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Solution Viscosities and Unperturbed Dimensions of Poly(vinylidene chloride)[1]

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ABSTRACT: Light-scattering molecular weights and dilute-solution viscosities have been measured for a series of unfractionated homopolymers of vinylidene chloride in tetramethylene sulfoxide and in *N*-methylpyrrolidone. From these results the characteristic ratio is estimated to be $C_\infty = 8 \pm 1$, which is somewhat larger than the accurately known value of 6.6 for poly(isobutylene). The larger value for poly(vinylidene chloride) can be rationalized as largely due to electrostatic dipole interactions.

Poly(vinylidene chloride) (PVDC) has long been an important commercial material,[2] but knowledge of its chain conformational properties is still relatively slight. The exact crystal structure is not yet settled,[2-4] and determinations of chain dimensions in solution have previously been published only for several copolymers of vinylidene chloride.[5,6] The lack of solution data is fundamentally due to the high crystalline melting point of the polymer (202°) which severely limits solubility at room temperature, and to thermal instability which prevents accurate work at higher temperatures. Recently, however, a wide search by Wessling[7] has revealed the existence of several solvents suitable for solution study of the homopolymer at ordinary temperatures. Here we report on light-scattering and viscosity measurements of a series of unfractionated samples of PVDC in several of Wessling's solvents, and from the results we estimate the unperturbed chain dimensions.

Apparently the only polymer of the structural type $(\text{-CH}_2\text{CR}_2\text{-})_x$ for which conformational properties are well known at present is poly(isobutylene) (PIB), and it is clearly worthwhile to study at least one more member of this class. Furthermore, the relatively small difference between the van der Waals radii of the methyl group and the chlorine atom suggests that differences in conformational behavior between PVDC and PIB might be attributed in considerable part to the electrostatic dipolar interactions present in the former polymer. We have made calculations which lend some support to this suggestion.

Experimental Section

Vinylidene chloride (Polysciences, Inc.) was distilled over anhydrous magnesium sulfate. Polymerizations were effected with benzoyl peroxide initiator (1.5 mol % on monomer) at 60° in the presence of varying amounts of carbon tetrachloride as diluent and transfer agent. The customary freeze–pump–thaw cycle was used. Polymerization in sealed tubes was allowed to proceed for several days, after which the solid polymer was rinsed thoroughly with methanol before drying under vacuum to constant weight.

Tetramethylene sulfoxide, TMSO (Aldrich, bp 60–61° (0.3 mm)), and 1-methyl-2-pyrrolidone, MP (Eastman Kodak, bp 68° (8 mm)), were distilled under reduced pressure before use. Hexamethylphosphoramide, HMPA (Aldrich), was used for viscosity measurements as obtained. Solution viscosities were determined in Ubbelohde dilution viscometers at 25° in a bath controlled to ±0.02°. A Brice-Phoenix Differential Refractometer, Model BP-1000V, was used to obtain refractive-index increments, d*n*/d*c*, for PVDC of 0.0494 (±0.0004) cm^3 g^{-1} in TMSO and 0.0799 (±0.0004) in MP at a wavelength of 546 nm. Light-scattering intensities of PVDC solutions in TMSO and MP were measured at room temperature for unpolarized incident light (546 nm) with a Brice-Phoenix Model 1000 Light Scattering Photometer.

Usually it was necessary to warm the polymer–solvent mixtures to about 50 or 60° for 3 to 4 min in order to produce homogeneous solutions, but these could then be kept at room temperature without phase separation for at least some hours, quite long enough for the measurements. Absence of significant polymer degradation during the dissolution period was inferred from the fact that solutions raised to 70° for more than 5 min and then returned to 25° displayed negligible changes in solution viscosity. The MP solutions as measured usually were visibly very faintly yellow in color, but deliberate slight enhancement of this color by warming for short periods of time did not change the measured light scattering intensity, and no correction for absorption was applied. The TMSO solutions were colorless.

