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Random-Coil Dimensions and Dipole Moments of *p*-Chlorostyrene Chains

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Mean-square dimensions and dipole moments of *p*-chlorostyrene chains $\text{CH}_3\text{--}[\text{CH}(\textit{p}\text{-C}_6\text{H}_4\text{Cl})\text{--CH}_2\text{--}]_x\text{H}$ have been calculated as a function of their stereochemical structure, degree of polymerization x , and temperature. Theoretical arguments and experimental evidence indicate that *p*-chlorostyrene and styrene chains differ little in conformational energy. Therefore, the present investigation employs conformational energies of styrene chains recently obtained by Flory and co-workers from analysis of the stereochemical equilibrium compositions of styrene dimers and trimers. The calculations indicate that at large x the dimensions of *p*-chlorostyrene, or styrene, chains and the dipole moments of *p*-chlorostyrene chains should increase with increasing isotacticity and decreasing temperature. The marked differences in the configurational characteristics of *p*-chlorostyrene and vinyl chloride chains are shown to result from the large difference in size between *p*-C₆H₄Cl groups and Cl atoms. Theoretical results calculated for large x are, in general, in satisfactory agreement with published experimental results on poly(*p*-chlorostyrene). Several experimental results, as yet unconfirmed, seem however to evade interpretation in terms of the present model. Additional experimental investigations would be required to resolve this discrepancy and to provide a more definitive test of the calculated results.

INTRODUCTION

Calculations of the random-coil dimensions and dipole moments of vinyl chloride chains $\text{CH}_3\text{--}[\text{CHCl--CH}_2\text{--}]_x\text{H}$ have been reported in the preceding paper.¹ These calculations constitute the only interpretation of the dipole moments of a vinyl chain molecule using a realistic model, a rotational isomeric state representation with neighbor interactions. Vinyl chloride oligomers and polymers are, however, unusual vinyl chains in that the small size of the pendant substituent R, a Cl atom, gives these molecules access to a larger number of conformations^{1,2} than are available to "typical" vinyl chains, i.e., those having substituents the size of a methyl group or larger.³⁻⁷ For example, an isotactic

polymer of vinyl chloride would not be expected^{1,2} to exhibit as strong a preference for 3₁ helical sequences as would isotactic polymers of propylene or styrene.³⁻⁷

It is therefore of considerable interest to extend the earlier calculations to vinyl oligomers and polymers having significant dipole moments and sufficiently large R substituents to limit, by steric interactions, the conformations accessible to the chain backbone. Chains of *para*(*p*)-chlorostyrene units $\text{CH}_3\text{--}[\text{CH}(\textit{p}\text{-C}_6\text{H}_4\text{Cl})\text{--CH}_2\text{--}]_x\text{H}$ are ideally suited for this purpose. Because of the nature of the bonding⁸ and the symmetry of the *para* isomer, the resultant group dipole in each repeat unit should lie, to a very good approximation, along the C^α–C^β bond, as shown in Fig. 1. Furthermore, in both vinyl chloride and *p*-chlorostyrene chains, this dipole

will be oriented approximately tetrahedrally⁸ with respect to the skeletal bonds meeting at a C^α atom. Calculated dipole moments for these two vinyl chains will be expressed relative to the dipole moment of the saturated monomer unit. Therefore, comparison of such normalized dipole moments for these two types of chain molecules will directly yield information on the effect of intramolecular interactions on the conformations of vinyl oligomers and polymers. As is well known, the unperturbed dimensions of a chain molecule serve a similar and complementary purpose.⁴

In this paper we therefore present calculations of both the mean-square unperturbed dimensions $\langle r^2 \rangle_0$ and dipole moments $\langle \mu^2 \rangle_0$ of *p*-chlorostyrene chains as a function of their stereochemical structure, degree of polymerization x , and temperature. A preliminary test of the calculated results in the limit of large x will be provided by several previously reported experimental studies of poly(*p*-chlorostyrene).

