The Use of Dipole Moments to Characterize Chemical Sequence Distributions in Vinyl Copolymers

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Received February 25, 1972

Abstract: A rotational isomeric state scheme is developed in order to investigate the feasibility of using dipole moments to characterize chemical sequence distributions in vinyl copolymers. By means of this scheme, dipole moments of such chains may be calculated as a function of chain length, temperature, chemical sequence distribution, and stereochemical composition. The method is illustrated by application to the simplest case, vinyl copolymers in which the pendant groups have dipoles of different magnitude, but are of sufficiently similar chemical structure that the conformation energy of the chain is independent of chemical composition. The copolymers poly(*p*-chlorostyrene–*p*-methylstyrene) and poly(*p*-chlorostyrene–styrene) have this structural feature, and the conformational energies required in the calculation of their statistical properties have been reported by Williams and Flory. Dipole moments were calculated for these two copolymers, using chemical sequence distributions characteristic of the reactivity ratios determined for these two sets of comonomers and random stereochemical sequence distributions. The results are in good agreement with published experimental results obtained on a number of atactic samples, of varying chemical composition, of these copolymers in the bulk, nonglassy, amorphous state. Additional calculations are used to establish the conditions under which dipole moments could most reliably be used to characterize chemical sequence distributions in this class of vinyl copolymers; it is found that the dipole moments of such copolymers are most sensitive to chemical sequence distribution in the stereochemical region of high syndiotacticity.

During the past decade, a great deal of research has been carried out in order to provide a detailed molecular picture of the configurational statistics of chain molecules.[1] Theoretical studies, based on the rotational isomeric state model with neighbor interactions,[2] have in general concentrated on the configuration-dependent properties of either homopolymers or *stereochemical* copolymers such as vinyl polymers of variable *d,l* structure[2–5] or diene polymers of variable cis, trans structure.[6,7] In contrast, there have been very few satisfactory theoretical investigations of the configuration-dependent properties of *chemical* copolymers;[8] useful results to date seem to be limited to copolypeptides[9,10] and copolysaccharides.[11] It is of considerable interest to extend such calculations to "synthetic" (nonbiological) copolymers, particularly since the preparation and study of such chain molecules has become a very active area of polymer research.[12–14] At least part of the impetus for this activity seems to be due to the fact that when sequences of identical units in these chains are of sufficient *length* and of sufficiently different chemical structure, the copolymer frequently exhibits colloidal behavior;[14] when such unusual behavior includes microscopic phase separation, the resulting materials often have highly desirable physical properties. This particular circumstance simply underlines the crucial importance, in general, of obtaining detailed knowledge of chemical sequence distributions, in addition to the overall chemical composition, in any type of chemical copolymer.

It is the purpose of the present investigation, therefore, to initiate a general study of the configuration-dependent properties of copolymers of variable chemical composition. The subject chosen for this preliminary study is the dipole moments of copolymeric vinyl chains in which the repeat unit has a dipole moment independent of rotation of the pendant group relative to the chain backbone. The general methodology developed for the calculation of this quantity may be directly applied to the simplest case, vinyl copolymers in which the pendant groups have group dipoles of significantly different magnitude, but are of sufficiently similar chemical structure that the conformational energy of the chain is independent of chemical composition. Sufficient information is available on two copolymers of this type, poly(*p*-chlorostyrene–*p*-methylstyrene) and poly(*p*-chlorostyrene–styrene) to permit a comparison of theoretical and experimental results. Additional calculations may be used to determine the conditions of stereochemistry and temperature which might lead to a sufficiently strong dependence of the dipole moment on the chemical sequence distribution to permit its use in estimating average chemical sequence lengths in this class of vinyl copolymers.

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(1) For a recent summary, see ref 2.

(2) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

(3) Reference 4 and articles on vinyl polymers cited therein.

(4) J. E. Mark, *J. Chem. Phys.*, **56**, 451 (1972).

(5) J. E. Mark, *ibid.*, **56**, 458 (1972).

(6) Y. Abe and P. J. Flory, *Macromolecules*, **4**, 219 (1971).

(7) Y. Abe and P. J. Flory, *ibid.*, **4**, 230 (1971).

(8) U. Biskup and H.-J. Cantow [*Makromol. Chem.*, **148**, 31 (1971)] have recently calculated random-coil dimensions of a class of vinyl copolymers. Their model, however, involves so many assumptions, some mutually inconsistent, with regard to the equivalence of various interactions between pendant groups and the chain backbone that their results have little, if any, applicability and contribute almost nothing to the general problem of characterizing chemical copolymers.

(9) W. G. Miller, D. A. Brant, and P. J. Flory, *J. Mol. Biol.*, **23**, 67 (1967); P. R. Schimmel and P. J. Flory, *ibid.*, **34**, 105 (1968).

(10) S. Tanaka and A. Nakajima, *Polym. J.*, **2**, 725 (1971).

(11) S. G. Whittington, *Biopolymers*, **10**, 1617 (1971).