The preliminary light-scattering results reported earlier[8] have now been superseded by later measurements in which greater photometer sensitivity was achieved, in part by sacrificing angular resolution. Molecular weights were obtained by linear extrapolation based on the customary relation

$$Kc/R_{90} = (P_{90}M_w)^{-1} + 2A_2c + \ldots \qquad (1)$$

Corrections for depolarization of the scattered light were negligible. The molecular weights (all below 130 × 10^3) are too small for accurate measurement of angular dissymmetry, so the intramolecular scattering factors P_{90} were estimated as elsewhere[9,10] from the intrinsic viscosities. The figures reported in Table I are obtained as averages of the results obtained in the two solvents MP and TMSO. Second virial coefficients are not given for the lower molecular weights because of insufficient precision; for the two highest, the value of A_2 is 1.5×10^{-4} cm^3 mol g^{-2}, which is close to that expected on the basis of the standard two-parameter correlation.[11]

Results

The weight-average molecular weights M_w and intrinsic viscosities $[\eta]$ obtained for the various samples in both TMSO and MP are shown in Table I. The estimated angular scattering factors $1/P_{90}$ alter the molecular weights by 4% at most. The table also includes intrinsic viscosities in HMPA, although with this solvent we could not prevent

Table I
Molecular Weights and Intrinsic Viscosities of PVDC Samples

		$[\eta]$, dl/g		
$M_w \times 10^{-3}$	$M_v \times 10^{-3}$	(MP)[a]	(TMSO)[b]	(HMPA)[c]
9.1	8.5	0.0680	0.0712	0.094
12.3	11.4	0.0816	0.0886	0.112
15.2	14.1	0.0920	0.0949	0.122
32.4	30.1	0.161	0.168	
37.3	34.3	0.173	0.182	0.226
106	98.6	0.354	0.378	0.455
126	117.0	0.416	0.435	

[a] *N*-Methyl pyrrolidone. [b] Tetramethylene sulfoxide. [c] Hexamethylphosphoramide.

rather strong discoloration of the solutions and accordingly did not try to make light-scattering measurements.

From the slopes ν of double logarithmic plots of $[\eta]$ against M_w we transformed the molecular weights into viscosity-average values M_v, employing the relation[9]

$$M_v/M_w = [(1+\nu)\Gamma(1+\nu)]^{1/\nu}/2 \tag{2}$$

which corresponds to polydisperse materials with a "most probable" distribution. For the present systems this ratio is 0.93. The order of solvent power indicated by the magnitudes of the intrinsic viscosities in the three solvents is the same as that implied by Wessling's[7] observations of dissolution temperatures. The viscosity–molecular weight relations are

$$[\eta] = 1.31 \times 10^{-4} M_v^{0.69} \quad \text{(in MP)} \tag{3}$$

$$[\eta] = 1.39 \times 10^{-4} M_v^{0.69} \quad \text{(in TMSO)} \tag{4}$$

$$[\eta] = 2.58 \times 10^{-4} M_v^{0.65} \quad \text{(in HMPA)} \tag{5}$$

for intrinsic viscosities in dl/g. As always, these relations should not be used far beyond the range of molecular weight measured. Double logarithmic plots of $[\eta]$ against M_v are shown in Figure 1.

Lacking data at θ conditions, we estimate the unperturbed dimensions by resorting to the familiar approximate device of plotting $[\eta]/M_v^{1/2}$ against $M_v^{1/2}$. Omitting the HMPA data as less reliable, we obtain an intercept which gives $10^4 K_\theta = 6.0 \pm 1$ for PVDC. An extra note of caution about this procedure has recently been sounded by Pouchlý and Patterson.[12] They point out that the concentration dependence of the familiar thermodynamic interaction parameter χ_1, as inferred from osmotic, vapor pressure or phase equilibrium data, results in a contribution to $[\eta]/M^{1/2}$ which is independent of molecular weight and therefore in general could not be eliminated by any treatment based on an extrapolation to low molecular weight. The existence of this term, which was clearly recognized in the earlier work of Orofino and Flory,[13] has been largely ignored, owing perhaps to the appeal of the two-parameter concept. We have no alternatives in the present case, and must be content simply to take this consideration into account in assigning a somewhat larger uncertainty to our extrapolated result. Adopting the value of K_θ given above, we then find

$$\langle r^2\rangle_0/M = (K_\theta/\Phi)^{2/3} = (39 \pm 4) \times 10^{-18}\ \text{cm}^2\ \text{mol/g} \tag{6}$$

in which we have used $\Phi = 2.5 \times 10^{21}$, and finally we get

$$C_\infty = \langle r^2\rangle_0/nl^2 = 8 \pm 1 \tag{7}$$

at 25° for PVDC. If a lower Φ value of 2.1×10^{21} is used, the characteristic ratio is raised to 9 ± 1. This result may be compared with those given by Asahina, Sato, and Kobayashi,[5] who report $10^4 K_\theta$ figures from 6.6 to 7.3 at 50° for several copolymers containing about 15 mol % of alkyl acrylates, and by Wallach,[6] who found $K_\theta = 8.1 \times 10^{-4}$ in THF for copolymers containing 15 mol % acrylonitrile. The corresponding characteristic ratios range from about 8.5 to 9.3, slightly higher than our figure for the homopolymer, but in agreement to within our estimated uncertainty. It is moreover recalled that in general the apparent unperturbed dimensions of polar polymers cannot be expected to be precisely the same in all polar solvent systems.[14,15] Under the circumstances, agreement among the results for homopolymers and copolymers is regarded as satisfactory.

