz-Lorentz expression (10), and an improved form of the latter [eq. (12)], derived as follows.

The functions Z_i are replaced by the linear approximations $Z_i = p_i + q_i n_i$. Thus

$$Z = p + qn \quad (12)$$

and

$$Z_2 = p_2 + q_2 n_2$$

For the dilute protein solutions and the essentially aqueous solvents the refractive indices do not differ appreciably, ranging from ca. 1.33 to 1.36. Hence the same approximations are held to be valid for both, and

$$Z_1 = p + qn_1 \quad (13)$$

Distinct values for p_i and q_i are assigned to the protein itself in eqs. (12) as n_2 is generally ca. $0.30 > n$ or n_1 . The three expressions for Z , Z_1 , and Z_2 are valid only if applied between linear limits of n_i . Substituting for Z , Z_1 , and Z_2 from eqs. (12) and (13) into eq. (11) yields

$$n_2 = \left[n_1 + \frac{(n - n_1)d_2}{c} \right] \left(\frac{q}{q_2} \right) + \left(\frac{p - p_2}{q_2} \right) \quad (14)$$

The square-bracketed terms in eq. (14) are identical with n_2 calculated from the Gladstone-Dale equation. In other words the Gladstone-Dale equation results directly from eq. (14) only if $p_2 = p$ and $q_2 = q$. The following eq. (15) is the result of inserting numerical values of p , p_2 , q and q_2 calculated with the aid of approximation formulas into eq. (14):

$$n_2 = 1.2181 \{ n_1 + [(n - n_1)d_2/c] \} - 0.3238 \quad (15)$$

Experimentally the Gladstone-Dale equation is found to furnish values of n_2 variable in the second decimal place, whereas the two forms of the Lorenz-Lorentz equation concur within a few units of the third decimal figure.

Mixed Solvents

Ewart et al.,²⁵ Stockmayer,²⁶ and Read²⁷ were among the first to develop and test the theory of light scattering applied to solutions of polymers in binary solvents with the objective of determining measures of true molecular weight and the selective adsorption of the better solvent on to the

polymer. The results of a recent approach to the problem by Strazielle and Benoit^{28,29} are summarized briefly below. It will be observed that an indispensable requirement additional to \bar{n} is a knowledge of the variation of refractive index with composition for the solvent mixture.

Firstly it is shown that for a binary system

$$A - A_1 = 2\pi^2 n_1^2 c M \bar{n}^2 / \lambda^4 N_A \quad (16)$$

where M is the molecular weight of polymer present at a concentration c and N_A is the Avogadro number. A and A_1 are the 90° Rayleigh ratios* of solution and solvent,† respectively. For a ternary system it is proposed that each polymer molecule is surrounded by a sphere of sufficiently large radius that the composition of the solvent remains constant at its periphery. This composition may differ from that of a mixture of the pure solvents on account of preferential adsorption of one of them. (Studies referred to later render the universal applicability of this postulate somewhat questionable.) The expression corresponding to eq. (16) then derived for this case is

$$A - A_1 = (2\pi^2 n_1^2 c M / \lambda^4 N_A) [\bar{n} + (x_3 N_A / M) (dn_1 / d\nu_3)]^2 \quad (17)$$

where x_3 represents the number of solvent molecules of species 3 within a sphere that are additional to those which would be present in the absence of selective adsorption. It thus constitutes one quantitative measure of this effect. ν_3 is the number of molecules of the same species (3) per unit volume of the solvent mixture. Hence $dn_1 / d\nu_3$ merely expresses the variation of refractive index of the solvent-pair mixture with the concentration of one of its constituents. Relations (16) and (17) differ only by the additional term $(x_3 N_A / M) (dn_1 / d\nu_3)$ within the square brackets, the manifestation of which is dependent on the inequality

$$dn_1 / d\nu_3 \neq 0$$

Before considering the experimental examination of eq. (17) we note some reported cognate work.

Schultz,³⁰ in ascertaining the θ composition of a solvent for poly(vinyl acetate) (E-124, Part I), conducted light-scattering experiments with *n*-heptane/methyl isopropyl ketone mixtures, i.e., solutions of varying ν_3 . The value of ν_3 at which the second virial coefficient vanishes constitutes the θ composition. True, rather than apparent, molecular weights are found in this case for, as the two liquids comprise an isorefractive pair,

* The symbol A is adopted here for the Rayleigh ratio in place of the more customary R to avoid confusion with the Lorenz-Lorentz specific refraction appearing earlier in the text.

† For the sake of consistency we retain the subscripts 2 and 1 always to denote solute and solvent, respectively, whatever the complexity of the latter may be. Thus for a binary system the sole solvent is denoted by 1 in eq. (16). The two solvents in a ternary system will be designated 3 and 4, although only one of them is actually referred to specifically. No ambiguity should arise if it is realized that the liquids 1 in eq. (16) and 3 in eq. (17) are identical.

$dn_1/d\nu_3 = 0$. There are several known examples of such pairs of liquids but few of them are also solvent-precipitant systems for common polymers. Butanone and isopropanol do possess practically the same index of refraction over a considerable range of temperature and wavelength and are jointly good and bad solvents for poly(methyl methacrylate) (E-111, Part I). At any specified temperature between 4 and 40°C. the θ composition is found to have a particular value between 46.8 and 58.2% v/v of butanone (corresponding to ν_3). Likewise, for any specified composition within this range the θ temperature lies between the limits mentioned.¹⁶ The significance of a large value of $dn_1/d\nu_3$ have been discovered fortuitously³¹ during determinations of \bar{n} for substituted cellulose xanthates (E-33, Part I), in a mixture composed of 90% DMSO/10% water. Two series of overlapping experiments were performed with the use of different preparations of the solvent mixture for each series. Although the combined results displayed irregularities in the variation of \bar{n} with degree of substitution, the data for each individual series yielded self-consistent light-scattering results. As water and DMSO differ greatly in refractive index (1.3398 and 1.4928 at 436 $m\mu$), a small error inadvertently introduced into the batch make-up of solvent for a series incurs a significant alteration in $dn_1/d\nu_3$. Selective adsorption on to the solute is thus invoked to explain these anomalies.