THEORY

We adopt for the present calculations the rotational isomeric state model formulated for vinyl chains by Flory and co-workers.^{3,4} In this representation, each skeletal bond is restricted to a choice of one of three rotational states. These states are designated *trans* (t), *gauche* positive (g^+), and *gauche* negative (g^-) and, as a first approximation may be assumed to be located at rotational angles ϕ of 0°, 120°, and -120°, respectively. (The conventions employed in defining these rotational angles are described in the preceding paper.¹) On the basis of previous analyses of the properties of polystyrene chains,^{7,9,10} it is anticipated, however, that steric interactions in *p*-chlorostyrene chains are rather large. Calculations must therefore also be carried out for the case in which some of the rotational states are displaced from these cited locations by an amount $\Delta\phi$, as previously described for poly(α -olefins).³ The nature of these displacements may readily be comprehended by reference to Figs. 1 and 2. Rotational states for the two skeletal bonds leading into and out of a C^α atom of *d* configuration (e.g., bonds $i-2$ and $i-1$, respectively, of Fig. 1) are located at $-\Delta\phi$, 120, and $-120+$

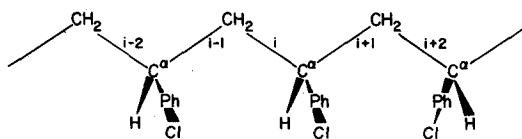


FIG. 1. The planar, all-*trans* conformation of a portion of a *p*-chlorostyrene chain consisting of an isotactic (*dd*) dyad followed by a syndiotactic (*dl*) dyad. In this diagram and in Fig. 7, bonds extending toward the reader are represented by lines of increasing thickness, and those extending away, by lines of decreasing thickness. The group dipole in each repeat unit is located along the line joining the C^α and Cl atoms. The symbol Ph stands for the *p*-phenylene (*p*-C₆H₄) group.

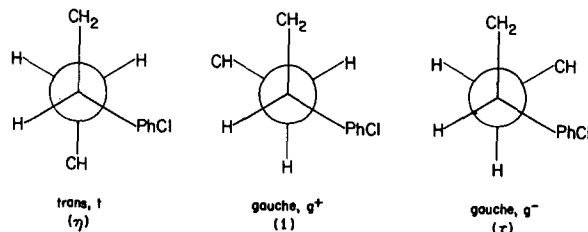


FIG. 2. Rotational states about skeletal bonds in *p*-chlorostyrene chains and the associated statistical weight factors.

$\Delta\phi^\circ$, 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 of *l* configuration (e.g., bonds $i+3$ and $i+2$, respectively).

As shown by Williams and Flory, several statistical weight factors are required in order to calculate configuration-dependent properties of vinyl chains having pendant substituents larger than methyl groups.⁵ In view of the large size of the *p*-C₆H₄ group,^{7,9,10} we adopt their scheme for the analysis of the conformations of *p*-chlorostyrene chains. Intramolecular interactions dependent on only one rotational angle in these chain molecules and the corresponding statistical weight factors (η , 1, and τ) are shown in Fig. 2 and are described in detail elsewhere.^{1,5} Interactions dependent on two consecutive rotational angles involve atoms or groups separated by four bonds. Except in the case where one of the interacting species is an H atom, these interactions are strongly repulsive. A single statistical weight factor $\omega \ll 1$ is therefore introduced to take into account the resulting suppression, or near suppression, of any conformation giving rise to such interactions.⁵

As outlined in the preceding paper,¹ these statistical weight factors, in conjunction with bond lengths, bond angles, and group dipole moments, may be used to calculate statistical mechanical averages (over all configurations) of the squares of the unperturbed dimensions and dipole moments of a vinyl chain of any length and stereochemical structure.³⁻⁵ As previously described,^{1,3} representative stereochemical sequences for any chosen replication probability p_r (i.e., probability of isotactic placement) may be generated by means of Monte Carlo methods. For convenience, the calculated results will be expressed as the *characteristic ratio* $\langle r^2 \rangle_0/nl^2$ and the *dipole-moment ratio* $\langle \mu^2 \rangle_0/xm^2$. In these ratios $n=2x$ is the number of skeletal bonds, each of length l , in the chain and x , being the degree of polymerization, is also the number of group dipoles, each of magnitude m . As is the case for vinyl chloride chains,¹ long-range interactions should have no effect on the mean-square dipole moments of *p*-chlorostyrene chains. The zero subscript in $\langle \mu^2 \rangle_0$ is therefore unnecessary and may be deleted, thus simplifying comparison of theoretical and experimental values of $\langle \mu^2 \rangle/xm^2$.

