

# Configurational characteristics of ethylene–vinyl chloride copolymers

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Rotational isomeric state theory has been used to calculate mean-square unperturbed dimensions  $\langle r^2 \rangle_0$  and dipole moments  $\langle \mu^2 \rangle$  of ethylene–vinyl chloride copolymers as a function of chemical composition, chemical sequence distribution, and stereochemical composition of the vinyl chloride sequences. As was previously found for several other copolymeric chains,  $\langle \mu^2 \rangle$  is much more sensitive to chemical composition and chemical sequence distribution than is  $\langle r^2 \rangle_0$ . The present calculations also indicate that both  $\langle r^2 \rangle_0$  and  $\langle \mu^2 \rangle$  are most strongly dependent on chemical sequence distribution for ethylene–vinyl chloride chains having vinyl chloride sequences which are significantly syndiotactic in structure. In the case of ethylene–vinyl chloride copolymers in which the chemical sequences are relatively short and the vinyl chloride sequences are significantly isotactic, both  $\langle r^2 \rangle_0$  and  $\langle \mu^2 \rangle$  depend on chemical composition in an unexpectedly complex manner; under the cited conditions both of these statistical properties display a maximum and minimum in their variation with chemical composition.

## INTRODUCTION

The rotational isomeric state theory of chain molecules<sup>1</sup> has recently been used to give a very satisfactory interpretation of the mean-square dipole moments  $\langle \mu^2 \rangle$  of styrene/*p*-substituted styrene copolymers<sup>2</sup> and the temperature coefficient of the unperturbed dimensions  $\langle r^2 \rangle_0$  of ethylene–propylene copolymers<sup>3</sup>. Similar calculations have also been carried out on propylene–vinyl chloride chains<sup>4</sup>. Of particular interest in such studies is the sensitivity of these statistical properties to chemical sequence distribution since it should be feasible, at least under some conditions, to use experimental values of  $\langle r^2 \rangle_0$  and  $\langle \mu^2 \rangle$  to characterize such distributions in copolymeric chains. In addition, it is very important in general to understand the configurational characteristics of chemical copolymers (as opposed to stereochemical copolymers) since many commercial materials now fall into this category<sup>5,6</sup> and most polymers of biological interest are, of course, chemically copolymeric.

It is therefore the purpose of the present study to obtain a scheme for calculating statistical properties for copolymers of ethylene with any vinyl comonomer. The method may then be illustrated by application to ethylene–vinyl chloride copolymers, materials the preparation and study of which has become an area of very great current interest<sup>7–9</sup>. More specifically, we wish to obtain and interpret values of  $\langle r^2 \rangle_0$  and  $\langle \mu^2 \rangle$  for ethylene–vinyl chloride chains, calculated as a function of chemical composition, chemical sequence distribution, and stereochemical composition of the vinyl chloride sequences.

## THEORY

The chemical and stereochemical structure of an ethylene–vinyl comonomer chain may be adequately characterized

by the probability  $p_2$  of occurrence of units of type 2, the reactivity ratio product  $r_1 r_2$  (which controls the chemical sequence distribution at the specified value of  $p_2$ ), and the stereochemical replication probability  $p_r$  (probability of isotactic placement) characterizing the vinyl comonomer sequences. As has already been described<sup>1, 2, 10, 11</sup>, Monte Carlo methods may be used in conjunction with these variables in order to generate representative chains of any length which have the desired chemical composition, chemical sequence distribution, and stereochemical composition of the vinyl sequences.

The rotational isomeric state model for chain molecules has been extensively discussed elsewhere<sup>1</sup> as has been its specific application to the random-coil unperturbed dimensions of polyethylene<sup>1, 12–14</sup> and to both the unperturbed dimensions and dipole moments of a variety of vinyl chains, including poly(vinyl chloride)<sup>11</sup>. Following the analyses of such homopolymers, we adopt the rotational states *trans* (*t*), *gauche* positive (*g*<sup>+</sup>), and *gauche* negative (*g*<sup>−</sup>) for the skeletal bonds of the copolymer. Since intramolecular steric interactions may be relatively large within ethylene units, we allow for the displacement of these rotational states by an amount  $\Delta\phi$  from their symmetric locations at 0, 120, and  $-120^\circ$ <sup>1, 12</sup>. Specifically, these states are thus located at 0,  $120 - \Delta\phi$ , and  $-120 + \Delta\phi^\circ$ , respectively. Displacements of rotational states within vinyl comonomer units are also frequently significant<sup>1, 10</sup>. In the specific case of vinyl chloride units they are generally relatively minor, however, because of the small size of the pendant Cl atom<sup>11, 15, 16</sup>; in the case of this particular comonomer, the rotational states are therefore assumed to occur at 0,  $\pm 120^\circ$ .