We revert now to the experimental examination of relation (17). If due cognizance is not made of $dn_1/d\nu_3$, the molecular weight and the second virial coefficient obtained will be apparent ones M_{app} and B_{app} when determined experimentally from

$$H_c/(A - A_1) = 1/M_{app} + 2cB_{app}$$

in which $A - A_1$ is given in eq. (16) with M replaced by M_{app} . Strazielle and Benoit find that for the system (E-119, Part I) consisting of polystyrene (2), benzene (3), and cyclohexane (4), M_{app} increases and B_{app} decreases (i.e., both the intercept and slope decrease in plots of reduced turbidity versus concentration) in solutions progressively richer in the poor solvent, cyclohexane (i.e., with decreasing ν_3). A 12% difference in the values of M_{app} is observed between solutions containing 100% and 25% of benzene, while the difference in B_{app} is far greater. Comparing relations (16) and (17) reveals that

$$M_{app} = M \left[1 + \frac{x_3 N_A}{M} \left(\frac{dn_1}{d\nu_3} / \bar{n} \right) \right] \quad (18)$$

Recalling that the definition of ν_3 appertains to the number of molecules of solvent 3 per unit volume of the solvent 3/solvent 4 mixture, the volume fraction ψ_3 is introduced in its place as it is more convenient practically. It is also the parameter adopted by other workers.²⁵ Because ν_3 and ψ_3 are related by

$$\nu_3 = \psi_3 (N_A/V_3)$$

in which V_3 is the molar volume of solvent 3, then

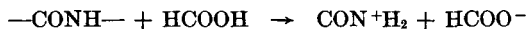
$$dn_1/dv_3 = (dn_1/d\psi_3)(V_3/N_A).$$

Substitution for dn_1/dv_3 into eq. (18) and rearrangement result in

$$x_3/M = (1/V_3)[(M_{app}/M)^{1/2} - 1][\bar{n}/(dn_1/d\psi_3)] \quad (19)$$

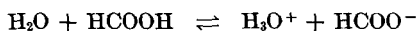
For any solvent mixture of given ψ_3 (or v_3), $dn_1/d\psi_3$ is obtainable via graphical differentiation of a plot of n_1 versus ψ_3 . The values of x_3/M calculated from eq. (19) are found to increase with decreasing ψ_3 (i.e., with increasing paucity of the solvent medium), passing through a maximum at $\psi_3 = 0.35$ and then decreasing. Similar behavior exhibited by polystyrene samples of different degrees of polymerization DP demonstrates that x_3/M is independent of M . x_3 , accordingly, is proportional to the length of the polymer chain and in this particular instance the maximum effect at $\psi_3 = 0.35$ corresponds to the adsorption of one molecule of benzene per five segments of polymer. Recent similar work^{32,33} on the same system with cyclohexane replaced by a variety of polar solvents indicates a much higher density of adsorption, which is unaltered on raising the temperature by 50°C.

The behavior of nylon in single solvents has already been referred to. Its light scattering in mixed solvents has been studied exhaustively by Saunders³⁴⁻³⁶ and is of especial interest, for the composition of the solvent mixture determines the extent to which the polymer manifests polyelectrolytic properties. In formic acid, a good solvent for nylon, protonation induces polyelectrolytic behavior thus:



The charge hereby introduced may be suppressed by either (a) decreasing the degree of ionization via an addition to the concentration of the counterions, and/or (b) increasing the ionic strength of the medium via the addition of a simple electrolyte.

Because the charge effects are so great in pure formic acid, the highest possible ionic strength is insufficient to depress them completely. The degree of ionization is therefore reduced to a minimum by the addition of water, which functions by increasing the concentration of formate ions thus:



After initial experiments with potassium chloride as the added electrolyte it was realized that addition of sodium formate to aqueous formic acid combines the desired features, for it is a simple electrolyte as well as a source of the counterions necessary to repress ionization. When considering the following summarized results it will be of advantage to bear in mind that the refractive index of water is less than that of formic acid and also that the index of aqueous formic acid is increased on adding potassium chloride.

(1) When potassium chloride is added to nylon in aqueous formic acid, \bar{n} decreases as the concentration of the salt increases. This observation

is accountable simply on the basis of an increase in the index of the solvent. Denoting salt-containing species by the subscript *s* and applying eq. (6) to salt-containing and salt-free solutions of nylon in aqueous formic acid, we obtain

$$\tilde{n} - \tilde{n}_s = (n_s - n_1)/d_2 \quad (20)$$

Taking as example the change in the specific increment caused by the addition of 1.0*M* KCl to 90% aqueous formic acid, $\tilde{n} - \tilde{n}_s = 0.145 - 0.136 = 0.009$ ml./g., which agrees well with the value (0.008 ml./g.) calculated from the appropriate values of d_2 for nylon and the indices n_1 and n_s .

(2) For the same reason, a similar change is incurred in \tilde{n} when sodium formate is substituted for potassium chloride.

(3) In the absence of salt, \tilde{n} is lowered by increasing the aqueous content of the formic acid. We have noted that water has a smaller refractive index than the acid and this behavior is therefore contrary to any expectation based on the variation of \tilde{n} with the index of the solvent medium [as in (1) and (2) above]. It is, in fact, associated with the diminishing extent of ionization concomitantly with the changing polarizabilities of the amide groups and their counterions.

(4) When potassium chloride is present at any fixed concentration in system (3), similar behavior is exhibited; i.e., \tilde{n} falls with the rise in concentration of water.

(5) If potassium chloride is replaced by sodium formate at any fixed concentration in system (4), \tilde{n} remains sensibly constant up to about a 20% aqueous content. As the specific increment does not, at least, decrease, it is likely that the same general explanation as for (4) applies here.

Since \tilde{n} depends on the nature of the solvent in these systems, different values of the light-scattering factor *H* obtain for each composition of the solvent. Notwithstanding this, plots of reduced turbidity HC/τ versus concentration are all found to extrapolate to the same intercept at zero concentration. The independence of the magnitude of intercept on the composition of solvent (ν_3) is indicative of little or no preferential adsorption of formic acid round the polymer.