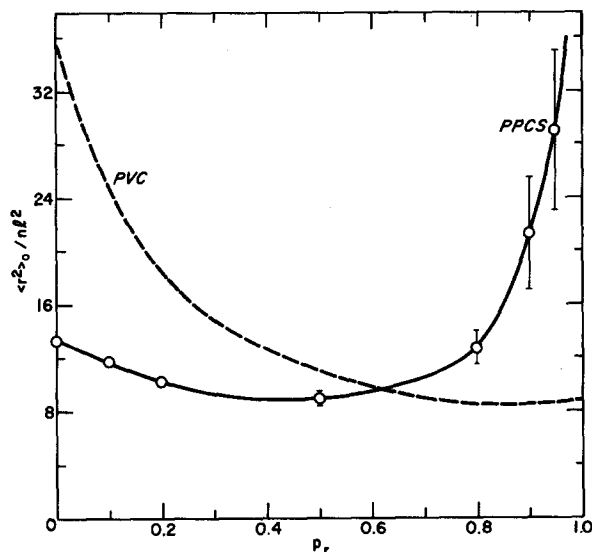


FIG. 3. The characteristic ratio shown as a function of stereochemical composition for poly(*p*-chlorostyrene) chains having a degree of polymerization of $x = \frac{1}{2}n$ of 100. In this and the following figures the temperature is 25°. In the case of stereoirregular chains, each point in these figures represents the average result of calculations on five Monte Carlo chains having the specified value of the replication probability p_r ; lines through the points have been drawn with a length twice the standard deviation in that set of results. Included for purposes of comparison are previously calculated results¹ for poly(vinyl chloride) chains at the same degree of polymerization.

CALCULATED RESULTS AND DISCUSSION

The statistical weight factors required for the averaging⁴ of the properties of *p*-chlorostyrene chains may be obtained, to good approximation, from the corresponding factors determined for (unsubstituted) styrene chains,⁵ as shown by the following theoretical arguments and experimental results. Interactions between groups separated by three bonds should be approximately the same in these two chain molecules for the following two reasons. The Cl atom is too far from the chain backbone to change significantly the steric interactions present in styrene chains and, in any case, there is little difference between the van der Waals radius of a Cl atom [1.75 Å¹¹] and the thickness of the C₆H₄ group (1.70 Å for a C atom¹¹). Second, any electrostatic effects between the *p*-C₆H₄Cl group and the hydrocarbon backbone should be very small. Similarly, interactions between groups separated by four bonds should be unchanged by the presence of the Cl substituent: Conformations in which *p*-C₆H₄Cl groups are sufficiently close for strong steric or electrostatic interactions are already largely excluded due to the previously mentioned steric repulsions between the C₆H₄ groups.⁵ The above arguments are supported by experimental results on several, presumably "atactic" polymers: most importantly, poly(*p*-chlorostyrene) (PPCS) has a value of the characteristic ratio, 10.6