The characterization of intramolecular interactions and the assignment of the corresponding statistical

weight factors is relatively simple in the case of copolymers of ethylene [CH<sub>2</sub>-CH<sub>2</sub>-] with a vinyl comonomeric unit [CH<sub>2</sub>-CHR-] where the pendant group R could be CH<sub>3</sub>, CH<sub>2</sub>-CH<sub>3</sub>, Cl, phenyl, etc. In the approximation that CH and CH<sub>2</sub> are sterically equivalent<sup>1,10</sup>, there are no intramolecular interactions occurring in such copolymeric chains not already characterized in analyses of the two homopolymers. Since, for example, such information is available for both polyethylene<sup>12-14</sup> and poly(vinyl chloride)<sup>11,15,16</sup>, both  $\langle r^2 \rangle_0$  and  $\langle \mu^2 \rangle$  can be directly calculated for ethylene-vinyl chloride chains without the need for additional approximations. The following analysis is therefore directly based on the schemes<sup>11-16</sup> developed for two such homopolymers. We consider first those interactions dependent on only one bond rotational angle. Conformations in which a CH or CH<sub>2</sub> group is *syn* to a CH<sub>2</sub> group are assigned a statistical weight factor of  $\sigma$ , whereas those in which a CH group is *syn* to an R group are given the factor  $\tau$ . Therefore, conformations in which CH is *syn* to both CH<sub>2</sub> and R are characterized by the product  $\sigma\tau$ . To facilitate comparison of the present analysis with that of the vinyl homopolymer itself, we normalize the factors  $\tau$ ,  $\sigma$ ,  $\sigma\tau$  to  $\eta$ , 1,  $\tau$  where  $\eta = \tau/\sigma$ <sup>11,15,17</sup>. If R is an articulated group such as CH<sub>2</sub>-CH<sub>3</sub>, then a pair of *trans* states about the bonds preceding and succeeding a substituted skeletal carbon atom give rise to interactions between the R group and the chain backbone which require the additional factor  $\tau^{*1,10}$ . 'Pentane-type' interactions, dependent on rotational states of two consecutive skeletal bonds, are characterized by the factors  $\omega$ ,  $\omega'$ , and  $\omega''$ . The first of these,  $\omega$ , is introduced for conformations engendering interactions between a pair of CH or CH<sub>2</sub> groups. The second,  $\omega'$ , is associated with interactions between one of these groups and an R group, and the third,  $\omega''$ , with interactions between two R groups. Various combinations of these factors may be used to represent overall statistical weights for all possible conformations in ethylene-vinyl comonomer chains.

For the purpose of calculating configuration-dependent properties such as  $\langle r^2 \rangle_0$  and  $\langle \mu^2 \rangle$ , these statistical weights are used to construct statistical weight matrices  $U_i$ . In such matrices, rows are associated with rotational states about skeletal bond  $i-1$  and columns, with rotational states about skeletal bond  $i$ . Both rows and columns are indexed in the order  $t$ ,  $g^+$ ,  $g^-$ . For CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub> (ethylene) bond pairs, the statistical weight matrix is designated  $U_e$  and has the form:

$$U_e = \begin{bmatrix} 1 & \tau/\eta & \tau/\eta \\ 1 & \tau/\eta & \tau\omega/\eta \\ 1 & \tau\omega/\eta & \tau/\eta \end{bmatrix} \quad (1)$$

For a pair of bonds meeting at a CHR group, the atomic configuration of the group must be specified. Adoption of the arbitrary  $d$ ,  $l$  convention previously employed<sup>1,10,11</sup> yields for the statistical weight matrix characterizing bonds meeting at a C atom of  $d$  configuration:

$$U_d = \begin{bmatrix} \eta\tau^* & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{bmatrix} \quad (2)$$