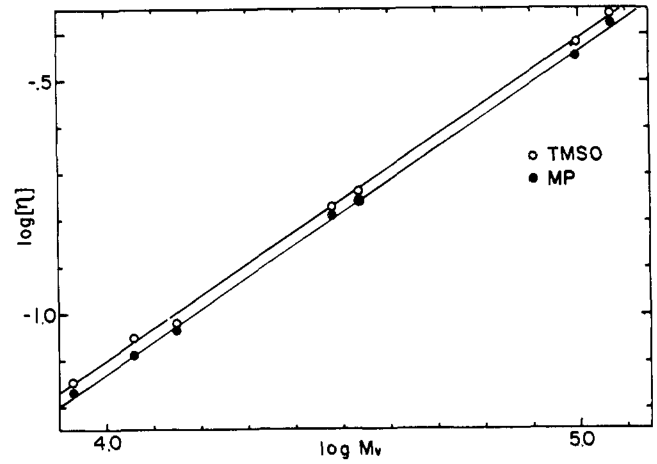

Figure 1. Intrinsic viscosity–molecular weight data for PVDC at 25°.

Discussion

The characteristic ratio found experimentally for PVDC is definitely larger than that for PIB, which is[16] about 6.6 at 24°. Of the numerous models which have been used[16-19] for the latter polymer, we find it most convenient for the present purpose to adopt that of Allegra, Benedetti, and Pedone,[17] modifying it for application to PVDC by the addition of electrostatic interactions among the polar C–Cl bonds. Formally the treatment of Allegra and coworkers is that of a three-state model, although it is recognized in assigning the statistical weights that a strictly planar all-trans conformation of the chain is sterically greatly hindered.[16] The method of assigning these weights also differs from the now conventional one recommended by Flory.[16]

Proceeding to our adaptation of the Allegra calculation, we take the two statistical-weight matrices to be

$$U' = \begin{array}{c|ccc} & t & g^+ & g^- \\ \hline t & 1 & \alpha & \alpha \\ g^+ & \alpha & \beta & \gamma \\ g^- & \alpha & \gamma & \beta \end{array} \tag{8}$$

$$U'' = \begin{array}{c|ccc} & t & g^+ & g^- \\ \hline t & 2 & \eta & \eta \\ g^+ & \eta & \epsilon & 0 \\ g^- & \eta & 0 & \epsilon \end{array} \tag{9}$$

Here the first matrix describes the statistical weights for a pair of neighboring chain bonds emanating from a CH_2 group, and the second matrix refers to a pair of bonds leading from an intervening CCl_2 group. The latter matrix U'', with elements given by

$$\begin{aligned} \epsilon &= \exp(-E/RT) \\ \eta &= 1 + \exp(-E_1/RT) \end{aligned} \tag{10}$$

is identical in form with that in PIB, and is thus conceived to be steric in origin. The elements of the former matrix U′ reflect differences in electrostatic energy.

$$\begin{aligned} RT \ln \alpha &= W(\mathrm{tt}) - W(\mathrm{tg}^{\pm}) \\ RT \ln \beta &= W(\mathrm{tt}) - W(\mathrm{g}^{\pm}\mathrm{g}^{\pm}) \\ RT \ln \gamma &= W(\mathrm{tt}) - W(\mathrm{g}^{\pm}\mathrm{g}^{\mp}) \end{aligned} \tag{11}$$

To represent the electrostatic effects, partial point charges $q_i e$ (where e is the electronic charge) are placed at the carbon and chlorine nuclei of a CCl_2 group. With a dipole moment of 2.0 D per repeat unit, a Cl–C–Cl bond angle of 112°, and a C–Cl bond length of 1.76 Å, we find $q(\mathrm{C}) = -2q(\mathrm{Cl}) = +0.42$. The electrostatic energy in a given conformation is then

$$W = (e^2/4\pi\epsilon_0 D) \sum_{i \neq j} q_i q_j / r_{ij} \tag{12}$$

where D is the effective dielectric constant. If the distances r_{ij} are in ångströms, the factor $(e^2/4\pi\epsilon_0)$ has the value 332 kcal mol^{-1}. Since eq 8–11 necessarily restrict correlations of conformation to those between nearest-neighboring bonds in the chain backbone, it is clear that the electrostatic interactions considered can be only those between adjacent CCl_2 groups. This does not imply that interactions between more distant pairs of polar groups are absent, but only that their dependence on chain conformation is neglected. In view of other crudities of the model, this neglect does not seem serious.