Friedberg et al.³⁷ present results on hydroxyethylcellulose in two sets of mixed solvents, water/DMSO and water/formamide. Where a maximum would have displayed the effect of preferential adsorption in the former, a minimum is actually observed when the apparent molecular weight is plotted against solvent composition. Although present, the influence of adsorption is masked by molecular aggregation emanating from strong dipole-dipole interaction between water and DMSO, which lessens the opportunity for interaction with the solute. Anomalous effects also obtain in mixtures of water (good solvent)/formamide (nonsolvent). Over a wide range of solvent composition the intrinsic viscosity $[\eta]$, Huggins viscosity slope factor k' , molecular weight, and radius of gyration $(\overline{S^2})^{1/2}$ are unaffected. The constancy of $(\overline{S^2})^{1/2}$, in particular, is indicative of similar structures of the solvent sheath in each mixture. In contrast to the postu-

late of Strazielle and Benoit mentioned earlier, it appears that the solvent environment of a polymer molecule does not differ from that of the bulk solvent mixture, which, however, may not be structurally what it seems. Here for example the hydrogen-bonded association of pure formamide, disrupted by the presence of water, is invoked to elucidate this behavior. Details have also been reported^{38,39} on the light scattering of proteins in aqueous organic mixtures (differing by at least 0.11 in n_1), from which it is not possible to derive information on the degree of hydration of the polymers.

Generally, then, when elucidating the properties of polymers in mixed solvents, the situation should be approached with some degree of caution if one of the solvents is water, for the polarity may induce on the mixture vastly different properties from those of the pure solvents.

Specific Refractive Increment in Copolymers

The specific refractive index increment for solutions of copolymers, like that for homopolymers, depends solely on the weight concentration. Hence for a copolymer composed of species A and B,

$$\tilde{n} = \tilde{n}_a[C_a/(C_a + C_b)] + \tilde{n}_b[C_b/(C_a + C_b)] \quad (21)$$

As before, denoting weight function by w_i , eq. (21) becomes

$$\tilde{n} = w_a\tilde{n}_a + (1 - w_a)\tilde{n}_b \quad (22)$$

Thus \tilde{n} can be calculated for a copolymer of known composition, provided the specific increments are known for the homopolymers. Krause⁴⁰ has verified eq. (22) for block copolymers of styrene/methyl methacrylate in butanone (E-150, Part I), obtaining the values of w_a from infrared analysis. The relation has also been deployed to obtain the composition of copolymers⁴¹ for when \tilde{n}_a and \tilde{n}_b are both known, measurement of \tilde{n} for a copolymer affords its weight composition directly.

An interesting example is provided by partially alcoholized poly(vinyl acetate) in water [E-125]. Beresiewicz⁴² quotes values of $(\tilde{n})_{546}$ for samples of different degree of alcoholysis α . We think it illuminating to test the validity of eq. (22) by considering these polymers as random copolymers of poly(vinyl acetate) (A) and poly(vinyl alcohol) (B). It is readily shown that

$$w_a = 86(1 - \alpha)/(86 - 42\alpha)$$

as the molecular weights of A and B are 86 and 44, respectively. The calculated values of w_a yield a straight line of negative slope when plotted against the reported experimental figures for \tilde{n} . The specific increments derived for A and B are 0.117 and 0.164 ml./g., respectively. The latter figure accords exactly with that quoted for poly(vinyl alcohol) in water at 546 m μ and 30°C. No significance can be attached to the value of 0.117 ml./g. for poly(vinyl acetate), as this polymer is insoluble in water. Other substituted polymers listed in the preceding paper,¹ such as cellulose ni-

trate, cellulose xanthate, and sodium carboxymethyl cellulose, should in principle be readily amenable to a similar treatment.

In a binary copolymer the presence of differing scattering elements leads to an apparent molecular weight M_{app} greater than the true one M_w . Work on such systems has been directed towards an evaluation of M_w and the molecular weights M_a and M_b of the segments of poly-A and poly-B comprised within. It is also possible to gain some measure of the polydispersity of the copolymer. The treatment of Bushuk and Benoit¹⁹ summarized below is selected rather than the earlier one of Stockmayer et al.⁴³ for no reason other than it combines all these aspects and presents them in an eminently comprehensive and experimentally verifiable form. The only system to have been studied in any detail is the copolymer of polystyrene (A)/poly(methyl methacrylate) (B).

Firstly it is shown that

$$M_{app} = [\tilde{n}_a \tilde{n}_b / \tilde{n}^2] M_w + [\tilde{n}_a (\tilde{n}_a - \tilde{n}_b) / \tilde{n}^2] w_a M_a + [\tilde{n}_b (\tilde{n}_a - \tilde{n}_b) / \tilde{n}^2] w_b M_b \quad (23)$$

From separate measurements in three different solvents (each yielding a different specific increment) three simultaneous equations of relation (23) can be set up and solved for M_w , M_a , and M_b . Thus for a copolymer bearing the composition $w_a = 0.68$ and $w_b = 0.32$: in butanone, $\tilde{n} = 0.185$ ml./g., $\tilde{n}_a = 0.220$ ml./g., $\tilde{n}_b = 0.111$ ml./g., $M_{app} = 2.21 \times 10^5$; in CCl_4 , $\tilde{n} = 0.103$ ml./g., $\tilde{n}_a = 0.146$ ml./g., $\tilde{n}_b = 0.023$ ml./g., $M_{app} = 2.81 \times 10^5$; in C_6H_5Cl , $\tilde{n} = 0.045$ ml./g., $\tilde{n}_a = 0.079$ ml./g., $\tilde{n}_b = -0.026$ ml./g., $M_{app} = 9.59 \times 10^5$; whence $M_w = 1.83 \times 10^5$, $M_a = 1.74 \times 10^5$, and $M_b = 0.82 \times 10^5$.

Similar examples are provided by the data of Krause.⁴⁰ It will be apparent both from eq. (23) and from the numerical examples that M_{app} (or more usefully the deviation of M_{app}/M_w from unity) increases with increase in \tilde{n} . Minimal departure of the observed molecular weight from the actual one can only be achieved by the use of large specific increments. These in turn are dictated by the most appropriate selection of solvent. As $n_1 \rightarrow n_2$, so $\tilde{n} \rightarrow 0$ and $M_{app}/M_w \rightarrow \infty$. By introducing parameters P and Q some insight into the polydispersity of the copolymer may be obtained:

$$M_{app} = M_w + 2P[(\tilde{n}_a - \tilde{n}_b)/\tilde{n}] + Q[(\tilde{n}_a - \tilde{n}_b)/\tilde{n}]^2 \quad (24)$$

where

$$P = \sum \gamma_i M_i \delta w_i$$

$$Q = \sum \gamma_i M_i \delta w_i^2$$

in which definitions γ_i and M_i are, respectively, the relative concentration and molecular weight of species having composition w_i , and δw_i is the deviation in composition of these molecules from the average one. Via the use of three simultaneous equations as before, M_w (as well as P and Q) can

equally well be calculated from expression (24). A parabolic plot is produced from M_{app}/M_w (ordinate) versus $(\tilde{n}_a - \tilde{n}_b)/\tilde{n}$ (abscissa), the slope of which is $2P/M_w$ at $(\tilde{n}_a - \tilde{n}_b)/\tilde{n} = 0$ and which in general gives the value of P and Q fitting most closely to the experimental points. The maximum possible value of Q is $w_a(1 - w_a)$ [or equally well $w_b(1 - w_b)$], which in this example equals 0.22. The value obtained by either of the two methods indicated is 0.16, and consequently the ratio $0.16/0.22 = 0.72$ is a quantitative measure of the polydispersity of composition.