(12) See, for example, ref 13 and 14.

(13) S. L. Aggarwal, Ed., "Block Polymers," Plenum Press, New York, N. Y., 1970.

(14) G. E. Molau, Ed., "Colloidal and Morphological Behavior of Block and Graft Copolymers," Plenum Press, New York, N. Y., 1971.

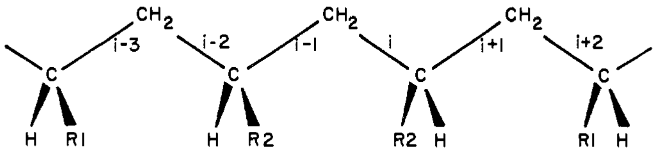

Figure 1. The planar conformation of a portion of a vinyl copolymer chain consisting of the chemical sequence, monomer units M1, M2, M2, M1, and the stereochemical sequence, isotactic (*dd*) dyad, syndiotactic (*dl*) dyad, isotactic (*ll*) dyad. The lines of increasing, and decreasing, thickness represent bonds extending toward, and away from, the reader, respectively.

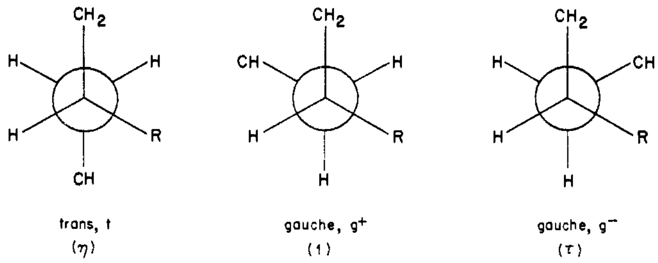

Figure 2. Newman projections of the three rotational states of $CHR\text{-}CH_2$ and $CH_2\text{-}CHR$ skeletal bonds, and the associated statistical weight factors.

Theory

In the investigation of the statistical properties of vinyl copolymers, it is necessary first to generate, or simulate, polymer chains which have chemical and stereochemical structures representative of copolymers actually prepared and experimentally investigated. In the case of the chemical composition, (binary) copolymerization theory[15-18] indicates that the probability, p_1, that a monomer unit being incorporated into a growing chain is of type 1 is

$$p_1 = (r_1F_1^2 + F_1F_2)/(r_1F_1^2 + 2F_1F_2 + r_2F_2^2) \quad (1)$$

where F_1 and $F_2 = 1 - F_1$ are the mole fractions of monomers M1 and M2, respectively, in the monomer mixture undergoing copolymerization. For very long chains, the fraction f_1 of units of type 1 in the chain will, of course, be equal to the value of the probability p_1, provided the monomer mixture is maintained at the composition F_1. The *reactivity ratios* r_1 and r_2 are defined by

$$r_1 = k_{11}/k_{12} \quad (2)$$

$$r_2 = k_{22}/k_{21} \quad (3)$$

where k_{ij} is the rate constant for the addition of monomer of type j to a growing chain end of type i. The *distribution* of monomer units along the chain is controlled by the conditional probabilities p_{ij} that a chain ending in monomer type i will add a unit of type j. In the case of (binary) copolymers, these probabilities are p_{11}, p_{22}, $p_{12} = 1 - p_{11}$, and $p_{21} = 1 - p_{22}$, and are specified by the equations[16,18]

$$p_{11} = r_1F_1/(r_1F_1 + F_2) \quad (4)$$

$$p_{22} = r_2F_2/(r_2F_2 + F_1) \quad (5)$$

The above set of equations indicates that specification of f_1 and r_1r_2 determines the value of F_1 and the values of p_{11} and p_{22} required to give a chain having the desired characteristics. Values of p_{11} and p_{22} thus calculated may be used in conjunction with a set of x random numbers ranging in magnitude from 0 to 1 to simulate a copolymerization leading to a chain of x monomer units. (The magnitude of the first number relative to p_1 is used to specify the chemical nature, or type, of the first unit in the chain; subsequent numbers are compared with either p_{11} or p_{22}, depending on the nature of the preceding unit, to determine the type of monomer used in subsequent additions.) The generation of the stereochemical structure can also be carried out using Monte Carlo methods, by consecutive comparison of another set of random numbers with the desired value of the replication probability p_r (probability of isotactic placement).[4,19] For very long chains, the fraction f_r of isotactic placements in the chain will be equal to the value chosen for p_r. In the general case of copolymer chains, however, four different replication probabilities may be required for the four different *chemical* sequences (M1,M1), (M1,M2), (M2,M1), and (M2,M2).