(±0.6),¹²⁻¹⁷ which is the same, within experimental error, as that of polystyrene, 10.0 (±0.2).⁴ In addition, even larger X substituents in CH₂-[CH(*p*-C₆H₄X)-CH₂]_xH seem to have only a modest effect on the unperturbed chain dimensions. For example, for X = Br, CH₃, and cyclohexyl, the van der Waals radii are 1.85,¹¹ ~2.0,¹⁸ and ≥2.0 Å, respectively, and the characteristic ratios are 12.3 (±1.1),^{17,19} 10.7 (±0.1),^{14,20} and 13.7,²¹ respectively. On the above grounds, we adopt without modification the statistical weight factors obtained by Williams and Flory⁵ by analysis of the stereochemical equilibrium compositions of styrene dimers²² and trimers.⁵ As a result, the calculated values of the characteristic ratio (but not, of course, the dipole-moment ratio) should pertain to styrene as well as *p*-chlorostyrene chains. At 25°, these factors are $\eta = 1.6$ and $\omega = 0$; the value of τ is relevant only when ω is nonzero. Both η and ω for *p*-chlorostyrene chains are smaller than the corresponding statistical weight factors for vinyl chloride chains at the same temperature ($\eta = 4.2$, $\omega = \omega' = 0.032$, and $\omega' = 0.071$). These differences are of course due to the difference in size between *p*-C₆H₄Cl groups and Cl atoms.^{2,5} Additional characteristics assumed for these chain molecules are (i) skeletal bond angles and lengths of 112° and 1.53 Å, respectively,⁸ (ii) tetrahedral orientation of the group dipoles with respect to the adjoining skeletal bonds,⁸ and (iii) group dipole moments of 1.68 D, the dipole moment of *p*-chloroethyl benzene in a variety of non-polar solvents.²³

Using the above information and methods, values

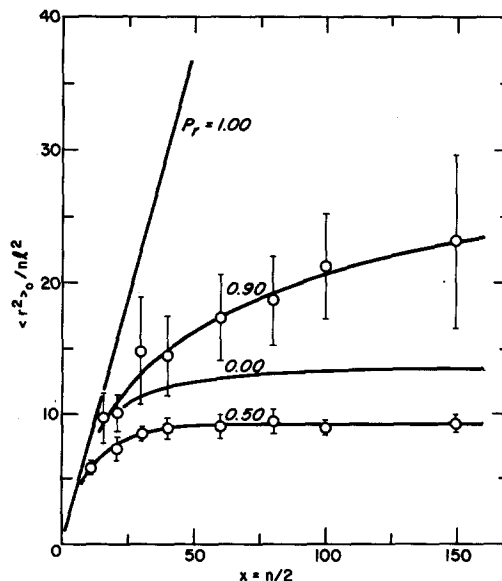


FIG. 4. The characteristic ratio of poly(*p*-chlorostyrene) chains shown as a function of the degree of polymerization. In this figure and in Fig. 8, each curve is labeled with the value of the replication probability used to generate the stereochemical structure of the chains.

of the characteristic ratio at 25° were calculated for PPCS chains having $x=100$ and $\Delta\phi=0$, over the entire range of stereochemical composition. These results are shown in Fig. 3; also shown for purposes of comparison are characteristic ratios calculated¹ for poly(vinyl chloride) (PVC) at the same temperature and value of x . The very different dependence of this ratio on the replication probability for these two vinyl polymers is obviously due to the large size of the *p*-C₆H₄Cl group relative to the Cl atom. In the region of high syndiotacticity, PPCS has a lower characteristic ratio than PVC because highly extended *trans* sequences are less favored in PPCS ($\eta=1.6$) than in PVC ($\eta=4.2$). For highly isotactic chains PPCS has the higher value of this ratio, since deviations from extended 3₁ helical conformations are permitted in PVC ($\omega, \omega', \omega'' > 0$) but not in PPCS ($\omega=0$).

Values of the characteristic ratio for PPCS chains are shown as a function of the degree of polymerization, for selected values of p_r , in Fig. 4. As was found to be the case for PVC chains, the larger the value of the ratio at $x=100$, the more protracted the convergence to its value in the limit of very large x . As shown in Fig. 5, displacement of some of the rotational states³ by $\Delta\phi=20^\circ$ was found to increase the characteristic ratio slightly for low values of p_r and to decrease it markedly for high values of p_r . Increase in ω from 0.00 to 0.05 at $\tau=0.5$ ²⁴ was found to decrease the characteristic ratio for all values of p_r , with the largest decrease occurring in the region of p_r approaching unity. Abe⁷ has used a similar model to obtain a limited number of calculated values of the characteristic ratio of styrene chains which, for reasons already cited, should pertain to *p*-chlorostyrene chains as well. The present

