The Use of Dipole Moments to Characterize Configurations of Chain Molecules

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The unique properties of polymeric materials both in solution and in the bulk, undiluted state result directly from the very large number of configurations or spatial arrangements which long-chain molecules can assume.[1,2] For example, the mechanical properties of materials as diverse as muscle fiber, partially crystalline polyethylene, and highly elastomeric natural rubber are largely due to the multitude of configurations accessible to these polymer chains and to rearrangements between such configurations in response to an imposed stress or change in environmental conditions. It is, therefore, highly desirable to obtain a quantitative understanding of the configurational characteristics of chain molecules, in particular, the dependence of configuration on the structural characteristics of the chain and the energetic effects accompanying changes from one configuration to another. There are a number of configuration-dependent properties which may be studied in pursuit of this goal, for example, the chain's mean-square end-to-end distance $\langle r^2 \rangle$, mean-square dipole moment $\langle \mu^2 \rangle$, optical rotation, and nmr spectrum.[1,2] Of these, the chain dimension $\langle r^2 \rangle$ has received by far the most attention, probably because of its relative ease of visualization and measurement through simple viscosity determinations.[1,3] In general, however, $\langle r^2 \rangle$ and several other properties can be determined reliably only in the case of relatively long chains. For this reason, and others to be presented below, there is a growing interest in the characterization of chain molecules through studies of their dipole moments,[1,2,4] even though this approach is obviously restricted to molecules of significant polarity. Analyses of such data in the case of small molecules have already given important structural information in the areas of both organic[5] and inorganic[6] chemistry.

The dipole moment of a polar chain molecule can readily be determined over the entire range of chain length from monomer through high molecular weight polymer, provided only that the chains be soluble in a nonpolar solvent, or be of sufficiently low polarity that they can be studied in the noncrystalline, nonglassy state in the absence of solvent. In addition, there is both theoretical[7-9] and experimental[10] evidence that dipole moments of many chain molecules are unaffected by excluded volume interactions.[1,3]

Such interactions have a significant effect on the chain dimensions and thus must be taken into account experimentally in order to obtain values of the chain dimensions which may be compared with results of theoretical calculations.

The purpose of the present Account is to survey theoretical studies which interpret dipole moments of chain molecules, including homopolymers, stereochemical copolymers, and chemical copolymers. Where appropriate for purposes of comparison, values of the dimensions of these molecules will be cited as well. The survey is concerned exclusively with equilibrium properties, to the exclusion of dielectric relaxation phenomena.[11] Since the subject of interest is the configuration of the chain itself, also excluded from consideration are chain molecules having polar groups capable of orientational motion independent of the chain backbone. This Account concentrates on the important results obtained from dipole moment investigations and detailed analysis of the advantages and disadvantages associated with the study of this particular configuration-dependent property.

Theory

In the study of stereochemical copolymers, such as vinyl chains $[CHRCH_2]_x$ of variable (d, l) structure, and chemical copolymers, which have variable chemical structure, it is necessary first to generate or simulate chain molecules which are closely similar in these structural features to polymers actually prepared and experimentally investigated. The stereochemical structure is generally characterized by the replication probability p_r, which is the probability of "isotactic" placements dd or ll rather than "syndiotactic" placements dl or ld. The chemical structure,

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(7) J. Marchal and H. Benoit, *J. Chim. Phys. Physicochim. Biol.*, 52, 818 (1955); *J. Polym. Sci.*, 23, 223 (1957).

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(10) S. C. Liao and J. E. Mark, *J. Chem. Phys.*, 59, 3825 (1973).

(11) Dielectric studies of the dynamic behavior of polymer chains in solution have recently been reviewed by Stockmayer, in ref 8 and in *Pure Appl. Chem. (Macromol. Chem.-8 Suppl.)*, 33, 379 (1973). See also L. De Brouckère and M. Mandel, *Advan. Chem. Phys.*, 1, 77 (1958).

on the other hand, is characterized by the probability p_1 that a given unit is of comonomer type 1 rather than type 2 and also by the average lengths n_1 and n_2 of sequences of the two types of units in the chain. As described in detail elsewhere[1,12-14] Monte Carlo techniques can be applied readily to p_r, and to p_2 and the reactivity ratio product[15] $r_1 r_2$ controlling the chemical sequence distribution, in order to generate chains of the desired stereochemical and chemical structure.

In the rotational isomeric state model[1,2,16,17] used in the analysis of the configuration-dependent properties of any type of chain, each rotatable skeletal bond is assumed to occur in one of a small number of discrete rotational states. This model for chain molecules has ample precedent in the study of small molecules.[18] (In addition, it has been shown recently[19] to give values of the dipole moments of the chloroethanes, molecules having only a single rotatable bond, which are essentially the same as those obtained by calculations carried out over the entire continuum of rotational angles.) In order to take into account the interdependence of rotational states, statistical weights must be assigned to *pairs* of conformations about consecutive skeletal bonds. Each such statistical weight u_{ij} is customarily expressed as a product of Boltzmann factors, each of the form[1] $\zeta_k = \exp[- E(\zeta_k)/RT]$, where $E(\zeta_k)$ is the energy characterizing one of the intramolecular interactions occurring in the associated conformation (*i.e.*, pair of consecutive rotational states) relative to some arbitrarily designated conformation of zero energy. The statistical weight of any particular pair of consecutive states will then be given by the appropriate product of such factors, one for each intramolecular interaction requiring characterization. The entire set of statistical weights required to describe all such conformations about a particular bond i in the chain is then used to construct a statistical weight matrix U_i.[1] (In many chain molecules, the rotatable skeletal bonds can exist in the three states trans (t), gauche positive (g+), and gauche negative (g−). These particular states generally occur at rotational angles φ of 0, 120, and −120°, respectively.) In this formalism, the configurational partition function for the chain may then be simply obtained by the appropriate sequential multiplication[1] of the U_i, one for each skeletal bond in the chain.