Mixtures of Polymers

The case of two homopolymers, poly-A and poly-B, dissolved in a single solvent is rarely encountered in practice and will be reviewed but briefly. Using the same concepts as they invoked for copolymers, Bushuk and Benoit¹⁹ obtain the following eq. (25) for the experimentally determined apparent molecular weight

$$M_{\text{app}} = [\tilde{n}_a^2 \gamma_a M_a + \tilde{n}_b^2 \gamma_b M_b] / \tilde{n}^2 \quad (25)$$

where the terms have their previous connotation. From this expression the principal features of these systems may be summarized as follows.

(1) M_{app} depends on n_1 because of the presence of the terms \tilde{n}_a , \tilde{n}_b , and \tilde{n} .

(2) When n_1 equals $(n_2)_b$, eq. (25) gives the molecular weight of poly-B because $\tilde{n}_b = [(\tilde{n}_2)_b - n_1]/(d_2)_b$.

(3) If $(n_2)_b > n_1 > (n_2)_a$, \tilde{n} can be adjusted to zero by suitable selection of the concentrations. Under these circumstances M_{app} is infinite, although light scattering is still exhibited by the solution.

(4) The effect of either γ_a or γ_b being equal to zero will be obvious from the definition of these terms, for the system is thereby reduced to a single-solute solution.

These points have been illustrated on characterized polystyrene-poly-(methyl methacrylate) mixtures.

Specific Refractive Increment and Wavelength

As for all transparent materials, a polymer, solvent and solution each exhibits dispersion or variation of refractive index with wavelength, which assumes the general form of the Cauchy relation

$$n_i = E + F/\lambda^2 + G/\lambda^4 \quad (26)$$

Normally the first two terms suffice to describe the variation within the wavelengths used. Dispersion D is often written in the form

$$D = D_{(\lambda)} - 1/[n_{(\lambda_2)} - n_{(\lambda_1)}] \quad (27)$$

where D is termed the reciprocal dispersion. It is large for materials of low dispersion and small for those which display a considerable dependence of refractive index on wavelength. Examples of dispersion among sol-

vents are legion. The quantitative form of the dispersion law for the solid polymers hemocyanin and amandine has been established²³ by obtaining n_2 at wavelengths 436, 546, 579, and 653 $m\mu$ via the use of the Lorenz-Lorentz equation. The most exhaustive study of dispersion by polymer solutions is probably that of Perlmann and Longworth,² who found that the proteins bovine, egg, human, and horse albumin as well as horse serum globulin and β -lactoglobulin all exhibited the same dispersive behavior in aqueous solution. Plotting $[\tilde{n}_{(\lambda)} - \tilde{n}_{(5790)}]/\tilde{n}_{(5790)}$ as a linear function of $1/\lambda^2$ they obtained the eq. (28) for the specific increment at any value of λ (in Angstroms):

$$\tilde{n}_{\lambda} = \tilde{n}_{5790} [0.940 + 2.00 \times 10^6/\lambda^2] \quad (28)$$

Having confirmed that \tilde{n} can be written in the form

$$\tilde{n}_{\lambda} = \tilde{n}_{436} [D' + D''/\lambda^2] \quad (29)$$

we have determined D' and D'' graphically for those examples in Part I which give data for at least three wavelengths. A reference wavelength of 436 $m\mu$ is taken, as it is the one most commonly employed. The values of D' and D'' for proteins have been recalculated on this basis and included in Table I.

TABLE I

Polymer	Solvent	D'	$10^{-4} \times D''$, $m\mu^{-2}$
Polycarbonates	Methylene chloride	0.823	3.42
"	THF	0.828	3.29
Polystyrene	MEK	0.826	3.34
Poly(vinyl alcohol)	Water	0.931	1.40
Proteins	Water	0.900	1.79
Actomyocin	Water	0.951	1.00
Poly(<i>n</i> -butyl methacrylate)	Acetone	0.969	0.560
"	MEK	0.968	0.529
Poly(methyl methacrylate)	Acetone	0.955	0.883
"	Butyl acetate	0.947	0.973
"	Chloroform	0.975	0.428
"	Dioxane	0.931	1.32
"	Ethyl acetate	0.950	0.991
"	THF	0.945	1.12

Writing dispersive equations complementary to expression (29) for the solvent (1) and polymer (2) and applying the Gladstone-Dale rule yields an interrelation between the dispersive constants of the form

$$(\tilde{n})_{436} [D'\lambda^2 + D'']d_2 = \{[(n_2)_{436} (D_2'\lambda^2 + D_2'')] - [(n_1)_{436} (D_1'\lambda^2 + D_1'')]\} \quad (30)$$

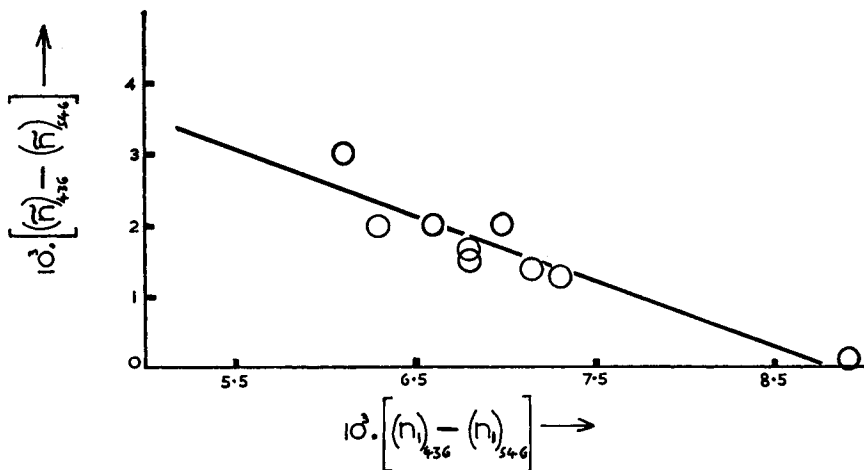


Fig. 2. Dispersion of solution between 436 and 546 $m\mu$ vs. dispersion of solvent for poly(methyl methacrylate) at 25°C.