By symmetry, the matrix  $U_l$  associated with a C atom

of  $l$  configuration is obtained by simple interchange of both the second and third rows and the second and third columns of  $U_d$ . In the case of pairs of bonds separating two CHR groups, the configuration of both groups must be specified. The statistical weight matrices for the dyads  $dd$  and  $dl$  are given by:

$$U_{dd} = \begin{bmatrix} \eta\omega'' & \tau\omega' & 1 \\ \eta & \tau\omega' & \omega \\ \eta\omega' & \tau\omega\omega'' & \omega' \end{bmatrix} \quad (3)$$

$$U_{dl} = \begin{bmatrix} \eta & \omega' & \tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\omega'' & \omega & \tau\omega'^2 \end{bmatrix} \quad (4)$$

The matrices  $U_{ll}$  and  $U_{ld}$  may be obtained from  $U_{dd}$  and  $U_{dl}$ , respectively, by the interchanges of rows and columns described above. Bond pairs CHR-CH<sub>2</sub>-CH<sub>2</sub> are characterized by the matrices  $U_{de}$  and  $U_{le}$  where:

$$U_{de} = \begin{bmatrix} \eta/\tau & \omega' & 1 \\ \eta/\tau & 1 & \omega \\ \eta/\tau & \omega & \omega' \end{bmatrix} \quad (5)$$

and  $U_{le}$  is related to  $U_{de}$  by the symmetry operations already described. Similarly, the matrices  $U_{ed}$  and  $U_{el}$  are associated with bond pairs CH<sub>2</sub>-CH<sub>2</sub>-CHR, with:

$$U_{ed} = \begin{bmatrix} \eta & \tau & 1 \\ \eta & \tau\omega' & \omega \\ \eta\omega' & \tau\omega & 1 \end{bmatrix} \quad (6)$$

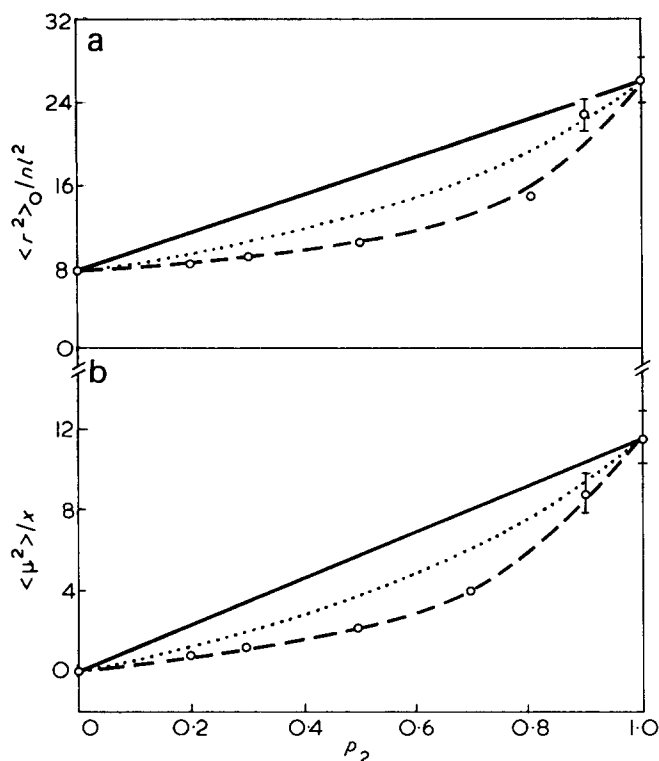
and  $U_{el}$  having the usual relationship to  $U_{ed}$ .

As described in detail elsewhere<sup>1,10-12</sup>, these matrices may now be used in conjunction with bond lengths, bond angles, and group dipole moment vectors to calculate values of the mean-square unperturbed dimensions and dipole moments of the ethylene-vinyl comonomer chains generated by the Monte Carlo method. For convenience, these results will be expressed as the characteristic ratio  $\langle r^2 \rangle_0/nl^2$  (where  $n$  is the number of skeletal bonds, each of length  $l$ ) and the mean-square dipole moment per unit  $\langle \mu^2 \rangle/x$  (where  $x=n/2$  is the number of monomer units in the chain). The absence of a subscript zero on  $\langle \mu^2 \rangle$  is in recognition of the fact that long-range interactions should have no effect on the mean-square dipole moments of the copolymers chosen for the illustrative calculations, namely those of ethylene with vinyl chloride.<sup>11,18,19</sup>