The statistical property of primary interest here is the mean-square value $\langle \mu^2 \rangle_0$ of the dipole moment averaged over all configurations of the chains. The zero subscript on such a statistical property indicates that this quantity will pertain only to chains unperturbed by excluded volume effects;[3] it will thus serve as a reminder that, in general, only those experimental values obtained under Θ conditions,[3] *i.e.*,

where the effects of such interactions are nullified, will be suitable for comparison with theoretical results. Theory,[7-9] however, indicates that excluded volume interactions should have no effect on the dipole moments of chain molecules which have the resultant dipole moment vector of each repeat unit directed along the bisector of a skeletal bond angle[7,8] or, more generally, which have symmetry planes, twofold symmetry axes, or symmetry points.[9] Most polar chain molecules meet these structural requirements and, in these cases, experiments need not be carried out under Θ conditions. Therefore, the restrictive subscript on $\langle \mu^2 \rangle_0$ will be unnecessary, unless stated otherwise. No corresponding simplification, however, occurs, for example, in the case of the "unperturbed dimension" $\langle r^2 \rangle_0$.

The desired mean-square dipole moment may be obtained by sequential multiplication of generator matrices G_i, where the G_i for a particular skeletal bond i contains the appropriate statistical weight matrix U_i, a coordinate transformation matrix T_i which depends only on the skeletal bond angle and allowed rotational angles φ_i, and the bond or group dipole vector m_i,[1,12] which is generally available from studies of small molecules. The same matrix methods serve for the calculation of $\langle r^2 \rangle_0$, when the dipole vectors m_i are replaced with bond vectors l_i. The matrices U_i and 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 to be used in such calculations are specified by Monte Carlo methods, as has been mentioned earlier.

The unperturbed dimensions will be expressed as the *characteristic ratio* $\langle r^2 \rangle_0 / n l^2$ where n is the number of skeletal bonds and l^2 is the mean of the squares of the bond lengths. The dipole moments of the homopolymers will be expressed as the analogously defined *dipole moment ratio* $\langle \mu^2 \rangle / n m^2$, where m^2 is the mean of the squares of the bond dipoles. Alternatively, the dipole moment ratio may be defined as $\langle \mu^2 \rangle / x m^2$, where x is the degree of polymerization, thereby making m^2 the mean of the squares of the resultant dipole moments of the repeat units. The characteristic ratio and dipole moment ratio are the factors by which the mean-square unperturbed dimension and dipole moment of an actual chain molecule differ from the values these quantities would have if the molecule were freely jointed along the entire chain backbone. For chemical copolymers, however, the most convenient quantity for theoretical interpretation is the ratio $\langle \mu^2 \rangle / x$, the mean-square dipole moment per repeat unit.[13,20,21] Finally, values of the temperature coefficient of any statistical property can, of course, be obtained from values of that property calculated as a function of the temperature-dependent Boltzmann factors ζ_k.[1,4]

Results

Homopolymers. Although polymethylene chains themselves, $H(CH_2)_{n-1}H$, are of negligible polarity, information on their configurational characteristics

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(17) T. M. Birshtein and O. B. Ptitsyn, "Conformations of Macromolecules," Interscience, New York, N. Y., 1966.

(18) See, for example, S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954.

(19) J. E. Mark and C. Sutton, *J. Amer. Chem. Soc.*, 94, 1083 (1972).

(20) J. E. Mark, *J. Polym. Sci., Polym. Phys. Ed.*, 11, 1375 (1973).

(21) J. E. Mark, *Polymer*, 14, 553 (1973).

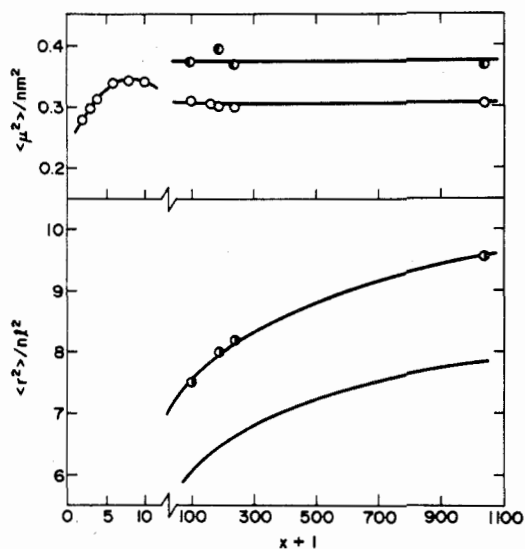**Figure 1.** Experimental values of the ratios $\langle\mu^2\rangle/nm^2$ and $\langle r^2\rangle/nl^2$ for dimethylsiloxane chains shown as a function of the degree of polymerization. In the upper portion of the figure, left-filled circles refer to dielectric results[10] obtained in cyclohexane at 25° and open circles to results[30,31] obtained on the undiluted chains at the same temperature. In the lower portion, the right-filled circles and the associated curve refer to viscometric results obtained in toluene at 25°; the other curve shown was calculated from the intrinsic viscosity–molecular weight relationship reported for dimethylsiloxane chains in benzene at 20°.[10,32]