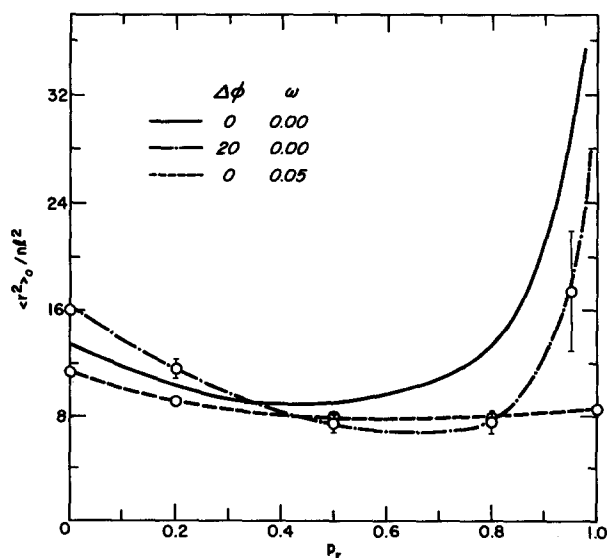


FIG. 5. The effect of $\Delta\phi$ and ω on the characteristic ratio of poly(*p*-chlorostyrene) chains of degree of polymerization 100; see text for details.

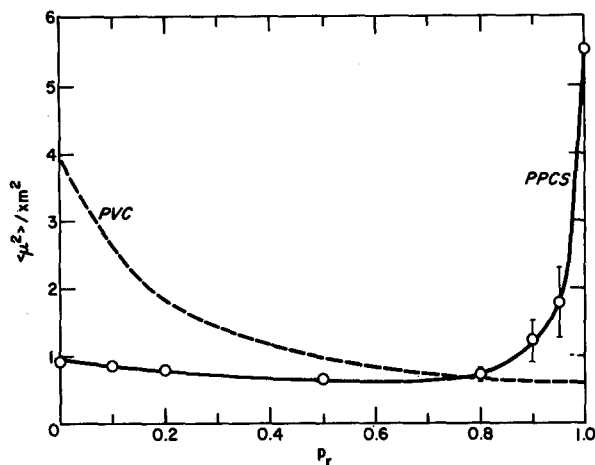


FIG. 6. The dipole-moment ratio for poly(*p*-chlorostyrene) chains and poly(vinyl chloride) chains having $x=100$, as a function the replication probability. In this figure and in Fig. 8, $\Delta\phi$ and ω have been restored to zero.

results are in excellent agreement with his results, which were obtained using $x=100$, $\eta=1.4$, $\Delta\phi=20^\circ$, and $\omega=0.01$. As expected, his results lie slightly below the curve in Fig. 5 corresponding to $x=100$, $\eta=1.6$, $\Delta\phi=20^\circ$, and $\omega=0.00$ except at values of p_r close to unity, where the assignment $\omega > 0.00$ causes a more marked decrease in the characteristic ratio. The dependence of the unperturbed dimensions on the statistical weight factors was calculated for PPCS chains at a temperature of 25° and a value of x of 100, for illustrative values of p_r , $\Delta\phi$, and ω . These results are shown in Columns 5-7 in the upper portion of Table I. Temperature coefficients of $\langle r^2 \rangle_0$, calculated in the usual manner,²⁵ are given in the last column of this portion of the table. Where approximate comparison of calculated values of the temperature coefficient of $\langle r^2 \rangle_0$ is possible, these results are in good agreement with those reported by Abe⁷ for polystyrene chains. The large negative values of this coefficient in the region of low p_r result of course from the fact that the lowest energy conformations in syndiotactic sequences, viz., *tt*, are also the most highly extended.