from which relation D'_2 and D''_2 for the pure polymer may be calculated via sets of simultaneous equations. By applying eq. (6) to two wavelengths λ_a and λ_b a simpler form of dispersion results:

$$[(\tilde{n})_{\lambda_b} - (\tilde{n})_{\lambda_a}] = [1/d_2] \{ [(n_2)_{\lambda_b} - (n_2)_{\lambda_a}] - [(n_1)_{\lambda_b} - (n_1)_{\lambda_a}] \} \quad (31)$$

In the case of polydimethylsiloxane in toluene,⁴ agreement to within 4% has been found between calculated and observed values of the left-hand side of eq. (31) with $\lambda_b = 436$ and $\lambda_a = 546 m\mu$. In Figure 2 we have plotted the difference between the specific increments (wavelengths 436 and 546 $m\mu$) for poly(methyl methacrylate) solutions against the differences in refractive indices of the solvents at 25°C. From the intercept at zero ordinate the refractive index of the pure polymer at 436 $m\mu$ is seen to be ca. 0.0089 greater than that at 546 $m\mu$, c.f. the literature value of 0.0090.

Influence of Temperature

Differentiation of eq. (6) with respect to temperature T yields eq. (32):

$$\partial\tilde{n}/\partial T = (1/d_2) [(\partial n_2/\partial T) - (\partial n_1/\partial T)] + (n_2 - n_1)[\partial(1/d_2)/\partial T] \quad (32)$$

Hence a knowledge of the thermal dependence of the indices of polymer and solvent coupled with the coefficient of cubical expansion of the polymer are required to ascertain the variation of \tilde{n} with temperature. Examination of published data¹ reveals that (1) $\partial\tilde{n}/\partial T$, $\partial n_2/\partial T$, and $\partial n_1/\partial T$ change very little with wavelength; e.g., for polystyrene $\partial n_2/\partial T = -1.41 \times 10^{-4}$ and $-1.34 \times 10^{-4}/^\circ\text{C}$. at 436 and 676 $m\mu$, respectively. For MEK $\partial n_1/\partial T = -4.8 \times 10^{-4}$ and $-4.7 \times 10^{-4}/^\circ\text{C}$. for 436 and 546 $m\mu$, respectively and for solutions of polystyrene in MEK $\partial\tilde{n}/\partial T = +2.3 \times 10^{-4}$ ml./g./ $^\circ\text{C}$. for both 436 and 546 $m\mu$. (2) Available values of $\partial\tilde{n}/\partial T$ lie from 0.9×10^{-4} to 5.6×10^{-4} ml./g./ $^\circ\text{C}$. with the exceptions⁴⁴ of

poly(acrylic acid), poly(methacrylic acid), polyacrylamide, and poly-methacrylamide in water, for which the specific increments are constant from 20 to 65°C.

Experimental agreement to within 4% of the calculated values at 436 and 546 $m\mu$ has been reported for solutions of polydimethylsiloxane in toluene.⁴ O'Mara and McIntyre⁴⁵ obtain acceptable, albeit less exact, accord in the case of polystyrene solutions (at the same wavelengths), using refractive index data⁴⁶ for the pure polymer at 589 $m\mu$. Taking ± 0.150 ml./g. and $+3.0 \times 10^{-4}$ ml./g./°C. as typical values for \bar{n} and $\partial\bar{n}/\partial T$, respectively, it is seen that a significant change in \bar{n} of one unit in the third decimal place is caused by a change in temperature of 3°C. and it is possible that the stringent temperature control often enforced may not be always essential.

Without detailed data on $\partial(1/d_2)/\partial T$ and $\partial n_2/\partial T$ for the exceptional polymers quoted, it is not possible to locate the root of the zero thermal coefficient of the specific increment. However by using $\bar{n} = 0.15$ ml./g. for polyacrylamide, taking approximate values for d_2 (1.2 g./ml.), n_1 (1.33) and n_2 (1.51) and noting that water has the unusually low value of $-1 \times 10^{-4}/^\circ\text{C}$. for $\partial n_1/\partial T$, it can be seen from eq. (32) that for $\partial\bar{n}/\partial T$ to be zero the thermal variation of n_2 must be equal to $-[1 \times 10^{-4} + 0.22 \partial(1/d_2)\partial t]$.

Effect of Pressure

Considerable fluctuation in atmospheric pressure has no effect on the value of \bar{n} . For solvents⁴⁷ $\partial n_1/\partial(\text{press}) \approx +3 \times 10^{-5}$ atm.⁻¹ and is less than this for pure polymers.

Molecular Weight

Certain entries (Part I) display values of \bar{n} which change with molecular weight M . Varying values of d_2 with M have been encountered with polyethylene, for example, and are associated with the extent of crystallinity. n_2 , however, for the same sample is less sensitive to the presence of microvoids. Two distinct sets of anomalous entries may be referred to: (1) E-95 and E-117 in Part I are solutions of high molecular weight (ca. 1×10^6) polymers and no explanation can be offered to elucidate the behavior; (2) E-76 and E-100 are cases of low polymers the solutions of which exhibit an increasing \bar{n} with increasing M . With regard to this second set the change in increment results from the well known increase of d_2 and n_2 in a homologous series. Consequently the attainment of a characteristic constant specific increment is dependent on the point at which these two similar properties assume limiting values and also on their relative rate of movement with respect to each other.

