138 Macromolecules 1981, 14, 138–142

Configurational Properties of Vinyl Chains. Dipole Moments of Poly(vinyl chloride)

F. Blasco Cantera and E. Riande*

Instituto de Plásticos y Caucho (CSIC), Juan de la Cierva 3, Madrid-6, Spain

J. P. Almendro and E. Saiz

Departamento de Química Física, Facultad de Ciencias, Universidad de Extremadura, Badajoz, Spain. *Received June 19, 1980*

ABSTRACT: The mean-square dipole moment, $\langle \mu^2 \rangle$, of two fractions of poly(vinyl chloride) has been measured in dioxane solution at different temperatures. The experimental values of $\langle \mu^2 \rangle$ increase with increasing syndiotacticity and show a negative temperature coefficient. Earlier theoretical calculations carried out assuming that the orientation of the vector dipole moment m corresponding to the repeat unit coincides with that of the C–Cl bond dipole moment gave values of $\langle \mu^2 \rangle$ significantly higher than the experimental results. The present analysis shows, however, that if the contribution to m from the vector dipole associated with the C–H bond of the HCCl group is taken into account, the theoretical calculations reproduce the experimental results.

Introduction

Ever-increasing emphasis is being placed on the analysis of the configurational properties of random-coil vinyl chains $CH_3-(CHRCH_2)_n-H$ which, as is known, depend on their stereochemistry, their degree of polymerization x, and the nature of the pendant group R.[1] Among these properties, the mean-square dipole moment assumes particular importance because it can be determined experimentally over the entire range of chain length, an advantage not shared by a number of other configuration-dependent properties such as chain dimensions and stress optical coefficients.[2] Moreover, theory indicates that long-range perturbations have no effect on the dipole moment of chain molecules which possess certain symmetry features;[3–6] for example, when the resulting dipole moment of each repeat unit lies in a plane bisecting one of the skeletal bond angles, as in the case of poly(oxyethylene), poly(dimethylsiloxanes), and poly(vinyl halides), or when the chains have appropriate symmetry elements (planes, axes, points), as in the case of polyacrylates, polymethacrylates, and polyamides. Therefore, the mean-square dipole moments of most polymers, at any given temperature and in any nonpolar solvent, coincide quite well with the unperturbed values.

Mark[7–10] has pioneered attempts to use dipole moments and chain dimensions of polymers dissolved in dilute solutions as a means to determine the monomer sequence distribution of copolymers as well as the stereochemical structure of vinyl chains. He has calculated the dimensions and dipole moments of poly(vinyl chloride) as a function of the stereochemical composition using the rotational isomeric state model.[8] Mark's results predict that the mean-square dipole moment of poly(vinyl chloride) decreases with increasing isotacticity and the dipole moment shows a negative temperature coefficient for each composition. The largest temperature dependence occurs in the case of perfectly syndiotactic chains.

Although the presence of a significantly large electric dipole in the repeat unit of poly(vinyl chloride) should permit the measurement of this parameter in an easy way, there are few experimental data to make reliable comparisons of theoretical and experimental values of the dipole moment ratio because of the insolubility of the polymer in most nonpolar solvents. For this reason, the present study was undertaken to determine reliable values of the dipole moment ratio $D_x = \langle \mu^2 \rangle / xm^2$, where $\langle \mu^2 \rangle$ is the mean-square dipole moment of the chain unperturbed by excluded-volume effects and x is the number of repeating units, each of them having a dipole moment of m. The approach taken, the study of characterized samples soluble in dioxane, is probably the only method available for this purpose. Actually, dioxane is the only common nonpolar medium in which slightly syndiotactic poly(vinyl chloride) chains are sufficiently soluble.

Experimental Section

Polymer Fractions. Polymerizations of purified vinyl chloride were carried out in bulk and initiated by UV radiation and 2,2′-azobis(isobutyronitrile) at +60 and −50 °C. The polymerization was stopped after a conversion less than 10%. The resulting products were purified by precipitation from a solution in tetrahydrofuran followed by drying under vacuum at 50 °C for 48 h. Dioxane-soluble fractions of the polymer obtained at 60 °C (fraction A) and at −50 °C (fraction B) were used in this study. Both fractions were extracted at 50 °C with dioxane and the resulting solutions were centrifuged at 16 000 rpm to eliminate undissolved material. The solutions were then poured into an excess of methanol with constant stirring. After filtration, washing with methanol, and air-drying, the precipitates were kept under vacuum. Finally, the fractions were freeze-dried from dioxane to eliminate low molecular weight material.