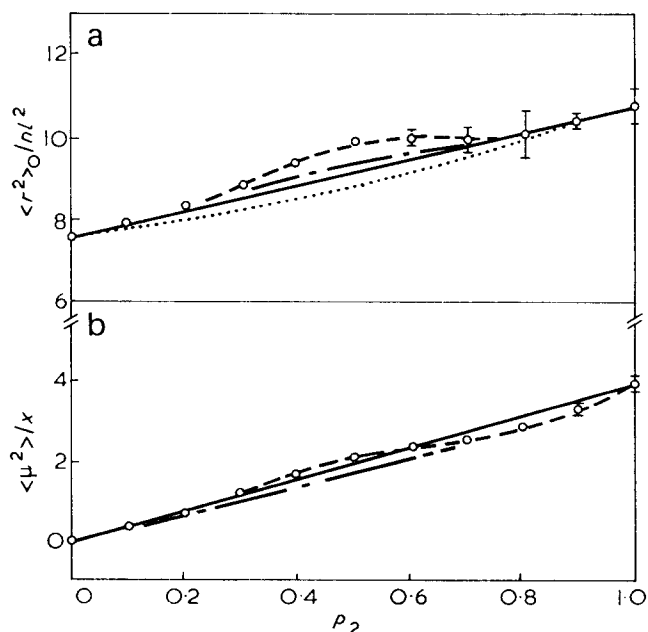
## RESULTS AND DISCUSSION

Calculations of  $\langle r^2 \rangle_0/nl^2$  and  $\langle \mu^2 \rangle/x$  for the ethylene-vinyl chloride copolymers were carried out using: (i) skeletal bond lengths of 1.53 Å and skeletal bond angles of 112°<sup>1,10,12</sup>; (ii) ethylene group dipole vectors of magnitude zero and vinyl chloride group dipole vectors of magnitude 2.00D, lying along C-Cl bonds tetrahedrally oriented with respect to the adjoining skeletal bonds<sup>11</sup>; (iii)  $\Delta\phi=0$  and 10°; (iv)  $p_r=0.05, 0.50$ , and 0.95 for the vinyl chloride sequences; (v)  $r_1r_2=0.01, 1.0, 100, 1000$ , and  $\infty$ ; (vi)  $x=n/2=100$ ; and (vii) values of the statistical weight factors appropriate for 25°C. These values are  $\eta=4.2$ ,  $\tau=0.45$ ,  $\tau^*=1.0$ ,  $\omega=\omega''=0.032$ , and  $\omega'=0.071$ <sup>1,10-12,15,16</sup>.

Figures 1, 2 and 3 show some of the calculated results as a function of the chemical composition variable  $p_2$  (fraction of units which are vinyl chloride) and the



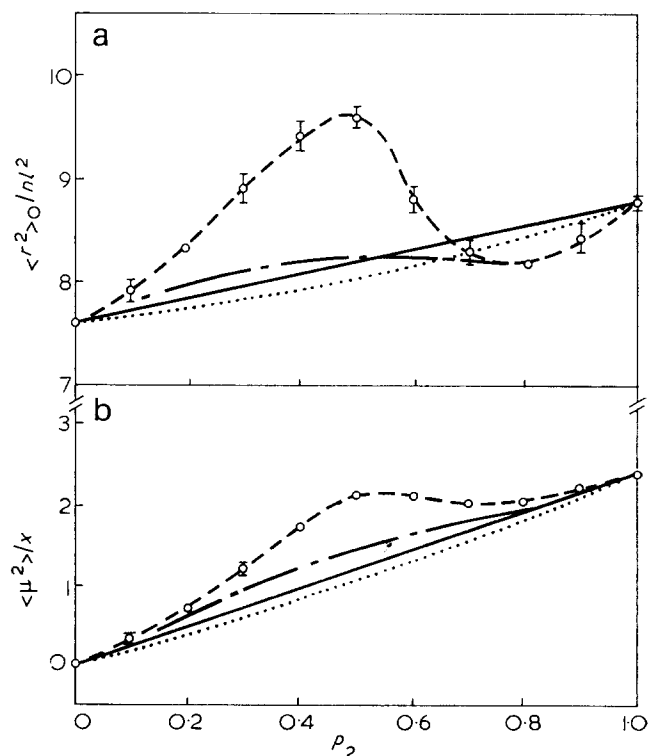
**Figure 1** Effect of chemical composition and chemical sequence distribution on (a) the characteristic ratio and (b) mean-square dipole moment per monomer unit of ethylene-vinyl chloride copolymers having vinyl chloride sequences of highly syndiotactic structure, at 25°C;  $p_r = 0.05$ . In this and the following Figures,  $p_r$  is the stereochemical replication probability and  $p_2$  is the probability that a given unit is of type 2 (vinyl chloride). In Figures 1-3, results are shown for rotational states located at  $\phi = 0, \pm 120^\circ$  (displacement  $\Delta\phi = 0^\circ$ ) and for selected values of the reactivity ratio product:  $r_1 r_2 = 0.01$  (---),  $1.0$  (-·-·-),  $100$  (·····), and  $\infty$  (—). Each circle (○) shown locates the average result calculated for five Monte Carlo chains, and the vertical lines through these points represent standard deviations. For purposes of clarity, calculated points and standard deviations are shown only for the case  $r_1 r_2 = 0.01$  in Figures 1-3, and for the case  $\Delta\phi = 0^\circ$  in Figures 4-6