has been obtained from the analysis[22] of the dipole moments of the α,ω-dibromoalkanes $Br(CH_2)_{n-1}Br$, in which significant polarity is introduced through the two terminal bonds. Experimental values of the dipole moment $\mu = \langle\mu^2\rangle^{1/2}$ have been reported[23] for relatively short chains of this type, with n ranging from 4 through 11. Theoretical values of μ have been calculated using a rotational isomeric state model based on conformational energies obtained from previous studies[1,24,25] of polyethylene, the long-chain limit in the n-alkane series. These conformational energies indicate that gauche rotational states about CH_2–CH_2 bonds have an energy approximately 0.5 kcal mol^{-1} higher than trans states, and that pairs of gauche states ($g^{\pm}g^{\mp}$) of opposite sign, which give rise to "pentane-type interferences" between CH_2 groups, are almost completely suppressed. Values of μ thus calculated are in satisfactory agreement with the experimental values, thus giving strong support to the basic features of this model, which is widely used to interpret the configuration-dependent properties of n-alkane chains in general.[1]

The same approach has been used to study the configurational statistics of perfluoroalkane chains $F(CF_2)_{n-1}F$. Dipole moments have been determined for α,ω-dihydroperfluoroalkanes, $H(CF_2)_{n-1}H$, having values of n in the range 5–11.[26] These experimental results were successfully interpreted using a model similar to that of n-alkane chains, but with gauche states about CF_2–CF_2 bonds approximately

1.0 kcal mol^{-1} higher than trans. This increase in the gauche–trans energy difference is very plausible in view of the fact that the van der Waals radius of an F atom is significantly larger than that of an H atom (1.35 *vs.* 1.20 Å)[1,27] and C–F bonds are considerably more polar than C–H bonds (1.2 *vs.* 0.4 D).[19,28] Since gauche states are relatively compact, their low occurrence in such molecules causes chains of poly(tetrafluoroethylene) (Teflon) to be of very high spatial extension. This circumstance may well account for the very high melting point ($\sim$330°) of this polymer and the unusually high viscosity of its melt.[1,29]

The chain molecules most extensively studied with regard to the dependence of the dipole moment on chain length, temperature, and the nature of the solvent medium are the dimethylsiloxanes, $(CH_3)_3Si[OSi(CH_3)_2]_xOSi(CH_3)_3$. Figure 1 presents values of the dipole moment ratio of these molecules at 25°, in both the undiluted state[30,31] and in cyclohexane,[10] as a function of the degree of polymerization $x + 1 = n/2$. For purposes of comparison, values[10] of the ratio $\langle r^2\rangle/nl^2$ are similarly displayed in the lower portion of this figure. The first notable feature of these experimental results is the fact that the dipole moment ratio $\langle\mu^2\rangle/nm^2$ is very much smaller than both the analogously defined ratio $\langle r^2\rangle/nl^2$ and, more importantly, the characteristic ratio $\langle r^2\rangle_0/nl^2$, which is approximately 7.0 for long dimethylsiloxane chains.[32] This is true for chain molecules in general, with values of the dipole moment ratio typically in the range 0.4–1.0,[4] while those of the characteristic ratio are typically approximately an order of magnitude higher.[1] This difference is directly traceable to the well-known characteristics of chemical bonding, which make it much more likely for bond dipole vectors to be in relative orientations where a great deal of mutual attenuation occurs, than is the case for skeletal bond vectors. For example, consecutive skeletal bond vectors rarely, if ever, occur at (bond) angles of less than 90°. In the case of bond dipole vectors, however, such attenuating orientations occur frequently, as is shown most directly in chains of the type

$$A \overset{B}{\nearrow}\searrow A \nearrow\searrow A \nearrow\searrow A$$
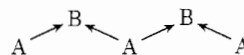
where the arrows specify the directions of the bond dipoles. The relatively small values generally obtained for $\langle\mu^2\rangle/nm^2$ are thus a direct reflection of such attenuation. A second feature of interest is immediately apparent from these experimental results; as shown in Figure 1, it is quite feasible to obtain values of the dipole moments of chain molecules in the region of very short chains ($x + 1 < 10$), where techniques used to obtain chain dimensions are generally totally inapplicable.