Solution viscosities of the two fractions were measured in cyclohexanone. Viscosity-average molecular weights were calculated from the measured intrinsic viscosities with the equation[11]

$$[\eta] = 2.4 \times 10^{-4} M_v^{0.72}$$

which was obtained by Danusso from viscosity and molecular weight measurements.

Stereoregularity of the Fractions. Infrared spectra were recorded at 25 °C on KBr pellets with a Perkin-Elmer 457 spectrometer. The normalized intensity of syndiotactic dyads, $P(S)$, was calculated by Germar's equation[12] (eq 1), where λ is

$$P(S) = \frac{1 + \exp(-\Delta E/RT)}{1 + \lambda} \qquad (1)$$

the ratio of the two infrared absorption bands at 1428 and 1434 cm^{-1} (A_{1428}/A_{1434}) and ΔE is the energy difference between the two syndiotactic conformations gg and tt. Pham et al.[12] have studied the variation of tacticity of radical poly(vinyl chloride) as a function of the polymerization temperature by ^{13}C NMR and infrared spectroscopy and they found that, within experimental error, the radical propagation of vinyl chloride in bulk may be considered Bernouillan over the temperature range −30 to +25 °C. That is

$$P(I) \approx P(I/I) \approx P(I/S)$$

$$P(S) \approx P(S/S) \approx P(S/I)$$

Since the fractions used in this study were obtained at temper-

Table I
Normalized Intensities of Isotactic Dyads

fraction	A_{1428}/A_{1434}	P(I)
A	1.09	0.47
B	1.28	0.41

atures not too far from those indicated above, the statistics of the chains was also assumed to be Bernouillan. The values of P(I) are given in Table I.

Dielectric Measurements. Capacitance measurements were made with a capacitance bridge (General Radio Co. Type 1620 A) and a three-terminal platinum cell which is composed of two coaxial cylindrical electrodes.[13] The electrode assembly is mounted within a double-walled cell made of Pyrex glass. The cell was calibrated with benzene, cyclohexane, and toluene, all of these being substances of known dielectric constant.[14] Temperature was controlled by immersing the cell in an oil bath, where the oil circulated around both the inner and outer walls of the cell, so that the temperature was controlled within ±0.1 °C. All the measurements were carried out at a frequency of 10 kHz, at which the dielectric constant obtained is, to a good approximation, the static value.

Dioxane (Merck, 99% pure), refluxed over sodium about 48 h and distilled in a column of about 20 theoretical plates, was used as solvent in the dielectric measurements. Each concentration was prepared with freshly purified dioxane and the dielectric constant of the solvent at the temperature of interest was measured before measuring those of each solution.

The difference between the square of the refractive index of the solution n^2 and that of the solvent n_1^2 was measured in a Brice-Phoenix differential refractometer at each stated temperature.

Results

The dipole moment ratio was calculated from the dielectric constant data by means of the equation of Guggenheim[15] and Smith[16]

$$\frac{\langle \mu^2 \rangle}{xm^2} = \frac{27kTM}{4\pi N_A \rho_1 (\epsilon_1 + 2)^2 xm^2} \left[\frac{\mathrm{d}(\epsilon - \epsilon_1)}{\mathrm{d}w} - \frac{\mathrm{d}(n^2 - n_1^2)}{\mathrm{d}w} \right] \tag{2}$$

where k is the Boltzmann constant, T is the absolute temperature, $M = xM_0$ (where $M_0 = 62.5$ is the molecular weight of the repeat unit), N_A is Avogadro's number, and ρ_1 is the density of the solvent; ϵ, ϵ_1, n, and n_1 are the static dielectric constants and refractive indices of solution and solvent (index 1), respectively. The magnitude of the dipole moment corresponding to the repeat unit was taken to be 2.00 D, the observed dipole of ethyl chloride in the gas phase.[17]