Figure 6 shows the dependence of the dipole-moment ratio on p_r for PPCS and PVC chains at a temperature of 25°, a value of $x=100$, and with $\Delta\phi$ and ω restored to zero. The relatively low value of this ratio for highly syndiotactic PPCS is due to the significant fraction of $(g^\pm g^\pm)(tt)(g^\pm g^\pm)$ sequences in such chains.⁵ As shown in Fig. 7, all-*trans* conformations would have large dipole moments; $(g^+ g^+)(tt)(g^+ g^+)$ sequences [and $(g^- g^-)(tt)(g^- g^-)$ sequences], however, would have almost zero dipole moments because of the near cancellation of neighboring pairs of group dipoles in such conformations. The high values of the dipole-moment ratio at large p_r are due to the fact that each group dipole in a helical sequence has a component pointing

TABLE I. The effect of the statistical weight factors and temperature on the mean-square unperturbed dimensions and dipole moments of poly(*p*-chlorostyrene).^a

$\langle V^2 \rangle$	$\Delta\phi$ (deg)	ω	p_r	$\partial \ln \langle V^2 \rangle / \partial \ln \eta$	$\partial \ln \langle V^2 \rangle / \partial \ln \tau$	$\partial \ln \langle V^2 \rangle / \partial \ln \omega$	$-10^3 d \ln \langle V^2 \rangle / dT$
$\langle r^2 \rangle_0$	0	0.00	0.0	0.960	3.78
			0.2	0.628	2.48
			0.5	0.346	1.36
			0.9	0.011	0.039
			1.0	0.000	0.000
	20	0.00	0.0	0.618	2.44
			0.2	0.476	1.87
			0.5	0.216	0.850
			0.9	0.001	0.005
			1.0	0.000	0.000
	0	0.05	0.0	0.894	-0.091	-0.118	4.92
			0.2	0.694	-0.052	-0.064	3.50
			0.5	0.410	-0.040	-0.104	2.75
			0.9	0.077	-0.065	-0.269	3.16
			1.0	0.019	-0.090	-0.367	3.97
$\langle \mu^2 \rangle$	0	0.00	0.0	1.80	7.09
			0.2	1.21	4.77
			0.5	0.512	2.02
			0.9	0.017	0.066
			1.0	0.000	0.000
	20	0.00	0.0	1.50	5.89
			0.2	1.07	4.23
			0.5	0.446	1.76
			0.9	0.007	0.027
			1.0	0.000	0.000
	0	0.05	0.0	1.51	0.015	-0.043	6.35
			0.2	1.00	0.009	-0.012	4.04
			0.5	0.556	0.003	0.011	2.07
			0.9	0.134	-0.033	-0.079	1.40
			1.0	0.090	-0.068	-0.155	2.07

^a Calculated for a degree of polymerization of 100, temperature of 25°C, and values of the statistical weight factors given in the text.

in the same direction along the helix axis, as is readily apparent from the examination of suitable models.

The dependence of the dipole-moment ratio of PPCS chains on the degree of polymerization is shown in Fig. 8. The rate of convergence of this ratio to its limiting value for large x is very similar to that shown by the characteristic ratio of these chains, at the same values of p_r . As shown in Fig. 9, increase in $\Delta\phi$ from 0° to 20° or increase in ω from 0.00 to 0.05 decreases the dipole-moment ratio, with the largest decrease being observed for the change in ω , in the region of large values of p_r . The dependence of $\langle \mu^2 \rangle$ on the statistical weight factors and on temperature are given in the lower portion of Table I. These coefficients are very similar to those obtained for $\langle r^2 \rangle_0$ because of the general correspondence, in these molecules, between high chain extension and large dipole moments.