It is also important to note that the dipole moment ratio becomes independent of chain length[10]

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once one has exceeded the region of very short chain length where the chains are not representative because end groups contribute significantly to the properties of the molecule. For purposes of comparison, the very marked increase in $\langle r^2 \rangle / nl^2$ with chain length in two solvents similar to cyclohexane is shown in the lower portion of the figure;[10] such a dependence on chain length is directly due to excluded volume effects.[3] These experimental results thus clearly establish that in the case of dimethylsiloxane chains excluded volume interactions, which have a pronounced effect on $\langle r^2 \rangle / nl^2$, have no effect at all on $\langle \mu^2 \rangle / nm^2$. As is obvious from the schematic diagram of the dimethylsiloxane chain shown in Figure 2, this experimental result is in agreement with theory[7-9] in that these molecules do meet the symmetry conditions required for such independence from excluded volume effects. Each group dipole $\mathbf{M}_i$ is perpendicular to the direction of the chain backbone and lies in a plane which bisects one of the skeletal bond angles.[33]

Earlier studies of the dimensions of high molecular weight poly(dimethylsiloxane) established that gauche states in these molecules are approximately 0.85 kcal mol^{-1} higher in energy than trans, and that conformations giving rise to pentane-type interferences are completely suppressed when the interacting species are pairs of Si(CH$_3$)$_2$ groups, and partially suppressed when they are pairs of O atoms.[1,34] It has also been demonstrated that it is essential to recognize the fact that the unequal bond angles about Si and O atoms in these molecules have the unusual effect of making the low-energy, all-trans conformation approximate a series of closest polygons,[1,33,34] as is shown in Figure 2. Dipole moment ratios calculated[33] from this information are in excellent agreement with experiment for the undiluted molecules[30,31] in the region of very short chain length; in this region, satisfactory agreement is also obtained for the temperature coefficient of the dipole moment.[31] Comparison of theory with experiment for significantly larger values of $x + 1$ is complicated by the presence of "specific solvent interactions." Such interactions are known to affect the dimensions of poly(dimethylsiloxane) chains both in solution[32] and in swollen networks,[35] and their effect on the dipole moment ratio is shown in Figure 1 by the difference in values obtained for $\langle \mu^2 \rangle / nm^2$ in the undiluted state and in cyclohexane.[10]

Displaying the dimethylsiloxane chain in the planar all-trans form, of minimum conformational energy, also permits explanation of two additional, interesting aspects of the dipole moments of these chains. The particularly low value of the dipole moment ratio for these chains is obviously due to the fact that the dipole moment of a closed polygon such as is shown in Figure 2 is essentially zero.[33] Also, in the dependence of $\langle \mu^2 \rangle / nm^2$ on degree of polymerization shown in Figure 1, the maximum observed in the vicinity of $x + 1 = 8$ is probably due to the fact that addition of group dipoles beyond $\mathbf{M}_4$ in the low-ener-
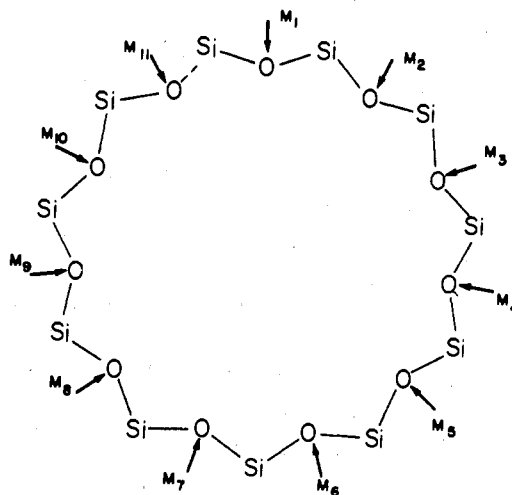

Figure 2. A segment of a dimethylsiloxane chain in its minimum energy, all-trans, planar conformation. The arrows represent group dipoles $\mathbf{M}_i$ for each Si(CH$_3$)$_2$–O–Si(CH$_3$)$_2$ pair of bonds.[33]

gy conformation decreases the dipole moment of the chain until the polygon is closed at $x + 1 \cong 12$. In any case, this analysis of dipole moments does greatly increase confidence in the conformational characteristics cited for dimethylsiloxane chains.

The polyoxides [(CH$_2$)$_y$O]$_x$ are another series of chain molecules the configurational characteristics of which have been studied extensively.[1,7,36-49] Studies have been carried out on the members of this series corresponding to $y = 1$–4 and have yielded the following conformational information. Gauche states which bring into proximity pairs of O atoms are approximately 0.4 kcal mol^{-1} lower in energy than the corresponding trans states.[36,37] When the interacting species are an O atom and a CH$_2$ group, gauche states are lower in energy by 0.2 kcal mol^{-1} for bond sequences C–C–C–O[38,39] and by 1.7 kcal mol^{-1} for the sequences C–O–C–O.[40] For interactions involving a pair of CH$_2$ groups, however, gauche states have higher energies than trans states; the energy difference is 0.5 kcal mole^{-1} for C–C–C–C sequences[24,39] and 0.9 kcal mol^{-1} for C–O–C–C sequences.[36-39] Conformations giving rise to pentane-type interferences are partially suppressed when the interacting species are a pair of O atoms, or an O atom and a CH$_2$ group, and are completely suppressed in the case of a pair of CH$_2$ groups.[1,36-40]

Polyoxymethylene, the first member ($y = 1$) of this series, has not been extensively studied from an experimental point of view because of its high melt-

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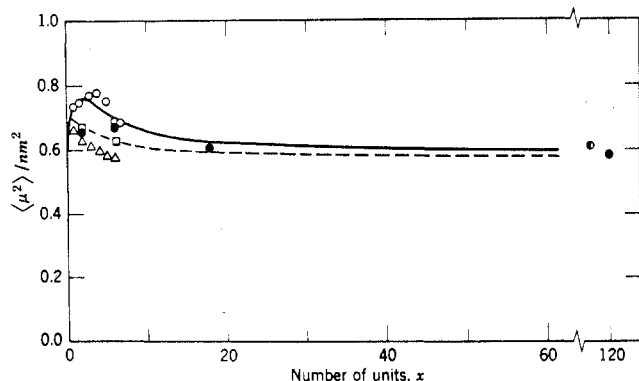(49) M. Kurata, H. Utiyama, and K. Kamada, *Makromol. Chem.*, 88, 281 (1965).