The rotational isomeric state model for vinyl chains has been extensively discussed elsewhere,[2,3] as has also been its specific application to the calculation of the dipole moments of homopolymers of vinyl chloride[4] and *p*-chlorostyrene.[5] The present development follows very closely that formulated for poly(*p*-chlorostyrene) chains.[5] As is customary, rotational states are designated trans (t), gauche positive (g+), and gauche negative (g−). In anticipation of the application of this model in the present study to vinyl chains having relatively large R substituents, we allow for the displacement of these rotational states by an amount $\Delta\phi$ from their symmetric locations at 0, 120, and −120°. Such displacements are due to steric repulsions between various groups, and their nature can be comprehended from Figures 1 and 2. Specifically, for the two skeletal bonds leading into and out of C^α atom of *d* configuration, these states are located at $-\Delta\phi$, 120, and $-120 + \Delta\phi$°, and $\Delta\phi$, $120 - \Delta\phi$, and −120°, respectively; the same two sets of rotational angles pertain to the two skeletal bonds leading respectively out of and into a C^α atom of *l* configuration.[5] In the case of vinyl copolymers in which the monomer units have R groups of significantly different size, different values of $\Delta\phi$ would be required for different monomer units.

The configuration partition function Z for a vinyl chain of n bonds, or $x = n/2$ repeat units, is given by the now-familiar expression[2,4]

$$Z = \mathbf{J}^*\left[\prod_{i/2=1}^{n/2-1} \mathbf{U}_i'\mathbf{U}''_{i+1}\right]\mathbf{J} \quad (6)$$

where $\mathbf{J}^* = [100]$, $\mathbf{J}$ is the transpose of [111], and the U's are statistical weight matrices, the elements of which are statistical weights characterizing all possible conformations about consecutive pairs of bonds in the chain backbone.[2] Single and double primes in this equation, and in eq 7, characterize quantities associated with $CH_2\text{-}CHR\text{-}CH_2$ and $CHR\text{-}CH_2\text{-}CHR$ bond pairs, respectively. Calculation of mean-square

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(15) See, for example, ref 16–18.

(16) T. Alfrey, Jr., J. J. Bohrer, and H. Mark, "Copolymerization," Interscience, New York, N. Y., 1952.

(17) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter V.

(18) G. E. Ham, "Copolymerization," G. E. Ham, Ed., Interscience, New York, N. Y., 1964.

(19) P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966).

dipole moments requires construction of generator matrices $\mathbf{G}_i$ each of which contains the appropriate statistical weight matrix $\mathbf{U}_i$, group dipole vector $\mathbf{m}_i$ and magnitude m_i, and transformation matrix $\mathbf{T}_i$. The detailed forms of all of these matrices are extensively discussed elsewhere.[2,5] The mean-square unperturbed dipole moment[5] is the given by[2,5]

$$\langle\mu^2\rangle_0 = 2Z^{-1}\mathbf{I}^*\mathbf{G}_1\left[\prod_{i/2=1}^{n/2-1}\mathbf{G}'_i\mathbf{G}''_{i+1}\right]\mathbf{G}'_n\mathbf{I} \qquad (7)$$

where $\mathbf{I}^*$ is the row vector consisting of a single unity followed by 14 zeros, and $\mathbf{I}$ is the column vector consisting of 12 zeros followed by three unities. The matrices $\mathbf{U}_i$ and $\mathbf{G}_i$ depend, in general, on the chemical and stereochemical nature of both the monomer unit in which bond i is located and its predecessor along the chain. The precise sequences of U's and G's appearing in eq 6 and 7 are specified by Monte Carlo methods, as already described.

The above model and equations can readily be adapted to the case of interest in the present study, vinyl copolymers in which the pendant groups have dipoles of different magnitude, but are of sufficiently similar chemical structure that the conformational energy of the chain is approximately independent of chemical composition. For such chains, $\Delta\phi$, p_r, and the U matrices are, to good approximation, independent of chemical composition and the G matrices depend on chemical composition only with respect to the group dipoles $\mathbf{m}_1$ or $\mathbf{m}_2$ contained therein. In a previous study,[5] it was demonstrated that members of the series of homopolymers $CH_3[CH(p\text{-}C_6H_4X)\text{-}CH_2)_xH$ corresponding to X = H, Cl, or CH_3 have very nearly the same conformational energy;[20] therefore, copolymers prepared from these monomers represent examples of the special class of vinyl chains under consideration. For this reason, statistical weight factors and overall chain statistical weights for the copolymers poly(*p*-chlorostyrene–*p*-methylstyrene) and poly(*p*-chlorostyrene–styrene), for example, should be independent of chemical composition and should simply be those characterizing *p*-chlorostyrene homopolymers.[5] These factors and the interactions they represent are (i) unity, for a CH group syn to a CH_2 group, (ii) η, for a CH group syn to an R pendant group, (iii) τ, for a CH group syn to both a CH_2 group and an R group, and (iv) ω, for interactions between any groups, other than H atoms, involved in "pentane-type" interferences. As outlined above, these statistical weight factors, in conjunction with structural information such as the orientation and magnitude of the group dipoles, may be used to calculate the mean-square unperturbed dipole moment $\langle\mu^2\rangle_0$ of vinyl copolymers of this type, at any temperature, as a function of their length, chemical sequence distribution, and stereochemical composition. Because of the very similar nature of these monomer units, it is probably a good approximation to assume that the chemical and stereochemical distributions are independent of one another.