To illustrate this point we have selected some calculated rather than experimental values for polydimethylsiloxanes. Literature values⁴⁸ of d_2 at 25°C. and $(n_2)_{589}^{25}$ versus M are plotted in Figures 3a and 3b, respectively. Using these figures and $(n_1)_{25}^{589}$ for toluene we have calculated the

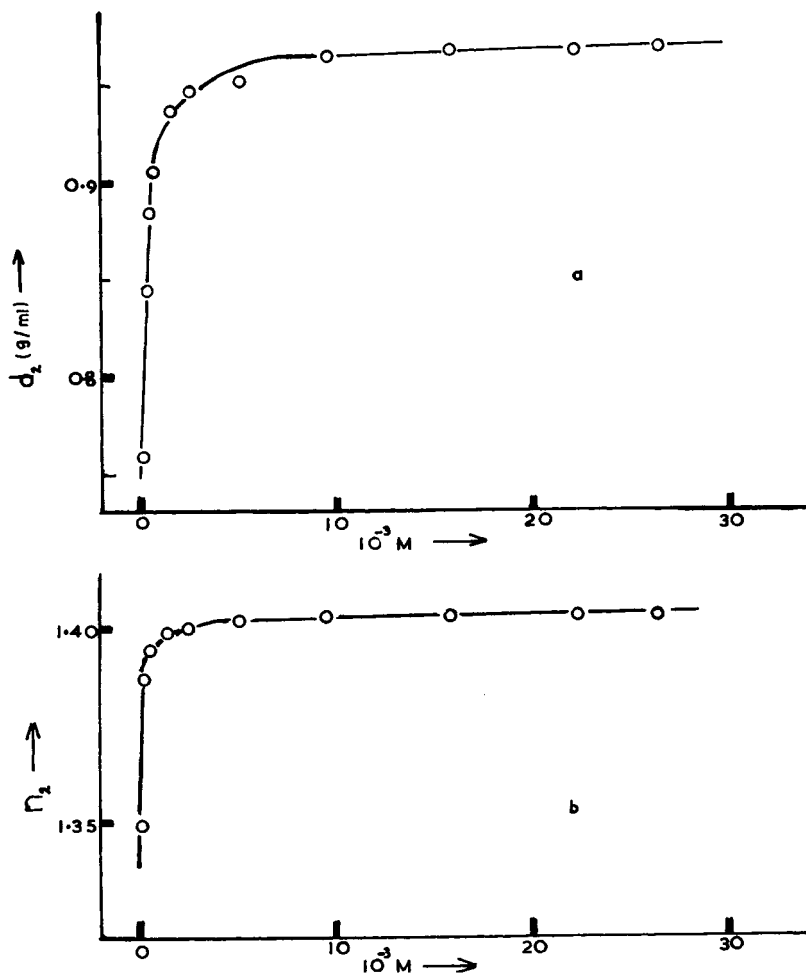


Fig. 3. Dependence of (a) density and (b) refractive index ($589\text{ m}\mu$) on molecular weight for polydimethylsiloxanes at 25°C .

value of $(\bar{n})_{589}^{25}$ which would obtain for each molecular weight. The variation of this specific increment with M follows the same curve as Figures 3a and 3b.

Initially \bar{n} increases very rapidly and then decreases gradually after a molecular weight of 5,000. From $M = 5000$ to $M = 36,900$ \bar{n} increases from -0.0955 to -0.092 ml./g. Assuming an inverse square dispersion law, the value of $(\bar{n})_{589}^{25}$ for the same polymer of molecular weight 63,000 in the same solvent, interpolated from the data of Nilsson and Sundelöf,⁴ is -0.0919 ml./g. The change of \bar{n} with M can be shown to be due to increases in both d_2 and n_2 and not solely d_2 , for the specific refractivity $r_2 [= (n_2 - 1)/d_2]$ falls from 0.459 to 0.417 ml./g. throughout the range of M . Empirically (c.f. also the variation of $1/d_2$ with M for polystyrene

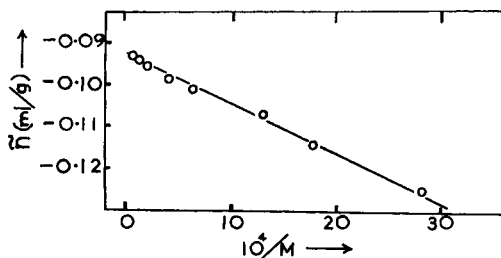


Fig. 4. Variation of specific refractive index increment (589 $m\mu$ and 25°C.) with reciprocal molecular weight for polydimethylsiloxanes.

studied by Fox and Flory⁴⁹), we find a linear relationship between \tilde{n} and $1/M$, in Figure 4, which yields the value of -0.0919 ml./g. on extrapolation to infinite molecular weight, i.e., $1/M = 0$. Similarly, $(n)_{436}$ for poly(ethylene glycol) in water and $(n)^{22}$ for *p*-oligophenylenes in toluene are determined as 0.143 and 0.292 ml./g., respectively.

Refractive Index Increment in Polyelectrolytes

The extrapolation of reduced turbidity to zero concentration is difficult for charged macromolecules because the electrostatic attraction causes the particle scattering factor and the second and third virial coefficients to change with concentration. When ionization is suppressed by the addition of a mineral acid such as HCl, poly(acrylic acid and poly(methacrylic acid) are un-ionized and behave as neutral polymers. When there is ionization it produces a significant increase in \tilde{n} , which varies linearly with the degree of ionization α . For poly(methacrylic acid) (neutralized to varying degrees with NaOH), the extrapolated value of \tilde{n} at zero α is found⁵⁰ to be 0.159 ml./g. which is in excellent agreement with 0.158 ml./g. reported by Silberberg et al.⁴⁴ for the same polymer in which ionization is repressed by the presence of 0.02*N* HCl. The molecular weights of ionized and un-ionized samples of the same polymer accord with each other provided that the appropriate refractive increment is used at any degree of ionization. Ideally this ought to be the value of n for the true scattering unit of (polyion + its double layer), which cannot, however, be measured. Practically the satisfactory increment is that corresponding to the (polyacid + its counterions). Hence at any value of α the appropriate specific refractive increment is determined from the measured $(n - n_1)$ and the concentration of polymer H^+P^- corrected to include that of the associated sodium ions.

Although of no direct utilitarian relevance, the values of \tilde{n} for H^+P^- alone have been calculated by Alexander and Stacey⁵⁰ using the method of Dismukes and Alberty⁵¹ (for electrolytes rather than polyelectrolytes), which is formally analogous to the Kohlrausch law of limiting ionic mobilities:

$$(K)_{H^+P^-} = (K)_{Na^+P^-} - (K)_{Na^+Cl^-} + (K)_{H^+Cl^-}$$

in which $(K)_i$, termed the integral increment of electrolyte i , is defined as $(n - n_i)/C_i$; where C_i is the molar concentration of i . As $(K)_{\text{Na}^+\text{Cl}^-} > (K)_{\text{H}^+\text{Cl}^-}$, the observed increment including the sodium ions is greater for each value of α than that calculated for the acid H^+P^- alone, which corresponds qualitatively with the greater size of the scattering unit.