Figure 3. Values of the dipole moment ratio shown as a function of the degree of polymerization for $HO[CH_2CH_2O]_xH$ and $C_2H_5O[CH_2CH_2O]_xC_2H_5$ chains in the vicinity of 25°.[1] For the former series of molecules, the theoretical results[1,37] are shown by the solid line and the experimental results by the open,[43] half-filled,[45] and filled[7] circles. The corresponding results for the latter series are given by the dashed line[1,37] and by the squares[7] and triangles.[44]

ing point (198°). Conformational energies have, however, been estimated for these molecules from studies[41] of the dipole moment of the oligomer corresponding to $x = 3$, and the dipole moment and its temperature dependence for the oligomer corresponding to $x = 2$. Although the comparison of theory with experiment is very tentative in this case, these energies[40,41] do give values of the dipole moment ratio and characteristic ratio which are in satisfactory agreement with preliminary experimental values of these quantities.[1,42] In contrast, there is a great deal of experimental information[7,36,43-47] on the polyoxyethylenes ($y = 2$), chain molecules which may be prepared with either hydroxyl or ethoxy terminal groups. Dipole moments for both types of oxyethylene chain are shown in Figure 3. There is excellent agreement between theory[37] and both the typical experimental results[7,43-45] presented here, and other experimental results as well.[46,47] Similarly good agreement is obtained for the temperature coefficient[45] of the dipole moment ratio and the characteristic ratio[36] and its temperature coefficient.[36] The results shown in Figure 3 also illustrate the fact that the dipole moment ratio very rapidly reaches its limiting value for very long chain length, thus simplifying somewhat the comparison of theoretical and experimental values of this quantity. Poly(trimethylene oxide) ($y = 3$) has been studied experimentally only with regard to its unperturbed dimensions. Calculations[38] carried out for this chain molecule give an estimate of the characteristic ratio which is in good agreement with the experimental result;[48] the same calculations yield predictions for the dipole moment ratio as well. In the case of poly(tetramethylene oxide) ($y = 4$), theoretical[39] and experimental[45] values of the dipole moment ratio are in excellent agreement, and values of the temperature coefficient of this ratio are in fair accord.[45] Very good agreement is obtained for both the characteristic ratio and its temperature coefficient.[39,45,49]

The most interesting aspect of the configurational characteristics of the polyoxide chains is the manner in which the dipole moment ratio and characteristic ratio in the limit of long chain length vary with the number y of methylene groups in the repeat unit. In

the case of polyoxymethylene, all of the skeletal bonds show a strong preference for gauche states, the energy of which is 1.7 kcal mol^{-1} below that of the trans states. This strong conformational preference requires long stretches of the chain to be in helical segments comprising sequences of gauche bonds of the same sign.[1,40] In these helical segments, group dipoles are in almost perfectly compensating orientations, thus explaining the very low value, ~0.2,[42] reported for its dipole moment ratio. Such helical segments are, however, of very high spatial extension, giving rise to a relatively large value, ~10,[1] for its characteristic ratio. For $y = 2$, 3, and 4, the skeletal bonds are no longer all identical; gauche states are preferred about some bonds and trans states about others.[36-39] Conformations of these chains are therefore not nearly as regular as those of polyoxymethylene. This circumstance causes values of the dipole moment ratio for $y = 2$-4 to be very much larger than that of polyoxymethylene (0.5-0.6 *vs.* 0.2),[37,42,45] and the values of the characteristic ratio to be considerably smaller (4-6 *vs.* 10).[1,36,48,49]

Dipole moments have also been calculated[50] for poly(hexamethyleneadipamide), $[NH(CH_2)_6NHCO-(CH_2)_4CO]_x$, a typical polyamide. The dipole moment ratio predicted for this molecule is very close to the value of unity characterizing a freely jointed chain, since the relatively long sequences of nonpolar CH_2 units between the polar NHCO groups cause the group dipoles to be essentially uncorrelated in direction.[50] Similar suppression of correlations between group dipoles can be attained by incorporation (copolymerization) of essentially nonpolar units into an otherwise polar chain molecule.[51]

Of the polyesters, only poly(ω-hydroxydecanoic acid), $[(CH_2)_9COO]_x$, has been studied experimentally in any detail.[52] As expected,[50] for reasons just cited, its dipole moment ratio is also in the vicinity of unity, having the value 1.3 (± 0.1).[52] The fact that this value somewhat exceeds unity may be due to excluded volume interactions, since this is one of the very few molecules studied which lack the symmetry required for immunity from this effect. Other chain molecules for which an excluded volume effect on the dipole moment has been demonstrated are poly(hexene 1-sulfone), $[CH_2CH(n\text{-}C_4H_9)SO_2]_x$,[53] and poly($\epsilon$-caprolactone), $[(CH_2)_5COO]_x$.[54]