In order to calculate the dipole moment ratio by eq 2, it is necessary to measure the difference between the static dielectric constant of the solution and that of the solvent at temperatures and concentrations of interest. The measurements presented some difficulty because of the solvent. The chief impurities in p-dioxane are acetic acid, water, and glycol acetal.[18] When the acetal is present in only small amounts, prolonged heating with sodium is adequate to remove it. Therefore, the solvent was refluxed about 48 h with sodium and then additional purification was effected by careful fractional distillation. However, purified dioxane is only stable when protected from an oxygen atmosphere. The measurements were made in an air atmosphere; the static dielectric constant of the fresh solvent at 25 °C, purified on different days, changed in the third decimal place, giving values intermediate between 2.2070 and 2.2094. Given the uncertainties involved in the values of ϵ_1, we have measured the dielectric constant of the solvent before preparing each solution and computed the differences $\Delta\epsilon = \epsilon - \epsilon_1$. The value of ϵ_1 used in the denominator of eq 2 was the average of all the values obtained in different measurements of freshly purified dioxane. This quantity, 2.2077 at 25 °C, is slightly lower than that reported in the literature (2.209).[18] Moreover, the temperature coefficient of ϵ_1 turned out to be -1.7×10^{-3} K^{-1}. Solutions were prepared by dissolving the polymer in dioxane in the vicinity of 90 °C; no separation of polymer was observed when the solutions were centrifuged at 16 000 rpm.

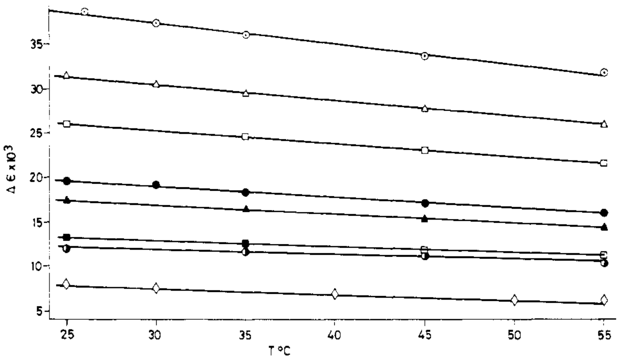

Figure 1. Difference $\Delta\epsilon = \epsilon - \epsilon_1$ of dielectric constants of solution (ϵ) and solvent (ϵ_1) vs. temperature for solutions with different weight factors w of poly(vinyl chloride) (fraction A): (◊) $w = 1.3 \times 10^{-3}$; (◑) $w = 2.13 \times 10^{-3}$; (■) $w = 2.2 \times 10^{-3}$; (▲) $w = 3.4 \times 10^{-3}$; (●) $w = 3.6 \times 10^{-}3$; (□) $w = 4.3 \times 10^{-3}$; (△) $w = 5.2 \times 10^{-3}$; (⊙) $w = 7.0 \times 10^{-3}$.

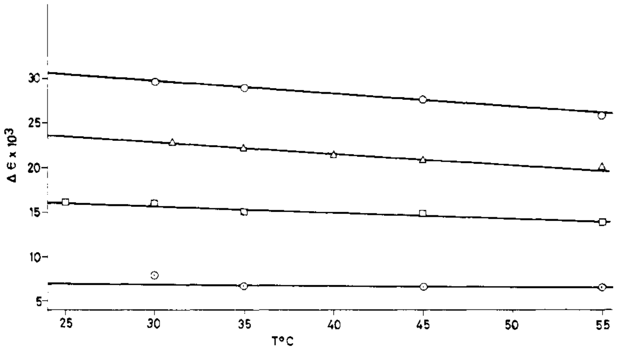

Figure 2. Difference $\Delta\epsilon = \epsilon - \epsilon_1$ of dielectric constants of solution (ϵ) and solvent (ϵ_1) vs. temperature for solutions with different weight fractions w of poly(vinyl chloride) (fraction B): (⊙) $w = 1.2 \times 10^{-3}$; (□) $w = 2.61 \times 10^{-3}$; (△) $w = 4.12 \times 10^{-3}$; (○) $w = 5.18 \times 10^{-3}$.