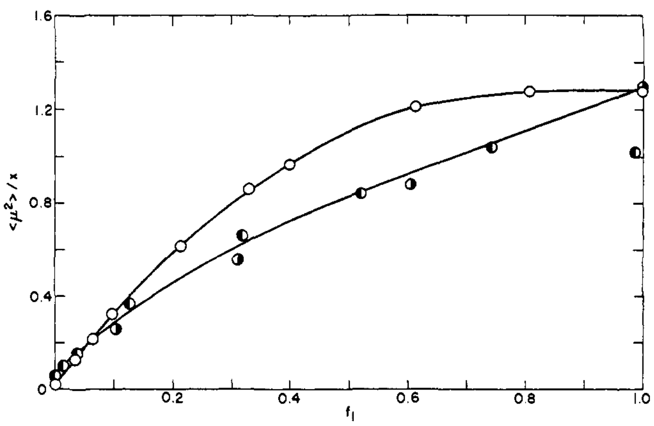

Figure 3. Experimental values of the mean-square dipole moment per monomer unit of atactic poly(*p*-chlorostyrene–*p*-methylstyrene) [○ (ref 23, 24)] and poly(*p*-chlorostyrene–styrene) [◐ (ref 25, 26) and ◑ (26)] shown as a function of the mole fraction of *p*-chlorostyrene in the copolymer. Results pertain to bulk, nonglassy, amorphous samples at 428 and 403°K, respectively.

For convenience, both calculated and experimental results will be expressed as the mean-square dipole moment per monomer unit, $\langle\mu^2\rangle_0/x$; since x is the degree of polymerization, it is also the number of group dipoles, each of magnitude m_1 or m_2. As is the case for *p*-chlorostyrene homopolymers,[5] long-range interactions should have no effect[21] on the mean-square dipole moments of these copolymers. The zero subscript of $\langle\mu^2\rangle_0$ may therefore be deleted, thus simplifying comparison of theoretical and experimental values of $\langle\mu^2\rangle/x$.

Experimental Results

Experimental values of $\langle\mu^2\rangle/x$ have been reported for poly(*p*-chlorostyrene–*p*-methylstyrene) copolymers by Smith, Corrado, and Work[22–24] and for poly(*p*-chlorostyrene–styrene) copolymers by Work and Tréhu,[25] and by Birshtein, Burshtein, and Ptitsyn.[26] In these studies a number of samples of varying chemical composition were studied; each of these samples was presumably atactic (stereochemically random) judging from the conditions used in its preparation, and therefore also noncrystallizable. Although the copolymerizations had not been carried out at constant monomer composition, this composition would not be expected to vary significantly during the copolymerization[25] because the reactivity ratios for these monomer pairs are not very different from unity.[27] The dipole moment measurements were carried out above the glass transition temperatures of the samples, *viz.* at 428°K for the poly(*p*-chlorostyrene–*p*-methylstyrene) copolymers,[23,24] and at 403°K for the poly(*p*-chlorostyrene–styrene) copolymers.[25,26,28] In Figure 3, these

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(20) This circumstance in conjunction with the fact that all vinyl units have skeletal bonds and skeletal bond angles of essentially the same length and magnitude, respectively, leads to the prediction that the unperturbed dimensions $\langle r^2\rangle_0$ of the three homopolymers specified should be the same, which is indeed the case.[5] It also, however, prevents the use of the unperturbed dimensions to characterize chemical sequence distributions in this type of vinyl copolymer.

(21) K. Nagai and T. Ishikawa, *Polym. J.*, **2**, 416 (1971).

(22) F. H. Smith, Ph.D. Thesis, The Pennsylvania State University, 1964; University Microfilms, Ann Arbor, Mich., No. 65-6767.

(23) L. C. Corrado, Ph.D. Thesis, Arizona State University, 1969; University Microfilms, Ann Arbor, Mich., No. 70-4853.

(24) F. H. Smith, L. C. Corrado, and R. N. Work, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **12** (1), 64 (1971).

(25) R. N. Work and Y. M. Tréhu, *J. Appl. Phys.*, **27**, 1003 (1956).

(26) T. M. Birshtein, L. L. Burshtein, and O. B. Ptitsyn, *Soviet Phys., Tech. Phys.*, **4**, 810 (1959).

(27) H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Beynon in ref 18, p 722.