A very limited number of studies have been carried out on the dipole moments of polypeptides, $[NHCHRCO]_x$. Although not obvious from this very schematic structural notation, polypeptides generally do[9] have the symmetry required to permit neglect of excluded volume effects. Theoretical[55] and experimental[56] values of the dipole moments of the

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charged oligomeric polyglycines $^+H_3NCH_2CO$-$[NHCH_2CO]_{x-1}NHCH_2CO_2^-$ have been shown to be in satisfactory agreement. In addition, similar calculations[57] have been carried out for uncharged glycine, L-alanine, and L-proline chains, but experimental values of the dipole moments of these chains have not yet been reported.

Stereochemical Copolymers. The two chain molecules in this category which have been most thoroughly investigated with regard to their dipole moments are poly(vinyl chloride), $[CHClCH_2]_x$, and poly(p-chlorostyrene), $[CH(p-C_6H_4Cl)CH_2]_x$. In the theoretical calculations[12,58] on these molecules, representative chains characterized by values of the stereochemical replication probability p_r of 0.05 (highly syndiotactic), 0.50 ("atactic" or random), and 0.95 (highly isotactic) were generated using Monte Carlo techniques, at a degree of polymerization, $x = 100$, sufficiently large, in general, for $\langle\mu^2\rangle/xm^2$ to have attained its limiting value for long chain length. In the case of poly(vinyl chloride), conformational energies are available from the stereochemical equilibration results obtained for vinyl chloride oligomers by Flory and coworkers.[59] The most important of these results are qualitatively summarized here. In syndiotactic sequences trans states are very strongly favored because interactions of the small Cl atom with the chain backbone are of relatively low energy in this conformation. Pentane-type interferences between Cl atoms separated by four bonds are sufficiently large to diminish significantly this preference in the case of isotactic sequences; they are not large enough, however, to restrict such sequences to conformations (e.g., tg),[1] giving rise to helices (3_1) to the extent shown by isotactic sequences of units having pendant groups the size of CH_3 or larger.[1,60]

The results of these circumstances are shown by the calculated values of the dipole moments of poly(vinyl chloride) shown in Figure 4.[58] As is readily evident from these results, the dipole moment ratio is very sensitive to stereochemical structure; it is very large in the region of high syndiotacticity, but very small in the region of high isotacticity. These differences are directly due to the relatively small size of the pendant Cl atom in these chain molecules. This is the origin both of the preference of trans conformations of high dipole moment[12] in syndiotactic sequences and the alleviation of the strong preference for helical conformations which would also be highly polar and which occur in isotactic polypropylene sequences because of repulsions between the relatively large CH_3 groups.[1] Unfortunately, comparison between experimental and theoretical values of the dipole moment ratio and its temperature coefficient are not feasible at the present time because of the very wide range of experimental values obtained for these qualities in the case of poly(vinyl chloride).[12]

As is obvious from the above discussion, poly(vinyl chloride) is not a typical vinyl polymer, because of
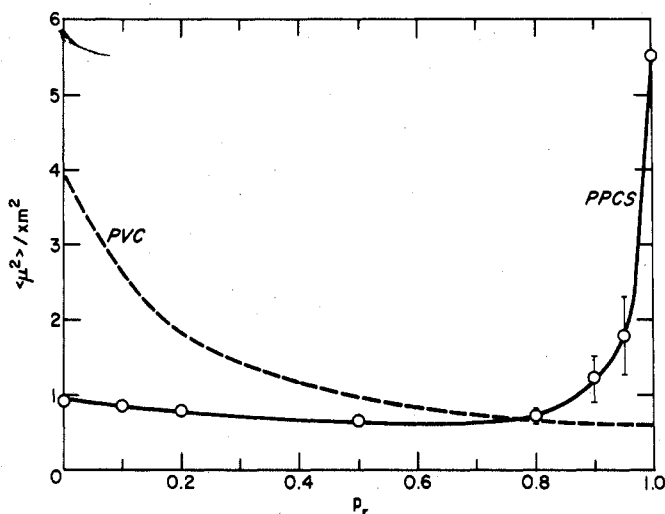
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Figure 4. Theoretical values of the dipole moment ratio at 25° for poly(vinyl chloride)[12] and poly(p-chlorostyrene)[58] chains of degree of polymerization $x = 100$, shown as a function of the probability p_r of stereochemical replication (isotactic placement). For clarity, the points and standard deviation lines used to locate the curve for poly(vinyl chloride) have been omitted.

the unusually small size of its pendant substituent. It is therefore of considerable interest that the para-substituted styrene chains are closely related polymers structurally, but have significantly larger side chains. Of interest here is the particular case of poly (p-chlorostyrene), where the para substituent is the Cl atom. Differences in dipole moment ratio between poly(p-chlorostyrene) and poly(vinyl chloride) should be due entirely to differences in conformational energy; in both molecules the group dipole vectors have a tetrahedral orientation relative to the chain backbone[12,58] and the difference between the two group dipole moments m is irrelevant since calculated dipole moments of the chains are expressed relative to the corresponding group dipole moments in ratios such as $\langle\mu^2\rangle/xm^2$.