Over a 100-fold change in salt concentration (NaCl) the specific increments for poly(acrylic acid) are found to be independent of the ionic strength I of the medium at any particular degree of neutralization (by NaOH). It should be noted that \bar{n} was calculated in terms of the polyacid rather than as previously indicated. The variation of \bar{n} with degree of neutralization (D.N.) is linear and extrapolates to $(\bar{n})_{436}^{30} = 0.144$ ml./g. c.f. $(\bar{n})^{20-65} = 0.146$ ml./g. reported elsewhere⁴⁴ for the same polymer, the ionization of which is repressed by 0.2M HCl and which was obtained, of course, in terms of the polyacid.

Orofino and Flory⁵² consider the application of \bar{n} in multicomponent systems exemplified by aqueous partially neutralized poly(acrylic acid) at a specified ionic strength determined by the concentration of added sodium chloride. The treatment is discussed in the light of the mixed solvent scheme of Ewart et al.,²⁵ which is conceptually similar to, but notationally different from, that already summarized (Strazielle and Benoit^{28,29}). The definition of components is somewhat arbitrary,* but may be conveniently regarded in this case as polysalt, water, and NaCl of specified molarity. The polymer molecules are treated as Donnan spheres, each containing its complement of gegenions, the number of which depends on the degree of neutralization. Essentially Orofino and Flory estimate the magnitude of the second term in square brackets of eq. (17). We write this term in the form $-YZ/M$, in which $Y = dn_1/d\psi_3$, previously defined; e.g. it is 0.01 for the mixed solvent considered here, 1M NaCl/water. Z is the variation of ψ (at the periphery of a sphere instead of in the bulk solvent mixture) with the concentration c and an expression is obtained for it at infinite dilution from the Donnan condition. The expression reveals that Z/M is negative and, as an approximation, it is proportional to $1/I$ and to D.N. Hence $-YZ/M$ is positive and is most significant at large D.N. and/or small I . An unfavorable case is taken to illustrate the order of magnitude of the whole term and thereby the factor to be added to \bar{n} , for poly(acrylic acid) of $M = 10^6$, $Y = 0.01$ and $Z/M \simeq 0.5$ at low I and high D.N. Whence $-YZ/M = +0.005$ ml./g., and the actual specific increment is this amount greater than \bar{n} .

Nature of the Polymer and Calculation of \bar{n}

Ivin et al.⁵⁵ observe that in the olefin polysulfones \bar{n} decreases as the alkyl group is lengthened (C_4 , C_6 , C_8 , and C_{12}). (The cyclohexyl group is not assimilated in this trend.) The values of $(\bar{n})_{436}^{20}$ in chloroform are, in the order just stated, 0.0970, 0.0790, 0.0732, and 0.0695 ml./g. and are thus

* For a rigorous exposition on these see papers by Casassa and Eisenberg.^{53,54}

tending to the value for an infinitely high ratio of hydrocarbon to sulfur dioxide; i.e., for polyethylene, which we interpolate to be about zero under the same conditions. Although other series exhibit similar trends, many do not, and it does not seem feasible to derive \bar{n} for a particular polymer from the specific increments of related compounds. Thus no regular variation of \bar{n} exists among solutions of the seven alkyl esters of poly(methacrylic acid) or among the four poly(vinyl alkyl ethers) for which data are available without invoking the density of the solution. With d_2 known, \bar{n} can be obtained from n_2 if the latter is either measured directly or calculated indirectly via the Lorenz-Lorentz specific refraction [eq. (9)]. In either case some accuracy is sacrificed compared to a direct experimental measurement of \bar{n} . Wiley⁵⁶ has compiled data for 26 pure polymers which give measured and calculated values of the Lorenz-Lorentz "segment" refractions ($R_2 \times$ mol. wt. of polymer segment). Measurements were made of $(n_2)_{589}^{25}$ and $(d_2)^{25}$ and calculated values obtained on the assumption of additivity of the constituent refractivities of the atoms in a segment. Agreement between observed and calculated figures was ca. $\pm 1\%$. Values of Lorenz-Lorentz atomic refractions appropriate to the wavelengths 656, 589, 486, and 434 $m\mu$ are available in the literature.⁵⁷ These values are the "segment" refractions, viz:

$$R_i = [(n_i^2 - 1)/(n_i^2 + 2)] \cdot (m_i/d_i) \quad (33)$$

where m_i is the molecular weight of the repeat unit. The error δn_2 for a polymer incurred by using R_2 and d_2 is

$$\delta n_2 = (\partial n_2 / \partial R_2) \cdot \delta R_2 + (\partial n_2 / \partial d_2) \delta d_2 \quad (34)$$

$$\delta n_2 = \{4(m_2 + 2R_2d_2)(m_2 - R_2d_2)\}^{-1/2} \{ (2d_2 + m_2d_2 + 2R_2d_2^2)\delta R_2 + (2R_2 + m_2R_2 + 2R_2^2d_2)\delta d_2 \} \quad (35)$$

Taking typical approximate values of 100, 25 ml./g.-segment, and 1 g./ml. for m_2 , R_2 , and d_2 , the absolute error in n_2 is given by

$$\delta n_2 \approx 0.0047 [80\delta R_2 + 3800 \delta d_2] \quad (36)$$

R_2 values, compiled from accurate data for the density and refractive index of simple substances, are quoted to three significant decimal figures, and δR_2 may legitimately be regarded as 0.001. Even with the highest accuracy the smallest value of δd_2 for a polymer is 0.0001 g./ml. and consequently for the most favorable case, eq. (36) yields $\delta n_2 < \text{ca. } 0.002$. This conclusion agrees with the experimental findings of Putzeys and Brosteaux.²³ The use of n_2 thus established to calculate \bar{n} from eq. (6) yields a minimum uncertainty of 1% in \bar{n} , where this increment assumes a favorably large value of 0.2 ml./g. We have calculated R_2 for polystyrene at 434 $m\mu$ from the atomic and bond refractions and their dispersions and have taken the most accurate experimental value⁴⁹ of d_2 at 25°C. From $R_2 = 34.378$ ml./g.-segment, $1/d_2 = 0.9432$ ml./g., $m_2 = 104.14$ the refractive index of polystyrene, referred to 25°C. and 434 $m\mu$ is calculated to be 1.6352. Con-

sidering \bar{n} for polystyrene in MEK, we have taken the most accurate literature values for n_1 and \bar{v}_2 , referred to 25°C. and 436 m μ and calculated \bar{n} via eq. (6). As $n_1 = 1.3843$ and $\bar{v}_2 = 0.9076$ ml./g., the specific refractive increment for this system is 0.228 ml./g. The most accurate literature results are 0.230 and 0.231 ml./g. and the predicted error of ca. 1% is confirmed.