Table II
Dielectric Results of Poly(vinyl chloride) Chains

	T, °C			
	25	35	45	55
Fraction A (M_v = 26 000)				
$\mathrm{d}(\epsilon - \epsilon_1)/\mathrm{d}w$	5.644	5.306	4.967	4.649
$\langle \mu^2 \rangle / xm^2$	0.679	0.670	0.658	0.645
Fraction B (M_v = 47 000)				
$\mathrm{d}(\epsilon - \epsilon_1)/\mathrm{d}w$	5.806	5.509	5.199	4.857
$\langle \mu^2 \rangle / xm^2$	0.699	0.697	0.690	0.681

In Figures 1 and 2 the quantities $\epsilon - \epsilon_1$ are plotted as a function of temperature at different weight fractions of polymer for fractions A and B. Values of the derivatives $\mathrm{d}(\epsilon - \epsilon_1)/\mathrm{d}w$ were obtained from plots of $\epsilon - \epsilon_1$ against w, and the resulting lines were located by least-squares analysis. The correlation factor was in all cases higher than 0.994, and the slopes of the straight lines are given in Table II. Illustrative plots of this kind are given in Figures 3 and 4. The term $\mathrm{d}(n^2 - n_1^2)/\mathrm{d}w$ was found to be independent of temperature and has a value of 0.26 for both fractions (Figure 5). The values of the dipole moment

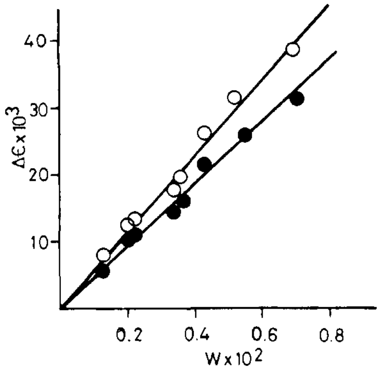

Figure 3. Concentration dependence of the increments in dielectric constant for fraction A: (○) 25 °C; (●) 55 °C.

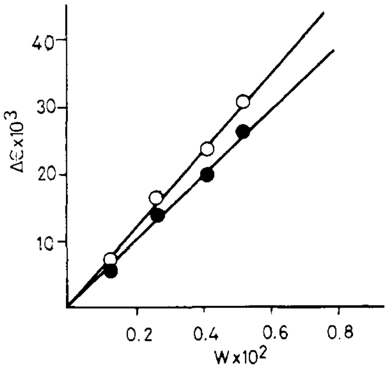

Figure 4. Concentration dependence of the increments in dielectric constant for fraction B: (○) 25 °C; (●) 55 °C.

Table III
Data of Le Fèvre and Sundaran[19] for Six Poly(vinyl chloride) Fractions with Decreasing Solubility

	fraction					
	I	II	III	IV	V	VI
$\langle\mu^2\rangle/xm^2$	0.662	0.669	0.674	0.679	0.671	0.717

ratio calculated therefrom are given in the third and fifth rows of Table II. These values agree satisfactorily with those reported by Le Fèvre and Sundaran,[19] who measured the dipole moment for a series of poly(vinyl chloride) fractions (fractions I–VI of Table III) which on the basis of their solubility characteristics would be expected to exhibit increasing syndiotacticity.

There are no published experimental data dealing with the influence of temperature on the dipole moments of poly(vinyl chloride) with the exception of those of Kotera et al.[20] These authors have found that the dipole moment ratio of poly(vinyl chloride) is independent of the measurement temperature. In contrast, our results indicate that this quantity has a negative temperature coefficient, as is shown in Figure 6, where the natural logarithm of $\langle\mu^2\rangle xm^2$ is plotted as a function of temperature.

Calculations

Following the RIS model, the mean-square dipole moment of a polymer chain consisting of n repeating units may be evaluated as[1,21]

$$\langle\mu^2\rangle = Z^{-1}\mathbf{F}_1\mathbf{F}_2^{(n-2)}\mathbf{F}_n \qquad (3)$$

where Z is the configurational partition function and **F** are matrices defined elsewhere.[21]

The use of eq 3 requires knowledge of the statistical weight matrices (i.e., matrices representing the stability of each conformation over two consecutive skeletal bonds).