The conformational energies appropriate for poly (p-chlorostyrene) chains are the same, to very good approximation,[58] as the corresponding energies for unsubstituted styrene chains, and these are available from stereochemical equilibration experiments carried out on styrene oligomers by Williams and Flory.[61] In brief, these energies indicate only a slight preference for trans states in syndiotactic sequences and the essentially complete suppression of conformations giving rise to pentane-type interferences. Calculations based on these conformational energies and pertinent structural information[58] give the values of the dipole moment ratio for p-chlorostyrene chains shown in Figure 4. Poly(p-chlorostyrene) has relatively small values of the dipole moment ratio in the region of high syndiotacticity but very large values at high isotacticity, the reverse of the situation pertaining to poly(vinyl chloride). The relatively large size of the C_6H_4Cl pendant group in poly(p-chlorostyrene) greatly diminishes the preference for extended trans states in syndiotactic sequences but also strongly suppresses departures from extended helical conformations in isotactic sequences. Both

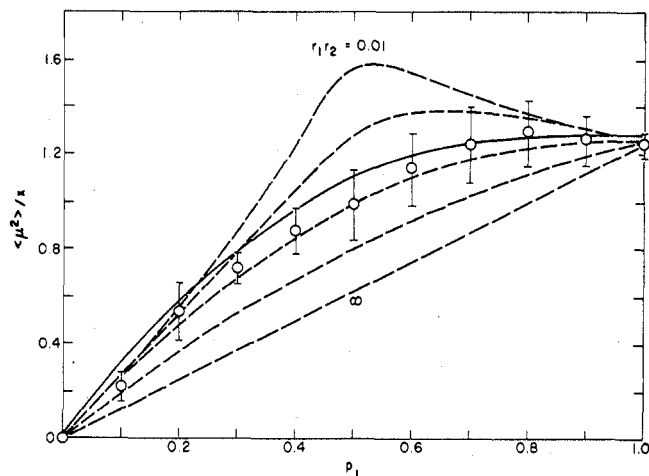(61) A. D. Williams and P. J. Flory, *J. Amer. Chem. Soc.*, 91, 3111 (1969).

Figure 5. The mean-square dipole moment per monomer unit for atactic poly(p-chlorostyrene-p-methylstyrene) copolymers at 155° shown as a function of the chemical composition variable p_1 (probability of occurrence of p-chlorostyrene units).[13] The solid curve shows the experimentally observed dependence. The circles and standard deviation lines locate theoretical results obtained using values of the replication probability and reactivity ratio product, r_1r_2, appropriate for such chains. The dashed curves represent additional, illustrative results calculated for values of r_1r_2 of 0.01, 0.10, 1.00, 10.0, and ∞, respectively.

Figure 6. Orientations of the group dipoles $m(R_1) > 0$ (*e.g.*, p-chlorostyrene) and $m(R_2) = 0$ (*e.g.*, p-methylstyrene) in the all-trans conformation of a syndiotactic vinyl copolymer. Dipoles extending toward the reader are represented by the solid arrows and those extending away, by the broken arrows. Case A ($r_1r_2 \rightarrow \infty$) represents a block copolymer and case B ($r_1r_2 = 0$) represents an alternating copolymer.[4]

such conformations correspond to large dipole moment.[58]

The calculated value of the dipole moment ratio for atactic poly(p-chlorostyrene) is 0.73, a result in good agreement with the average value 0.68 (±0.10) obtained from a number of experimental studies of this polymer.[58] There is also, in general, satisfactory agreement between theoretical and experimental values of the temperature coefficient of the dipole moment.[58] Finally, fair agreement is obtained between calculated and experimental values of the dipole moment ratio for p-fluorostyrene[62] and styrene itself.[13,63]

Chemical Copolymers

As already mentioned, the chemical sequence distribution in a copolymer may be characterized in part by the average sequence lengths n_1 and n_2 of chemically identical units of type 1 and 2, respectively. These characteristics are controlled by the chemical composition variable p_2 (fraction of units of type 2) and the reactivity ratio product r_1r_2.[13,14] Values of n_1 and n_2 for selected values of p_2 and r_1r_2 are tabulated in detail elsewhere,[13,14] but the following Monte Carlo results for equimolar copolymers ($p_2 = 0.50$) are presented here for purposes of illustration. For values of $r_1r_2 = 0.0, 1.0, 1000.0$, and ∞, the representative values of $n_1 = n_2$ are, respectively, 1.0 (perfectly alternating copolymers), 2.0 ("ideal" copolymers), 24.0 ("block" copolymers), and ∞ (mixtures of homopolymers).[13,14,21]