(28) Work, *et al.*, interpret these experimental results using a model only crudely related to molecular parameters in that, for example, it

Table I. Average Chemical Sequence Lengths in Copolymers of Degree of Polymerization $x = 100$

	$p_1 =$									
	0.1		0.2		0.3		0.4		0.5	
r_1r_2	n_1	n_2	n_1	n_2	n_1	n_2	n_1	n_2	n_1	n_2
0.01	1.04	11.50	1.00	4.78	1.01	2.45	1.02	1.59	1.15	1.08
0.10	1.06	11.47	1.05	4.98	1.11	2.52	1.21	1.79	1.34	1.35
0.75	1.10	11.01	1.22	4.62	1.35	2.99	1.50	2.17	1.84	1.76
0.85	1.11	12.03	1.26	5.61	1.48	3.39	1.59	2.44	2.04	2.09
1.00	1.12	12.70	1.25	5.63	1.48	3.62	1.71	2.59	2.03	2.10
10.0	2.93	24.28	3.69	11.69	4.07	8.68	4.02	5.32	4.30	4.59
100.0	5.60	49.57	6.65	21.31	6.67	14.78	8.90	11.56	8.73	7.84

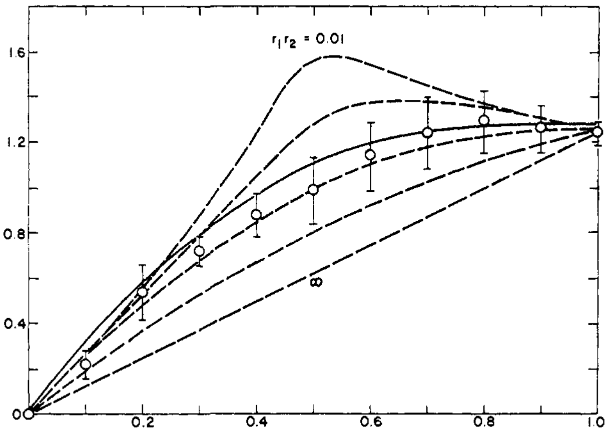

Figure 4. Values of $\langle\mu^2\rangle/x$ of poly(p-chlorostyrene–p-methylstyrene) copolymers at 428°K shown as a function of the chemical composition variable p_1, the probability of occurrence of p-chlorostyrene units. The solid curve shows the experimentally observed dependence.[23,24] Each circle shown locates the average result calculated for five Monte Carlo chains generated using (i) $x = 100$ random numbers, (ii) the specified value of p_1, (iii) a stereochemical replication probability p_r of 0.50, (iv) a reactivity ratio product r_1r_2 of 0.75,[23,27] and (v) values of the statistical weight factors appropriate for 428°K, with the approximation $\omega = 0.00$. The lines through the calculated points represent standard deviations (see text). The dashed curves in each of the Figures 4–7 represent additional calculated results for values of r_1r_2 of 0.01, 0.10, 1.00, 10.0, and ∞, respectively; calculated points and standard deviation bars have been omitted from these curves for purposes of clarity.

experimental results are shown as a function of the mole fraction f_1 of p-chlorostyrene units in the copolymer. The most noteworthy feature of the two curves is the marked positive departures from simple linearity between the values of $\langle\mu^2\rangle/x$ characterizing the corresponding homopolymers.

Calculated Results and Discussion

Average chemical sequence lengths n_1 and n_2 of comonomers 1 and 2 in chains of degree of polymerization $x = 100$ were obtained by Monte Carlo methods as described above. Sequences were accepted as being representative only if the differences between f_1 and p_1 and between f_r and p_r were both less than 0.05; other sequences were discarded. Results obtained are given as a function of p_1, for selected values of r_1r_2, in Table I; each entry is the average calculated from five acceptable chains. Values of n_1 and n_2 for $p_1 > 0.5$ can of course be obtained by simple interchange of the subscripts 1 and 2. Monte Carlo generation of stereochemical sequences for $x = 100$ and $p_r = 0.05$, 0.50, and 0.95 led, also in the case of five successful trials, to average isotactic sequence lengths of 1.067, 1.974, and 16.38, respectively.

The first set of calculations of $\langle\mu^2\rangle/x$ were carried out assuming (i) reactivity ratio product $r_1r_2 = 0.75$[23,27] for the comonomer pair p-chlorostyrene–p-methylstyrene; (ii) $r_1r_2 = 0.85$[16] for the pair p-chlorostyrene–styrene; (iii) $p_r = 0.5$ (stereochemical randomness); (iv) skeletal bond angles of 112°;[5] (v) $\Delta\phi = 10°$, the average value of the range 0–20° assumed appropriate for polystyrene chains;[29,30] (vi) group dipoles lying along the C^α–C^β bonds joining the R groups to the chain backbone, with tetrahedral orientation with respect to the adjoining skeletal bonds;[5] (vii) bond dipole moments m_1 (p-chlorostyrene units) = 1.68 D, the dipole moment of p-chloroethylbenzene;[31] (viii) bond dipole moments m_2 (p-methylstyrene units) = 0.0 D, the dipole moment of p-ethyltoluene;[32] (ix) bond dipole moments m_2 (styrene units) = 0.36 D, the dipole moment of ethylbenzene.[32] Since the experimental results were obtained on polymers of high molecular weight, all calculations were carried out using a degree of polymerization x of 100, a value sufficiently high in the case of atactic polymers that $\langle\mu^2\rangle/x$ is very close to its value in the limit of very large x.[4,5] For reasons stated above, we accept without modification the statistical weight factors obtained by Williams and Flory[33] by analysis of the stereochemical equilibrium composition of styrene dimers and trimers. On the assumption that these quantities may be expressed as Boltzmann factors in the conformational energy, the values are $\eta = 1.13$ at 428°K and 1.19 at 403°K. Assumed in the initial calculations is $\omega = 0.00$ (*i.e.*, complete exclusion of all "pentane-type" interferences not involving H atoms, thus requiring all isotactic sequences to be in 3_1 helical conformations[2]). Assignment of the value zero to ω makes irrelevant the value assigned to τ.[2]