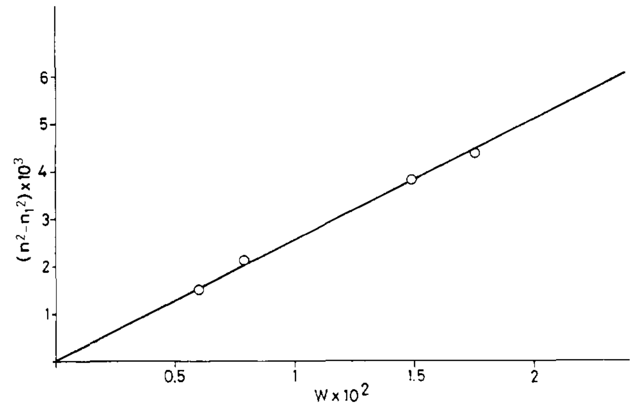

Figure 5. Concentration dependence of the increments in squared index of refraction for fractions A and B at 25 °C.

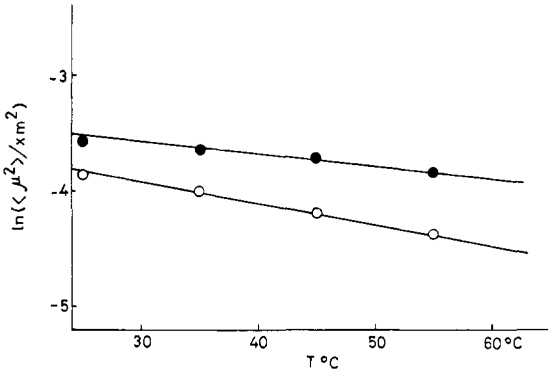

Figure 6. Dependence of the dipole moment ratio on temperature: (○) fraction A; (●) fraction B.

The three matrices required for the PVC chain may be written as[22]

$$\mathbf{U}_1 = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{pmatrix}$$

$$\mathbf{U}_\mathrm{m} = \begin{pmatrix} \omega''\eta^2 & \eta\tau\omega' & \eta \\ \eta & \tau\omega' & \omega \\ \eta\tau\omega' & \tau^2\omega\omega'' & \tau\omega' \end{pmatrix} \qquad (4)$$

$$\mathbf{U}_\mathrm{r} = \begin{pmatrix} \eta^2 & \eta\omega' & \eta\tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\tau\omega'' & \tau\omega & \tau^2\omega'^2 \end{pmatrix}$$

these matrices being equivalent to the ones previously used by Mark.[8]

The statistical weight factors needed to form eq 4 have been obtained by Flory and Williams[23] by qualitative estimates based on the relative sizes of interacting atoms and by analysis of the stereochemical equilibrium composition of 2,4-dichloro-*n*-pentane at 70 °C and were corrected to 25 °C by Mark,[8] yielding the values $\eta = 4.2$, $\tau = 0.45$, $\omega = \omega'' = 0.032$, and $\omega' = 0.071$.

In order to check these values, we have carried out some energy calculations. Three contributions to conformational energies were computed: *Rotational barriers* over C–C skeletal bonds were evaluated by using a threefold intrinsic potential with barriers of[24] 2.8 kcal mol^{-1}. *Electrostatic interactions* were computed by assigning partial charges[25] to Cl and C atoms so as to reproduce a dipole moment of 2.0 D for the C–Cl bond; a value of 3.0 was used for the dielectric constant of the medium.[26] *Nonbonded interactions* were calculated on the basis of the Lennard-Jones potential: $V_{ij} = (a_{ij}/r_{ij}^{12}) - (C_{ij}/r_{ij}^{6})$, wih the C_{ij} constants calculated according to the Slater–Kirkwood formula[27,28]

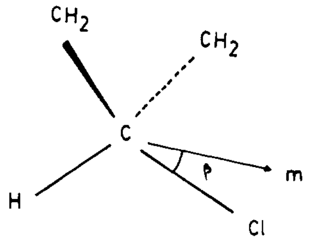

Figure 7. Orientation of the vector dipole moment m.

and the a_{ij} values assigned so as to minimize the pair potential V_{ij} for a given pair of atoms when their distance r_{ij} is set equal to the sum of the corresponding adjusted van der Waals radii;[28] following standard procedures,[28,29] this potential was truncated when the distance r_{ij} reached a given value σ in order to represent the effect of solvent molecules on the interaction between pairs of atoms.

Values of 1.53, 1.10, and 1.85 Å were taken for C–C, C–H, and C–Cl bond lengths, respectively.[30,31] The skeletal C–C–C bond angle was taken to be[30] 112° and a tetrahedral value was used for all remaining bond angles.