When the extent of annealing, orientation and crystallinity are variable factors in a polymer film of fixed molecular weight, both d_2 and n_2 will change, although R_2 remains constant. Schael⁸⁸ has recently obtained R_2 for the polyolefins polyethylene, polypropylene, and poly-4-methylpentene-1 by measuring n_2 and d_2 plotting $(n_2^2 - 1)/(n_2^2 + 2)$ versus d_2 , whence R_2 is obtained as the slope of the line. (For these anisotropic materials n_2 is actually the geometric mean of the indices $(n_2)_x$, $(n_2)_y$, and $(n_2)_z$ along three mutually perpendicular axes.)

Conventional experimental measurements yield \bar{n} accurate to 0.5%, while recent refined techniques⁹ allow it to be obtained to within 0.1%. Re-emphasizing that errors incurred in \bar{n} are doubly reflected in the molecular weight of the polymer deduced by light scattering, it is clear that experimental determinations of the increment are emphatically to be preferred.

Tacticity

n_2 and \bar{n} are essentially measures of local polarizability due to deformation of the electronic configuration about nuclei. They should, consequently, be insensitive to such detailed structure as stereoregularity. In Part I¹ comparative data on \bar{n} for atactic and isotactic forms of the same polymer corroborate this supposition.

Radiation

The effect of irradiation on polystyrene solutions has been studied by Pedemonte et al.⁵⁹ Instead of following chain scission via intrinsic viscosity it was considered more meaningful to measure M_w by light scattering. \bar{n} was checked and found to be unaltered after irradiation, simply confirming that it is independent of chain length.

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Résumé

Les résultats de la Partie I ont été étudiés à la lumière des théories admises. L'incrément de l'indice de réfraction spécifique \bar{n} pour la plupart des solutions de polymère se situe entre -0.2 et $+0.2$ ml/g, bien que des valeurs plus élevées puissent être obtenues dans des circonstances où l'unité diffusante est particulièrement grande, par ex. des solutions de polyacides partiellement neutralisés dont les unités contiennent des ions de signe contraire. \bar{n} dépend des indices du solvant n_1 et du polymère n_2 . Parmi les solvants habituels, l'eau et le 1-bromonaphthalène sont capables de fournir des valeurs respectivement fort positives et négatives pour \bar{n} . La règle de Gladstone-Dale s'applique rigoureusement aux solvants purs et en mélange mais l'expression de Lorenz-Lorentz est préférable pour l'évaluation de n_2 . On résume les résultats des théories actuelles appliquées aux solvants en mélange et aux copolymères. Dans le premier cas le poids moléculaire vrai M a été déterminé en utilisant la valeur de n et la variation de l'indice du solvant avec la composition. Pour un copolymère composé des monomères A et B, M aussi bien que M_a et M_b sont obtenables en utilisant \bar{n} , \bar{n}_a et \bar{n}_b . L'expression de la dispersion est exprimée par $(\bar{n})_\lambda = (\bar{n})_{436}[D' + D''/\lambda^2]$ pour une longueur d'onde λ et les constantes de dispersion D' et D'' ont été évaluées pour certaines solutions. $\partial n/\partial T$ est généralement égal à $3.2(\pm 2.3) \times 10^{-4}$ ml/g/°C et change très peu avec λ . Lorsque \bar{n} augmente en même temps que M , la valeur caractéristique limite est obtenue (pour $1/M = 0$) à partir d'un graphique de \bar{n} en fonction de $1/M$, \bar{n} ne peut être déterminé avec une précision maximum de 1% en employant n_2 calculé à partir de l'équation de Lorenz-Lorentz et du volume spécifique partiel expérimental.

Zusammenfassung

Die in Teil I angegebenen Daten werden im Lichte der bestehenden Theorie überprüft. Das spezifische Brechungsindexinkrement \bar{n} der meisten Polymerlösungen liegt zwischen $-0,2$ und $+0,2$ ml/g; allerdings können in Fällen, wo die Streueinheit ungewöhnlich gross ist, z.B. Lösungen von partiell neutralisierten Polysäuren, deren Einheit das Gegenion enthält, grössere Werte erhalten werden. \bar{n} hängt vom Brechungsindex des Lösungsmittels n_1 und des Polymeren n_2 ab. Unter den üblichen Lösungsmitteln sind Wasser und 1-Bromnaphthalin dazu befähigt, hohe positive bzw. negative Werte für n zu liefern. Die Regel von Gladstone und Dale ist auf reine und gemischte Lösungsmittel streng anwendbar, zur Ermittlung von n_2 ist jedoch der Lorenz-Lorentz-Ausdruck vorzuziehen. Die Ergebnisse bei der Anwendung der bekannten Theorien auf Mischlösungsmittel und Copolymere werden zusammengefasst. Bei ersteren wird bei Verwendung von \bar{n} und der Abhängigkeit des Lösungsmittelbrechungsindex von der Zusammensetzung das wahre Molekulargewicht M bestimmt. Für ein Copolymeres aus den Monomeren A und B kann sowohl M als auch M_a und M_b bei Verwendung von \bar{n} , \bar{n}_a und \bar{n}_b erhalten werden. Die Dispersion wird als $(\bar{n})_\lambda = (\bar{n})_{436}[D' + D''/\lambda^2]$ bei einer Wellenlänge λ ausgedrückt, und die Dispersionskonstanten D' und D'' werden für einige Lösungen ermittelt. $\partial \bar{n}/\partial T$ liegt allgemein bei $3,2 (\pm 2,3) \times 10^{-4}$ ml/g/°C und ändert sich mit λ nur wenig. Bei einem Anstieg von \bar{n} mit M wird der charakteristische Grenzwert (bei $1/M = 0$) aus einem Diagramm \bar{n} gegen $1/M$ erhalten. n kann unter Verwendung des aus der Lorenz-Lorentz-Gleichung und dem experimentellen partiellen spezifischen Volumen berechneten n_2 mit einer maximalen Genauigkeit von 1% bestimmt werden.

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