Calculated results for poly(p-chlorostyrene–p-methylstyrene) copolymers at 428°K are shown as a function of p_1 by the points in Figure 4. Each point represents the average of the results obtained on five Monte Carlo chains; in this and the following figures, lines

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totally neglects the stereochemical structure of the chain, a feature long recognized as being of paramount importance in the case of vinyl polymers.[2] In addition, it does not seem to be feasible to use the results obtained from their analysis to interpret other reported properties, nor to predict additional properties not yet measured for these chains. Their analysis will therefore not be considered further in the present discussion.

(29) Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, 3, 294 (1970).

(30) A. E. Tonelli, Y. Abe, and P. J. Flory, *ibid.*, 3, 303 (1970).

(31) L. L. Burshtein and T. P. Stepanova, *Vysokomol. Soedin., Ser. A*, 11, 2537 (1969); *Polymer Sci. USSR*, 11, 2885 (1969).

(32) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

(33) A. D. Williams and P. J. Flory, *J. Amer. Chem. Soc.*, 91, 3111 (1969).

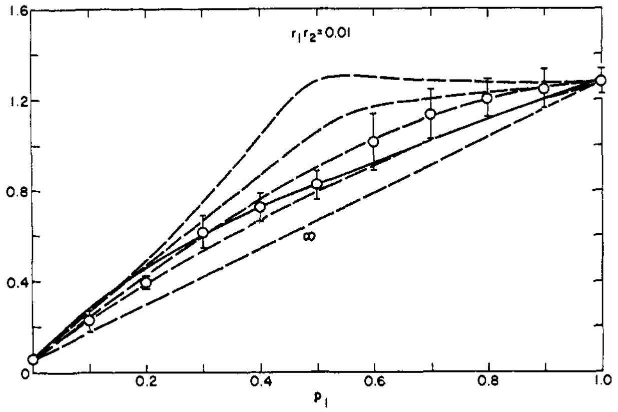

Figure 5. Values of $\langle\mu^2\rangle/x$ of poly(p-chlorostyrene–styrene) copolymers at 403°K shown as a function of chemical composition. The solid curve shows the experimental results[25,26] and the circles locate results calculated as described above, but with r_1r_2 assigned the experiment value 0.85[16] appropriate for these comonomers. The dashed curves represent additional, illustrative calculations; see legend to preceding figure.

of length twice the standard deviation in the set of results have been drawn through the points in those cases in which this length exceeded the diameter of the of the circles used to locate the points. Also represented, by the solid curve, are the experimental results on this polymer, which have been taken from Figure 3. As can readily be seen, there is good agreement between theoretical and experimental results, the average difference amounting to only 0.056 unit in $\langle\mu^2\rangle/x$. Additional, illustrative results calculated for values of r_1r_2 = 0.01, 0.10, 1.00, 10.0, and ∞ (corresponding to an increasing tendency to form long sequences or "blocks") are also shown. (The case $r_1r_2 = \infty$ yields a mixture of homopolymers in which the mole fraction of chains composed entirely of units of type 1 is simply p_1; this is the origin of the linear dependence of $\langle\mu^2\rangle/x$ on p_1 shown for this case in Figures 4–7.) These results indicate that if r_1r_2 had not been known for these comonomers, the dipole moment analysis would have led to the prediction $r_1r_2 \cong 0.7$, in fair agreement with the experimental value, 0.85. (As is well known,[34,35] there is a great deal of uncertainty in the reported values of r_1r_2 for many systems.) Since the experimental results shown in Figure 3 would seem to require a *decrease* in $\langle\mu^2\rangle/x$ with *increase* in m_2 from 0.0 D (p-methylstyrene units) to 0.36 D (styrene units), two additional calculations were carried out at 428°K, using $p_1 = 0.50$ and $r_1r_2 = 1.00$. The cited increase in m_2 does lead to a decrease in $\langle\mu^2\rangle/x$, from 0.944 to 0.848. This would indicate that the bulkiness of the C_6H_4 groups causes group dipoles to be largely in orientations in which a great deal of attenuation occurs. Such attenuation would be expected to be less in poly(p-chlorostyrene–p-methylstyrene) copolymers, in which the magnitude of one of the group dipoles is zero, thus explaining the observed dependence. This circumstance is of course also the origin of the convex nature of the curves shown in Figure 3; the cited attenuation is less in a copolymer of composition f_1 than in a mixture of homopolymers having the same overall composition.