Mean-square dipole moments per unit reported for atactic p-chlorostyrene-p-methylstyrene chains at 155° are represented by the solid line in Figure 5.[13] There is a very noteworthy feature in these experimental results that, as will be seen, can be under-
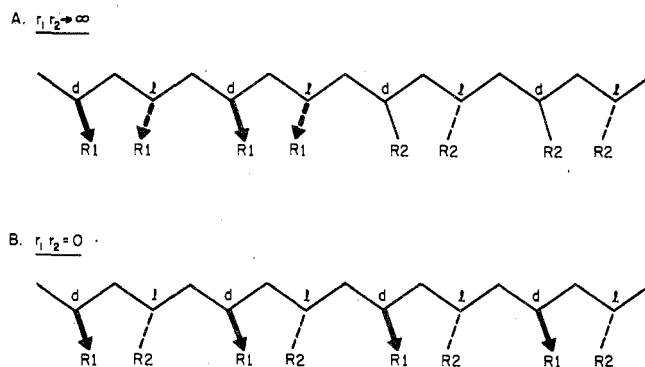
stood readily in terms of configurational calculations. Specifically, the dependence of $\langle\mu^2\rangle/x$ on the fraction p_1 of p-chlorostyrene units in the chain shows a marked positive deviation from simple linearity between the values of $\langle\mu^2\rangle/x$ characterizing the corresponding homopolymers. Calculations[13] for the correspondingly atactic p-chlorostyrene-p-methylstyrene copolymer gave the values of $\langle\mu^2\rangle/x$ shown by the points in Figure 5; they are seen to be in good agreement with the experimental relationship shown by the solid line. The dashed lines show results calculated for other, illustrative values of r_1r_2 and demonstrate that $\langle\mu^2\rangle/x$ is generally quite sensitive to sequence distribution at constant chemical composition. Therefore, in this case, measurements of dipole moments could have been used to obtain reliable values of r_1r_2, and thus values of the average chemical sequence lengths in the copolymer. Similarly satisfactory results are obtained for p-chlorostyrene-styrene chains;[13] calculated results of $\langle\mu^2\rangle/x$ for these copolymers are also in good agreement with experiment. Detailed analysis of the calculated results, in general, indicate that the bulkiness of the C_6H_4 groups causes neighboring group dipoles to be largely in orientations in which there is a great deal of attenuation. This is, of course, the origin of the convex nature of the curves shown in Figure 5; the attenuation would obviously be less in a copolymer than in a mixture of homopolymers having the same overall composition.[13] Additional results obtained for p-chlorostyrene-p-methylstyrene chains indicate that the dependence of $\langle\mu^2\rangle/x$ on chemical sequence distribution is particularly strong in the case of syndiotactic chains. This can be understood readily from the fact that trans sequences are low-energy conformations in chains of this stereochemical structure. In these conformations, as shown in Figure 6, decrease in r_1r_2 toward zero causes alternation in the placement of the group dipoles with the result that all of the larger [$m(R_1)$] dipoles assume parallel, perfectly additive orientations. The ratio $\langle\mu^2\rangle/x$ thus becomes very much larger than it is for the case of the corresponding block copolymer ($r_1r_2 \rightarrow \infty$) where there is considerable attenuation among group dipole vectors.[13]

Calculations[20] of both the dimensions and dipole moments of propylene-vinyl chloride chains have

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been carried out, in part to illustrate the relative sensitivity of these quantities to chemical sequence distribution. These results indicate that $\langle\mu^2\rangle/x$ is generally much more sensitive to both chemical composition and chemical sequence distribution than is $\langle r^2\rangle_0/nl^2$, a result of some importance with regard to the possible characterization of such distributions by measurements of configuration-dependent properties. 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. On the other hand, in the calculation of $\langle\mu^2\rangle/x$, *both* the conformational energy and the group dipole moment depend on the chemical nature of the comonomeric unit. Similarly calculated results[21] for ethylene–vinyl chloride chains confirm this enhanced sensitivity of the mean-square dipole moment to chemical composition and chemical sequence distribution.

Summary

It has been demonstrated clearly that analysis of the dipole moments of randomly coiled chain molecules by means of rotational isomeric state theory can provide very valuable information on the conformational energies and spatial configurations of such molecules. The main advantages of this approach are the possibility of extending measurements into the region of very short chain length and the absence of any effect of excluded volume on the dipole moments of most chain molecules. In addition, there is usually a very rapid convergence of the mean-square dipole moment per bond to its limiting value for infinite chain length and a marked sensitivity of the dipole moment to both the stereochemical and chemical structure of the chain.

Laser Measurement of Optical Absorption in Liquids

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When a laser beam passes through a material with finite optical absorption, the heat generated increases temperature, which changes the index of refraction, which in turn affects the optical beam. The results include a defocusing[1-4] or focusing[5,6] of the beam (depending upon the sign of the index change with temperature), a change in phase delay as index changes,[7] and a smearing of the beam due to free convection effects if the material is fluid.[8,9] Certain of the effects are observable for beams in the power range of only milliwatts to watts in materials normally thought to be "transparent" (absorption coefficients of 10^{-4} cm^{-1} or lower), and are thus useful for the measurement of low optical absorption coefficients with relatively simple experimental arrangements.[10-12] The methods give true absorption, as calorimetric methods do, not absorption plus scattering, as in transmission methods. The methods have been applied primarily to the measurement of

absorption in samples to be used for optical experiments, or for the study of materials considered for optical transmission. They should also play an important role in absorption spectroscopy.

Although we stress in this Account the aspects that are important for absorption measurements, there are also undesirable consequences of index changes from thermal absorption. For high average powers, the spreading or "thermal blooming" in passing through solid windows or fluid cells may be significant even when these materials are relatively transparent. High power beams in the atmosphere may suffer a thermal blooming and a distortion from

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