Calculations were carried out for meso and racemic dyads, allowing for rotations over two consecutive skeletal bonds. Partition functions ($Z_{\zeta\eta}$) and average energies ($\langle E_{\zeta\eta}\rangle$) were evaluated for a region of ±40° over each minimum ($\zeta\eta$) at intervals of 5° in both rotational angles. The statistical weight of each state $\zeta\eta$ appearing in eq 3 was then calculated as the ratio $Z_{\zeta\eta}/Z_{\mathrm{rac,gg}}$. Once the statistical weights are known, the factors η, τ, etc. can be determined in a straightforward way.

The results of these calculations agree with the values of Flory and Williams[23] corrected by Mark;[8] the calculated statistical factors are scarcely affected by the value of σ we choose (i.e., decreases by about 3% when σ varies from ∞ to 5 Å). We therefore conclude that Mark's values for these factors are adequate, since neither a rigorous calculation nor the incorporation of the solvent effect in the scheme of calculations would appreciably modify them.

However, the calculated values of the dipole moment ratio depend strongly on the orientation of the dipole moment of the repeat unit,[32a] m. If we assume that m lies in the HCCl plane, its orientation is given by the angle β that it makes with the C–Cl bond indicated in Figure 7. We have calculated the dipole moment ratio as a function of the angle β. Chains consisting of $x = 100$ repeat units having a preselected tacticity and Bernoullian placement of meso and racemic dyads were generated, their dipole moments were evaluated according to eq 2, and the ratios D_x were computed up to $x = 100$; these values were extrapolated to infinity by plotting D_x vs. $1/x$. Typical differences between D_x and D_∞ are on the order of 1%. The results of this calculation are shown in Figure 8 as function of the fraction of meso dyads in the chain (p_i); the values shown for $0 \leq p_i \leq 1$ are averages over the results of 10 chains generated as explained above. As can be seen on Figure 8, D_∞ for the racemic chain decreases about 43% when β changes from 0 to 10°; the value for the isotactic chain is reduced by about 20% for the same variation of β.

The large dependence of D_∞ on the value of β may be easily explained. Let us examine a racemic dyad in its preferred conformation tt; if we assume that the C–Cl bond makes an angle of 55° with its projection on the backbone plane, the dipole moment of the dyad, m_d, is related to the dipole moment of the repeat unit, m, by the expression[32b] $m_\mathrm{d} \simeq 2m \cos(55 + \beta)$. Therefore if $\beta = 0$, $m_\mathrm{d} \simeq 1.15m$, whereas if $\beta = 10°$, $m_\mathrm{d} \simeq 0.85m$. For a meso dyad the explanation is not as straightforward as it is for a racemic dyad, but at any rate, calculation of m_d in the preferred conformations shows that m_d decreases by about 12% when β changes from 0 to 10°.

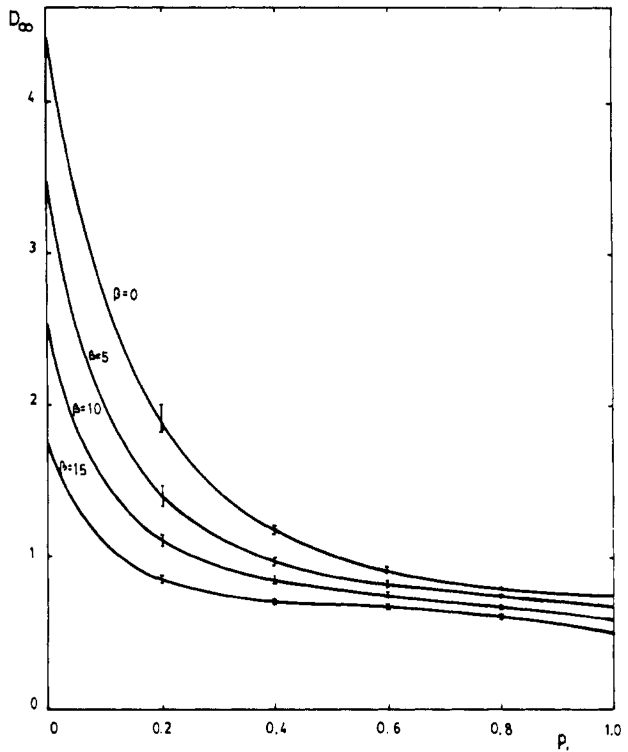

Figure 8. Dependence of the dipole moment ratio on the orientation of the vector dipole m corresponding to the repeat unit.