**Figure 2** (a)  $\langle r^2 \rangle_0 / nl^2$  and (b)  $\langle \mu^2 \rangle / x$  shown as a function of  $p_2$  for selected values of  $r_1 r_2$  for ethylene-vinyl chloride copolymers having atactic vinyl chloride sequences;  $p_r = 0.50$ . See caption to Figure 1

reactivity ratio product  $r_1 r_2$ . Results are given for illustrative values of the replication probability  $p_r$  of 0.05, 0.50 and 0.95. More detailed results which show the dependence of  $\langle r^2 \rangle_0 / nl^2$  and  $\langle \mu^2 \rangle / x$  on  $\log r_1 r_2$  at equimolar composition ( $p_2 = 0.50$ ), are given in the remaining three Figures. As documented in detail elsewhere<sup>2, 3</sup>, increase in  $r_1 r_2$  at constant  $p_2$  corresponds to an increasing tendency to form long sequences ('blocks') of uniform chemical structure. For example, at  $p_2 = 0.50$ , values of  $r_1 r_2$  of 0.0 and 1000 give average sequence lengths  $n_1 = n_2$  of 1.0 and  $\sim 24$ , respectively, for a chain of  $x = 100$  units.

These results indicate that  $\langle \mu^2 \rangle / x$  is much more sensitive to chemical composition and chemical sequence distribution at constant composition than is  $\langle r^2 \rangle_0 / nl^2$ , a result of considerable importance with regard to possible characterization of such distributions by measurements of configuration-dependent properties. This conclusion is in agreement with results of previous studies on styrene/*p*-substituted styrene copolymers<sup>2</sup>, ethylene-propylene copolymers<sup>3</sup>, and propylene-vinyl chloride copolymers<sup>4</sup>. As has been previously pointed out<sup>4</sup>, this enhanced sensitivity in the case of  $\langle \mu^2 \rangle / x$  is obviously due to the fact that, in the calculation of  $\langle r^2 \rangle_0 / nl^2$  chemically different units differ in conformational energy, but have essentially identical values of the quantity being averaged, the skeletal bond vector, as expressed in the skeletal-bond coordinate system<sup>3, 4</sup>. On the other hand, in the calculation of  $\langle \mu^2 \rangle / x$ , both the conformational energy and the group dipole moment vector depend on the chemical nature of the comonomer unit<sup>2, 4</sup>. In the case of both  $\langle r^2 \rangle_0 / nl^2$  and  $\langle \mu^2 \rangle / x$  for ethylene-vinyl chloride chains, the strongest dependence on chemical sequence distribution is found in the stereochemical region of high syndiotacticity ( $p_r = 0.05$ ) of the vinyl chloride sequences.