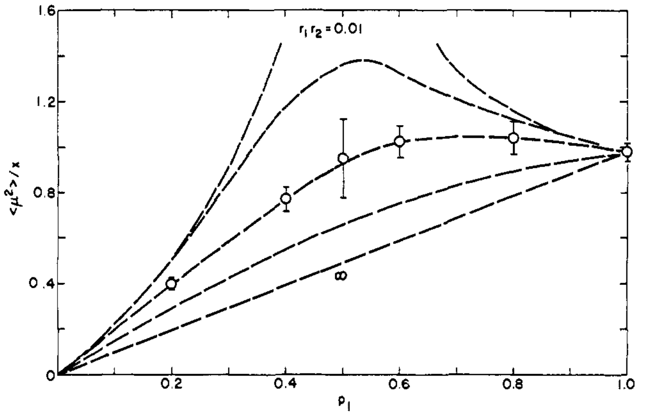

Figure 6. Calculated values of $\langle\mu^2\rangle/x$ at $x = 100$ for poly(p-chlorostyrene–p-methylstyrene) copolymers of high syndiotacticity (p_r = 0.05) at 428°K; the results are shown as a function of p_1 for values of r_1r_2 of 0.01, 0.10, 1.00, 10.0, and ∞, respectively. For purposes of clarity, only those points used to locate the curve corresponding to $r_1r_2 = 1.00$ are shown. In this and the following figure $\omega = 0.00$.

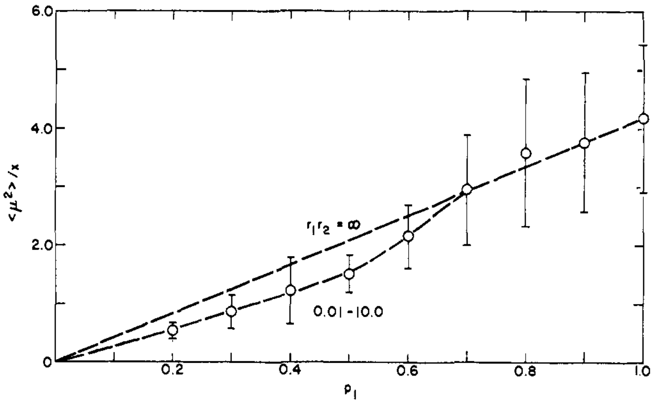

Figure 7. Calculated values of $\langle\mu^2\rangle/x$ at 428°K for poly(p-chlorostyrene–p-methylstyrene) copolymers of high isotacticity (p_r = 0.95). See legend to preceding figure.

Results for poly(p-chlorostyrene–styrene) copolymers at 403°K are shown in Figure 5; the points locate the results calculated for $r_1r_2 = 0.85$,[16] and the solid line represents the experimental data on this copolymer shown in Figure 3. The agreement between theory and experiment is satisfactory; the average difference between theoretical and experimental values of $\langle\mu^2\rangle/x$ is 0.071 unit if all the experimental points in Figure 3 are accepted, and 0.054 unit if the point corresponding to $p_1 = 0.99$ is rejected because of its disagreement with the other results. The dashed curves represent the results of additional, illustrative calculations as already described. The analysis of the dipole moments of these copolymers would lead to the prediction that $r_1r_2 \cong$ 1.0–5.0, a relatively poor result if the experimental values of both r_1r_2 and the dipole moments are correct.

Figures 6 and 7 show the results of illustrative calculations carried out for poly(p-chlorostyrene–p-methylstyrene) copolymers of high syndiotacticity (p_r = 0.05) and high isotacticity (p_r = 0.95), respectively; all results pertain to 428°K. (For purposes of clarity, only those points used to locate the curves corresponding to $r_1r_2 = 1.00$ are shown.) The ratio $\langle\mu^2\rangle/x$ at constant p_1 is seen to be very sensitive to r_1r_2 in the region of high syndiotacticity; this can readily be understood from

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[34] K. F. O'Driscoll, *J. Polymer Sci., Part B*, 3, 305 (1965).

[35] F. R. Mayo, *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, 12, (2) 14 (1971).