Numerical evaluations of C_∞ were made with the aid of the formula of Hoeve[19] and with the following structural parameters in addition to those specified above: C–C distance 1.54 Å; C–CH_2–C bond angle, $\theta_2 = 123°$; C–CCl_2–C bond angle θ_1 varying over the range 110 to 120°. Two different sets of values for the steric energies were tried: (1) $E = 2.0$ kcal mol^{-1} and $E_1 = 1.4$ kcal mol^{-1}, both near the lower limits of the ranges considered for PIB by Allegra and coworkers;[17] and (2) $E = 1.0$ kcal mol^{-1} and $E_1 = 0.5$ kcal mol^{-1}. The latter values were investigated because the van der Waals radius of Cl is somewhat smaller than that of CH_3 (1.8 Å compared with 2.0 Å in Pauling's table[20]). The effective dielectric constant was put at D = 1, 2, 4, and ∞; the infinite value is included because it affords a check, permitting recovery of the Allegra results for PIB.

Some calculated values of C_∞ are shown in Table II. Results (not shown) were also obtained for $\theta_2 = 124°$, but this produced a change of less than 0.1 in the characteristic ratio and thus showed that precise specification of θ_2 is not important. On the other hand, the calculation is quite sensitive to the value chosen for the bond angle θ_1, as can be seen in Table II and also in Figure 2, where calculated characteristic ratios are plotted against θ_1 for several values of D. For PIB, the value of θ_1 is[17] near 110°, but various models proposed for PVDC span the entire range covered in Table II. It is seen in the table or the figure that when the effective dielectric constant is in a physically reasonable range near $D = 2$ the experimental value of C_∞ can be reproduced with our model if θ_1 is in the range 111 to 115°, depending on the choice of E and E_1. It should of course be remarked that we assign θ_1 the same value in all rotational isomeric states, which is a serious oversimplification although it is common to most such calculations, including the treatment of PIB with which we compare our results for PVDC.

Mark[21] has made conformational energy calculations for poly(vinyl chloride) and poly(propylene) and concluded that the difference in van der Walls radius between Cl and CH_3, rather than polarity, is the principal cause of the dissimilarities in configurational and conformational equilibria between these polymers. In the case of PVDC, a reduction of the Allegra energy parameters E and E_1, which probably corresponds to reducing the van der Waals repulsions among the chain substituents, produces a decrease in the calculated characteristic ratio, and the electrostatic effects are then needed to raise it to the observed value. There is not necessarily a contradiction between our conclusions and those of Mark, because the geometry of the dipolar and steric interactions in vinyl and vinylidene chains is quite different.

We have evaluated the probabilities of the various bond-pair conformations by appropriate differentiation of the partition function (i.e., of the largest eigenvalue of the matrix U′U″),[16] but in view of the crudeness of the model the details do not seem worth presenting. In Table III the effect of the electrostatic terms is illustrated by the results for the case $E \doteq 2.0$ kcal mol^{-1}, $E_1 = 1.4$ kcal mol^{-1}, $\theta_1 = 112°$, and $\theta_2 = 123°$, for both $D = 2$ and $D \to \infty$. The magnitudes of the elements in the matrix U′ decrease in the order $\beta > \alpha > 1 > \gamma$; thus electrostatic repulsions actually diminish slightly the probability of a trans conformation for any one bond, but they also augment by a larger factor the probability of helical g^+g^+ and g^-g^- sequences. The attendant increase of characteristic ratio despite a reduction in trans population is similar to those displayed in Flory's model calculations for poly(oxymethylene) and poly(dimethylsiloxane) chains,[16] and as in the latter example the

Table II
Computed Characteristic Ratio C_∞

	θ_1, deg			
D	120	116	112	110
	(1) $E = 2.0$, $E_1 = 1.4$ kcal/mol			
1	11.443	9.974	8.634	8.016
2	11.104	9.651	8.302	7.677
4	10.749	9.275	7.923	7.302
∞	10.119	8.640	7.318	6.722
	(2) $E = 1.0$, $E_1 = 0.5$ kcal/mol			
1	9.575	8.560	7.587	7.122
2	9.608	8.377	7.379	6.875
4	9.284	8.094	7.003	6.500
∞	8.613	7.434	6.384	5.909