**Figure 3** (a)  $\langle r^2 \rangle_0 / nl^2$  and (b)  $\langle \mu^2 \rangle / x$  shown as a function of  $p_2$  for selected values of  $r_1 r_2$  for ethylene-vinyl chloride copolymers having highly isotactic vinyl chloride sequences;  $p_r = 0.95$ . See caption to Figure 1

It is interesting to note that in the case of ethylene-vinyl chloride copolymers in which the chemical sequences are relatively short and the vinyl chloride sequences are significantly isotactic, both the characteristic ratio and the mean-square dipole moment per unit depend on chemical composition in an unexpectedly complex manner. For such copolymers, both of these statistical properties display a maximum and minimum in their variation with chemical composition. This behaviour can be readily understood by considering in detail the effect of chemical composition and chemical sequence distribution on, for example, the characteristic ratio  $\langle r^2 \rangle_0/nl^2$  of an ethylene-vinyl chloride copolymer having highly isotactic vinyl chloride sequences. As is shown in Figures 1-3,  $\langle r^2 \rangle_0/nl^2$  for a vinyl chloride homopolymer is larger than that of polyethylene homopolymer. Furthermore, addition of vinyl chloride units to a polyethylene chain increases its value of  $\langle r^2 \rangle_0/nl^2$ , while addition of ethylene units to a vinyl chloride chain decreases its value of  $\langle r^2 \rangle_0/nl^2$ . The characteristic ratio of a vinyl chloride homopolymer which is highly isotactic ( $p_r=0.95$ ) is, however, not very much larger than that of polyethylene and, consequently, the dependence of  $\langle r^2 \rangle_0/nl^2$  on composition exhibits the pronounced maximum and minimum shown in Figure 3. The effect is most pronounced at small values of the reactivity ratio product because of two circumstances. Increase in the characteristic ratio of a polyethylene chain due to addition of vinyl chloride units is greatest if these units are widely dispersed along the chain (small average sequence length due to small

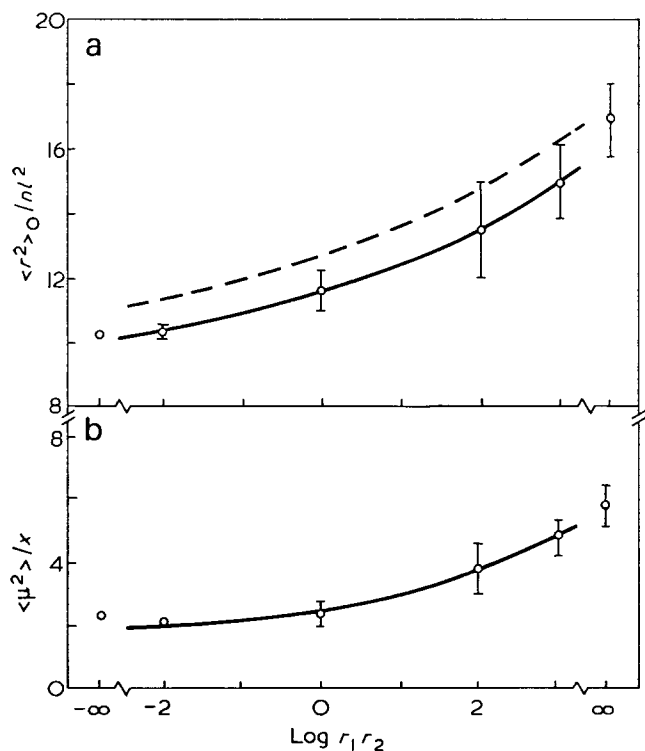


Figure 4 Dependence of (a) the characteristic ratio and (b) mean-square dipole moment per unit on the reactivity ratio product for ethylene-vinyl chloride chains of equimolar composition ( $p_2=0.50$ ) and highly syndiotactic vinyl chloride sequences, at  $25^\circ\text{C}$ ;  $p_r=0.05$ . Circles ( $\circ$ ) and solid lines (—) locate results calculated for  $\Delta\phi=0^\circ$ ; the broken lines (---) show results obtained upon alteration of  $\Delta\phi$  to  $10^\circ$  in the case of ethylene units, when these results differ significantly from those calculated for  $\Delta\phi=0^\circ$