Discussion

The theoretical calculations predict that the dipole moment ratio should increase with increasing syndiotacticity, in qualitative agreement with the experimental results. However, if we compare the experimental and the theoretical values of $\langle\mu^2\rangle/xm^2$ for a given stereochemical composition, the agreement is not satisfactory provided that the vector dipole moment of the repeat unit lies along the C–Cl bond, that is, $\beta = 0$. Actually, $\langle\mu^2\rangle/xm^2$ for fraction A with isotactic placement $p_i \simeq 0.47$ is 0.679, sensibly lower than the theoretical value which is in the vicinity of 1.10. In the same way, the experimental dipole moment ratio for fraction B in which $p_i \simeq 0.41$, is 0.699 at 25 °C, also much lower than the theoretical value 1.2.

The cause of the large discrepancy between the experimental and the theoretical dipole moment ratio might be due to the following: (a) the polymeric solutions used in the dielectric measurements were not completely homogeneous; (b) the angle β between the vector dipole moment of the repeat unit and the C–Cl bond is not zero. With regard to the first point Doty[33] reported, as early as 1947, the occurrence of molecular aggregates in poly(vinyl chloride) solutions. Later several authors observed these aggregates in a very convincing manner, using ultracentrifugation techniques.[34,35] Cragnola and Danusso[36] measured the percentage of aggregates in solution for a commercial product prepared in suspension and for three low-temperature products. These workers found an increase in molecular association with decreasing polymerization temperature so that it appears to follow the well-known increasing degree of crystallinity in the precipitated polymer. According to this, the occurrence of molecular aggregates in solutions of fraction A should be lower than in fraction B. Moreover, since the formation of molecular associations is time dependent, this dependence should be reflected in the dielectric data. However, the relatively good fit of the experimental data to a straight line in the plot of $\Delta\epsilon$ vs. w seems to indicate that either the presence of aggregates in our solutions is negligible or the entwined molecules forming the aggregates exhibit the same dielectric behavior as if they were isolated.

As shown in Figure 8, the parameter β, which gives the orientation of the vector dipole moment of the repeat unit, is very important in the calculation of the dipole moment ratio. Now the question is whether a value of $\beta \neq 0$ is physically acceptable or not. As explained above, we take $m = 2.0$ D, the experimental value of ethyl chloride in the gas phase; unfortunately the assigning of an orientation to m is not so straightforward. If we assume (as Mark does[8]) that the only contribution to m comes from the C–Cl bond dipole moment, m_{CCl}, of course β has to be zero. But the C–H bond also has an associated dipole moment,[32,37] m_{CH}, with the negative end in the C atom (opposite direction to that of the C–Cl vector dipole) and therefore it is enhanced because of the presence of m_{CCl}. These two contributions make an angle of 110° and since $m_{\mathrm{CCl}} \gg m_{\mathrm{CH}}$, $|m| \simeq m_{\mathrm{CCl}}$. However, although the contribution of m_{CH} to m is negligible, it has a large influence on its orientation (for instance, if we take $m_{\mathrm{CCl}} = 1.9$ D and $m_{\mathrm{CH}} = 0.4$ D, the results are $m = 2.07$ D and $\beta = 11°$). Therefore, if we assume that $m_{\mathrm{CH}} \neq 0$, we can adjust the contribution m_{CCl} so that $m \simeq 2.0$ D for values of β lying in the interval 0–20°. It may be argued that the chain contains other C–H bonds in the CH_2 groups and that these also have to be taken into account. However, as was shown in the case of poly(methyl acrylate),[32] the introduction of these dipoles would have small influence because of their direction and because their C atom is not joined to an electronegative atom as is the case of Cl in the HCCl group.

The theoretical calculations shown in Figure 8 indicate that there is excellent agreement between theoretical and experimental results for values of β lying in the range 10–15°. The experimental values of the temperature coefficient, -1.84×10^{-3} for fraction A and -1.05×10^{-3} K^{-1} for fraction B, are also in fair agreement with the theoretical results, which are in the neighborhood of -1.1×10^{-3} and -2.1×10^{-3} K^{-1}, respectively. Therefore it can be concluded that if the contribution to m from the vector dipole associated with the C–H bond of the HCCl group is considered, the theoretical calculations reproduce the experimental results.