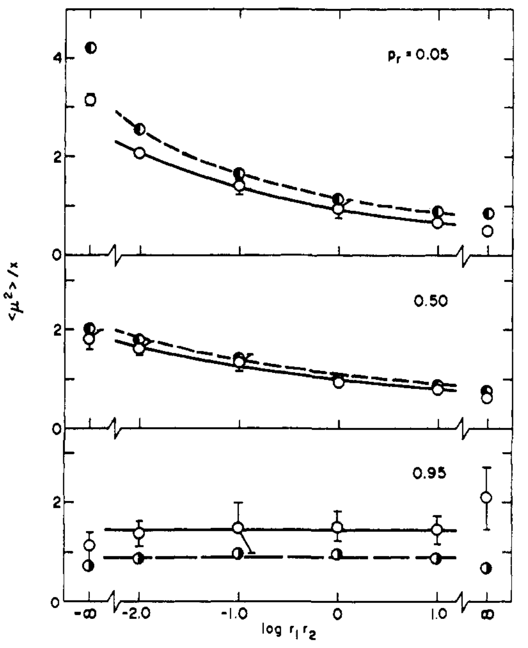

Figure 8. The dependence of $\langle \mu^2 \rangle / x$ on log r_1r_2 for poly(*p*-chlorostyrene–*p*-methylstyrene) copolymers having $x = 100$, at $p_1 = 0.50$; results are shown for selected values of p_r and temperature. For the curves obtained at $p_r = 0.05$ and 0.50, the open circles refer to a temperature of 428°K and left-filled circles refer to 298°K. In these cases, $\omega = 0.00$. For the curves obtained at $p_r = 0.95$, the open circles refer to either temperature and $\omega = 0.00$; the right-filled circles refer to a temperature of 298°K, $\omega = 0.05$, and $\tau = 0.50$.[36]

the fact that, in syndiotactic chains, trans sequences represent low-energy conformations. In these conformations, decrease in r_1r_2 toward 0.00 causes alternation in the placement of the m_1 and m_2 groups dipoles with the result that all of the nonzero (m_1) dipoles assume parallel, perfectly additive orientations and $\langle \mu^2 \rangle / x$ becomes very large. The dipole moment is, however, quite insensitive to r_1r_2 in the region of high isotacticity. In fact, as shown in Figure 7, all data for the highly isotactic polymer calculated for the range $r_1r_2 = 0.01$–10.0 could be represented by a single curve. This indicates that the extent to which a pair of group dipoles augment or attenuate one another depends only slightly on whether the two units are adjacent or widely separated within the helix.

The effect of temperature on the dependence of $\langle \mu^2 \rangle / x$ on r_1r_2 for poly(*p*-chlorostyrene–*p*-methylstyrene) chains was investigated by adjustment of the statistical weight factors to 298°K, again using the assumption that these quantities may be represented as simple Boltzmann factors. Results for $p_1 = 0.5$ (the only possible value for the limiting case $r_1r_2 = 0.00$) and $p_r = 0.05$, 0.50, and 0.95 are shown in Figure 8. In the case of $p_r = 0.05$ or 0.50, the open circles correspond to 428°K and left-filled circles to 298°K. Decrease in temperature enhances the dependence of $\langle \mu^2 \rangle / x$ on r_1r_2 in the case of the highly syndiotactic polymer (because of the increase in trans conformations) but has only a small effect in the case of the atactic polymer ($p_r = 0.50$). There is no change at all in the case of the highly isotactic polymer ($p_r = 0.95$) in the assumption that $\omega = 0.00$; results corresponding to both 428 and 298°K are represented by the open circles in this part of the figure. The effect of partially relaxing this requirement by increase in ω to 0.05 (with $\tau = 0.5$[36]) at $p_r = 0.95$ is shown by the right-filled circles. There is a decrease in $\langle \mu^2 \rangle / x$, as expected,[5] but the dipole moment remains relatively insensitive to r_1r_2 in this region of stereochemical structure.

Conclusions

The present calculations give a very satisfactory account of the experimentally determined dipole moments of the copolymers poly(*p*-chlorostyrene–*p*-methylstyrene) and poly(*p*-chlorostyrene–styrene) over a wide range of chemical composition. In this class of vinyl copolymers, however, in which the conformational energy is independent of chemical composition, analysis of dipole moment data to obtain values of r_1r_2 seems feasible only for copolymers significantly syndiotactic in stereochemical structure. Other types of vinyl copolymers [*e.g.*, poly(*p*-chlorostyrene–vinyl chloride) or poly(propylene–vinyl chloride)] would have conformational energies *dependent* on chemical composition and could quite conceivably have configuration-dependent properties more strongly dependent on r_1r_2. For such vinyl copolymers, the mean-square unperturbed dimensions $\langle r^2 \rangle_0$ as well as the mean-square dipole moments could serve to characterize the chemical sequence distributions.[37]

Acknowledgment. It is a pleasure to acknowledge the financial support provided for this research by Grant GP-16028 from the National Science Foundation.

(36) Y. Fujiwara and P. J. Flory, *Macromolecules*, 3, 43 (1970).

(37) Calculations on ethylene–propylene copolymers (R_1 = H, R_2 = CH_3) indicate that the unperturbed dimensions of these copolymers are particularly sensitive to chemical sequence distribution in the region of high isotacticity. On the other hand, both the unperturbed dimensions and dipole moments of propylene–vinyl chloride copolymers (R_1 = CH_3, R_2 = Cl) show the strongest dependence on distribution in the highly syndiotactic region.