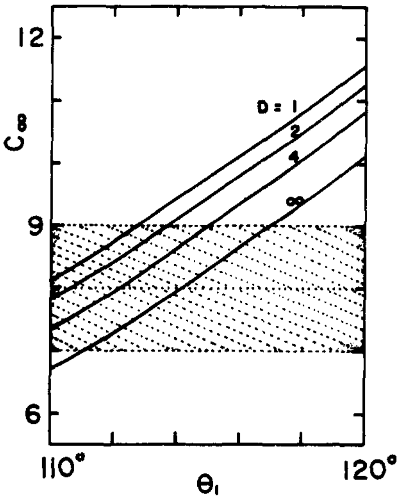

Figure 2. Calculated characteristic ratios for PVDC with several choices of bond angle θ_1 and effective dielectric constant D, for E = 2.0 kcal mol^{-1} and E_1 = 1.4 kcal mol^{-1}. Shaded area represents range of experimental results.

Table III
Bond Conformational Probabilities Calculated for a PVDC Chain with $E = 2.0$ kcal mol^{-1}, $E_1 = 1.4$ kcal mol^{-1}, $\theta_1 = 112°$, $\theta_2 = 123°$

	Infinite D	$D = 2$
$p_g = 1 - p_t$	0.3501	0.3922
$p_{g^+g^+} = p_{g^-g^-}$	0.0307, 0.0053[a]	0.0457, 0.0086[a]
$p_{g^+g^-} = p_{g^-g^+}$	0.0307, 0	0.0127, 0
$p_{g^+t} = p_{tg^+}$	0.1138, 0.1698	0.1378, 0.1875
p_{tt}	0.4223, 0.3103	0.3323, 0.2328

[a] First figure for bond pairs flanking CH_2; second figure for pairs flanking CCl_2.

effect in PVDC is somewhat augmented by the inequality of the chain bond angles θ_1 and θ_2. The results for other choices of E, E_1, and θ_1 are qualitatively similar.

In conclusions, we may advise the reader to regard the above calculations with mild skepticism, in view of the recognized difficulties[16] of dealing with such highly substituted chains. It would be illuminating to study the PVDC chain with a more sophisticated model, such as that of Boyd and Breitling.[18]

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Analysis of Polydispersity in Polymer Solutions by Inelastic Laser Light Scattering

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ABSTRACT: The autocorrelation function of light inelastically scattered from a polymer solution may be analyzed to determine the diffusion coefficient of the polymer. If the solution is polydisperse, the measured diffusion coefficient will be an average over all species. Koppel showed that if the autocorrelation function is analyzed in terms of its cumulants, the diffusion coefficient will be a z average. If the particle dimensions are not small compared with the wavelength of light, however, this conclusion will hold only in the limit of zero scattering angle, since at higher angles the form factors of the larger particles decrease their contributions relative to the smaller particles. We show how the slopes and intercepts of plots of K_1/K^2 and K_2/K^4 (where K_1 and K_2 are the first and second cumulants, and K is the scattering vector, $(4\pi/\lambda)\sin(\theta/2)$) can be analyzed to yield four z averages of the polymer radius distribution function: $\langle R^{-1}\rangle$, $\langle R^{-2}\rangle$, $\langle R\rangle$, and $\langle R^2\rangle$. The experimental behavior of the angular dependence of K_1/K^2 for synthetic mixtures of polystyrene latex spheres gives good agreement with theory.

Polymer solutions are often polydisperse. Attempts to use inelastic laser light scattering to analyze such polydispersity or, conversely, to estimate the complicating effects of polydispersity on scattering measurements are common in the recent literature. These attempts have generally concentrated on data analysis at a single scattering angle, and have characterized polydispersity effects in terms of deviations from a simple Lorentzian line shape or a simple exponential decay, depending on whether spectral or autocorrelation analysis is employed. In recent work, autocorrelation analysis has been particularly prominent.[1–5]

In this paper we show that a more detailed analysis of polydispersity is possible if autocorrelation functions are obtained at several scattering angles, and if the scattering particles are large enough that intramolecular interference effects are significant. Our treatment is an extension of the cumulant expansion technique introduced by Koppel.[1]

Theory

The electric field autocorrelation function of light scattered from a polydisperse solution of spherical particles is

$$g^{(1)}(\tau) = \frac{\sum_i M_i W(M_i) P(K,M_i) e^{-K^2 D_i \tau}}{\sum_i M_i W(M_i) P(K,M_i)} \tag{1}$$

where $W(M_i)$ is the weight fraction of species i with molecular weight M_i, diffusion coefficient D_i, and scattering form factor $P(K,M_i)$. K is the scattering vector, whose magnitude is $(4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of light in the scattering medium and θ is the scattering angle.

The first and second cumulants of the autocorrelation