Acknowledgment. Thanks are due to Drs. J. L. Millán and G. Martinez for supplying the PVC samples and for helpful discussions.

References and Notes

(1) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(2) Mark, J. E. *Acc. Chem. Res.* **1974**, *7*, 218. "Characterization of Materials in Research, Ceramics and Polymers"; Syracuse University Press: Syracuse, N.Y., 1975; Chapter 11.
(3) Marchal, J.; Benoit, H. *J. Polym. Sci.* **1957**, *23*, 323.
(4) Nagai, K.; Ishikawa, T. *Polym. J.* **1971**, *2*, 416.
(5) Doi, M. *Polym. J.* **1972**, *3*, 252.
(6) Liao, S. C.; Mark, J. E. *J. Chem. Phys.* **1973**, *59*, 3825.
(7) Mark, J. E. *J. Am. Chem. Soc.* **1972**, *94*, 6645.
(8) Mark, J. E. *J. Chem. Phys.* **1971**, *56*, 451. *Ibid.* **1972**, *57*, 2541.
(9) Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1375.
(10) Mark, J. E. *Polymer* **1973**, *14*, 553.
(11) Danusso, F.; Moraglio, G.; Gazzera, S. *Chim. Ind. (Milan)* **1954**, *36*, 883.
(12) Pham, P. T.; Millán, J. L.; Lòpez Madruga, E. *Makromol. Chem.* **1974**, *175*, 945.
(13) Riande, E. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2231.
(14) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1965; Vols. 1 and 2.
(15) Guggenheim, E. A. *Trans. Faraday Soc.* **1949**, *45*, 714. *Ibid.* **1951**, *47*, 573.
(16) Smith, J. W. *Trans. Faraday Soc.* **1950**, *46*, 394.
(17) McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, Calif., 1963; Vol. I. *Ibid.* Rahara Enterprises: El Cerrito, Calif., 1974; Vol. II.
(18) Riddic, J. A.; Bunger, W. B. "Organic Solvents"; Wiley: New York, 1970.
(19) Le Fèvre, R. J. W.; Sundaran, K. M. S. *J. Chem. Soc.* **1967**, 1494.
(20) Kotera, A.; Shima, M.; Fujisaki, N.; Kobayashi, T. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1117.
(21) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(22) Flory, P. J.; Sundarajan, P. R.; de Bolt, L. C. *J. Am. Chem. Soc.* **1974**, *96*, 5015.
(23) Flory, P. J.; Williams, A. D. *J. Am. Chem. Soc.* **1969**, *91*, 3118.
(24) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(25) Brant, D. A.; Miller, W. G.; Flory, P. J. *J. Mol. Biol.* **1967**, *23*, 47.
(26) Saiz, E.; Riande, E.; Guzmán, J.; de Abajo, J. *J. Chem. Phys.* **1980**, *73*, 958.
(27) Pitzer, K. *Adv. Chem. Phys.* **1959**, *2*, 49.
(28) Yoon, D. Y.; Sutter, U. W.; Sundarajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 784.
(29) Yoon, D. Y.; Sundarajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(30) Sutter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(31) Weast, R. C.; Astle, M. J., Eds. "Handbook of Chemistry and Physics", 59th ed.; CRC Press: Palm Beach, Fla., 1978.
(32) (a) Ojalvo, E. A.; Saiz, E.; Masegosa, R. M.; Hermández-Fuentes, I. *Macromolecules* **1979**, *12*, 865. (b) This relationship would be exact if the valence angles of the backbone were tetrahedral; however, for this qualitative discussion it may be considered accurate enough.
(33) Doty, P.; Wagner, H.; Singer, S. *J. Phys. Colloid Chem.* **1947**, *51*, 33.
(34) Oth, A. *XXVII Congr. Int. Chem. Ind. Brussels, 1954.*
(35) Hengstenberg, J.; Schun, E. *Makromol. Chem.* **1964**, *74*, 55.
(36) Cragnola, A.; Danusso, F. *J. Polym. Sci., Polym. Lett. Ed.* **1968**, *6*, 535.