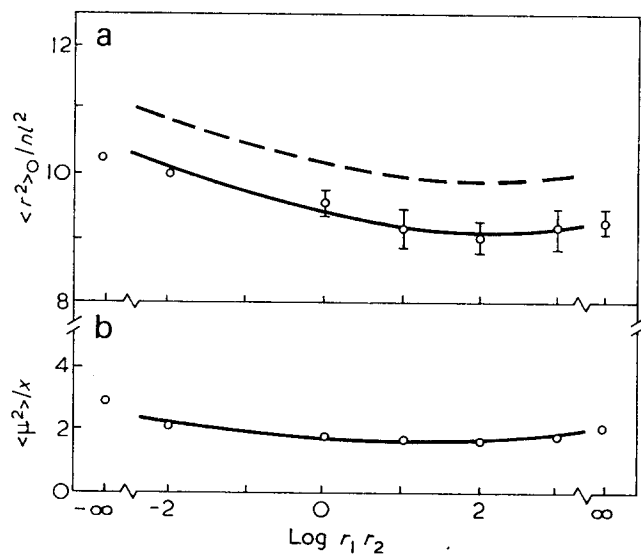


Figure 5 Dependence of (a)  $\langle r^2 \rangle_0/nl^2$  and (b)  $\langle \mu^2 \rangle/x$  on  $r_1 r_2$  for ethylene-vinyl chloride chains having  $p_2=0.50$  and atactic vinyl chloride sequences;  $p_r=0.50$ . See caption to Figure 4

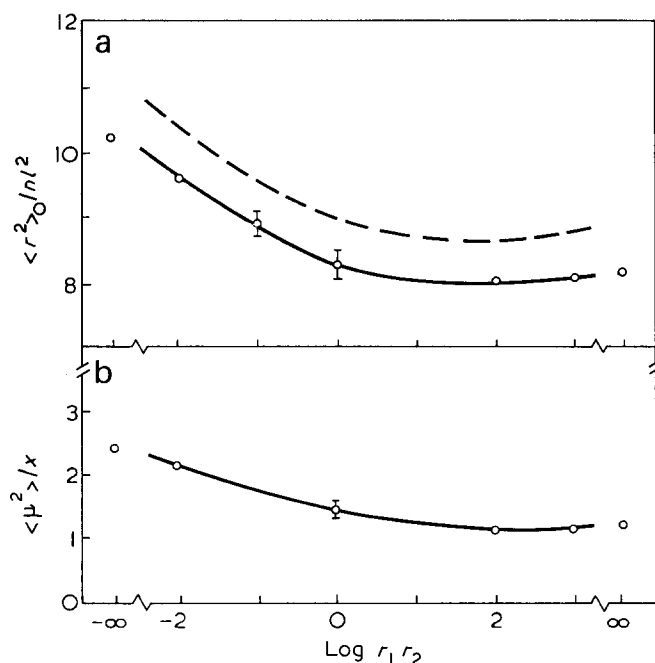


Figure 6 Dependence of (a)  $\langle r^2 \rangle_0/nl^2$  and (b)  $\langle \mu^2 \rangle/x$  on  $r_1 r_2$  for ethylene-vinyl chloride chains having  $p_2=0.50$  and highly isotactic vinyl chloride sequences;  $p_r=0.95$ . See caption to Figure 4

reactivity ratio product) since, in the case of highly isotactic vinyl chloride sequences, interactions between neighbouring vinyl chloride units decreases the preference for highly extended *trans* conformations in these units<sup>11, 15</sup>. Correspondingly, decrease in the characteristic ratio of an isotactic poly(vinyl chloride) chain upon incorporation of ethylene units is most pronounced when the ethylene units are widely dispersed, causing the largest number of disruptions of the extended helical conformations adopted by the isotactic vinyl chloride sequences<sup>11, 15</sup>. These maxima and minima would thus be expected to be less pronounced in the case of an ethylene-vinyl chloride copolymer having less highly isotactic vinyl chloride sequences and this is, in fact, shown by the results for the atactic case ( $p_r=0.50$ ) given in Figure 2. Similar arguments apply to  $\langle \mu^2 \rangle/x$  since, in vinyl chloride sequences, conforma-

tions of high chain extension are also of high dipole moment<sup>11</sup>.

It should be noted that the location of the rotational states is not of crucial importance in the present analysis. As can be seen from the broken lines in *Figures 4-6*, alteration of the displacement  $\Delta\phi$  from 0 to 10° in the case of ethylene units has only a relatively small effect on  $\langle r^2 \rangle_0/nl^2$  and no significant effect at all on  $\langle \mu^2 \rangle/x$ .

It is thus now apparent that although measurements of configuration-dependent properties of copolymers do show considerable promise, at least under some conditions, for use in characterizing chemical sequence distributions, the variation of such properties with chemical composition, chemical sequence distribution, and stereochemical composition can be exceedingly complex<sup>20</sup>.

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