COMPARISON OF THEORY AND EXPERIMENT

A number of experimental studies have been carried out on samples of PPCS prepared by free-radical polymerizations at temperatures in the vicinity of room temperature or higher; in the literature, such polymers are usually described as being "atactic," i.e., stereochemically random. Danusso and co-workers²⁶ have concluded from NMR measurements that a typical free-radically prepared polymer of styrene is indeed essentially random in its stereochemical structure. Bywater and co-workers²⁷ and Bovey and co-workers^{28,29} have obtained NMR results, however, that have led them to the contrary conclusion that an "atactic" styrene polymer is predominantly syndiotactic in structure, with the specific suggestion²⁸ that a replication probability p_r of ~ 0.2 is appropriate for such

chains. Pending resolution of this disagreement, one is apparently limited to the general statement that the value of p_r characterizing "atactic" styrene chains almost certainly lies in the range 0.2–0.5. In lieu of better information, we adopt this interval as appropriate for free-radically prepared PPCS as well. Fortunately, as shown in Figs. 3 and 6, the characteristic ratio and dipole-moment ratio of PPCS chains are not strongly dependent on p_r over this range of values. In addition, Figs. 4 and 8 indicate that the characteristic ratio and dipole-moment ratio for PPCS chains having stereochemical compositions in this interval are relatively insensitive to x for values of x exceeding approximately 50 and 20, respectively. Thus, since experimental results pertinent to the present study have been carried out on high-molecular-weight PPCS, the limiting values of these ratios, estimated from calculations using $x = 100$, will be used in the comparison of theory with experiment.

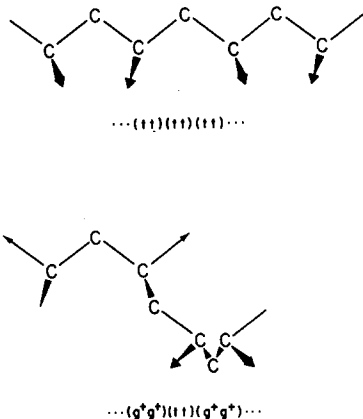


FIG. 7. Locations of the chain backbone and group dipoles in the low-energy conformations of a syndiotactic (*dl*) sequence in poly(*p*-chlorostyrene).

There is only one study^{15,30} reporting measurements on PPCS chains in a system at the Θ condition, i.e., the condition under which the effect of long-range interactions on the chain dimensions is nullified.³¹ Since these data¹⁵ show a great deal of scatter, the value of the characteristic ratio, 11.8, obtained from this study cannot be considered definitive. One must therefore also resort to results obtained by approximate correction³² for such interactions in the interpretation of viscosities measured in solvents lacking this characteristic. Use of a value of the hydrodynamic constant of $\Phi \approx 2.5 \times 10^{21}$ in the interpretation of such data in the vicinity of 25° yields values of the characteristic ratio for PPCS of 10.1,^{12,13,16} 10.6,¹⁴ and 11.2¹⁷; the average 10.6 (± 0.6) of all the experimental values is in good agreement with the range 10.3 to 9.0 indicated by theory for this temperature and for $p_r = 0.2$ to 0.5. It is perhaps appropriate to specify here the origin of the values of the characteristic ratio quoted for several other substituted styrene polymers in the preceding

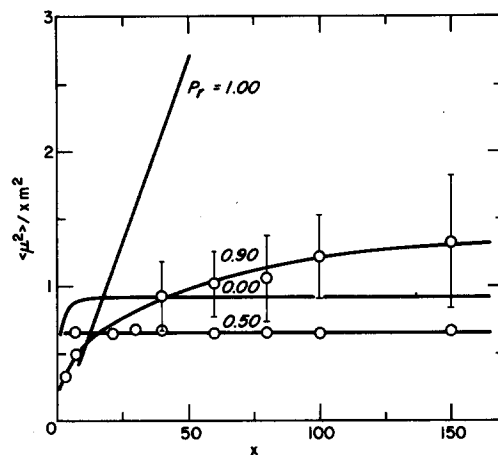


FIG. 8. The dependence of the dipole-moment ratio on degree of polymerization for poly(*p*-chlorostyrene) chains.

section. Measurements on solutions of poly(*p*-bromostyrene) and poly(*p*-methylstyrene) at their respective Θ points gave values of the characteristic ratio of 13.4¹⁹ and 10.8,²⁰ respectively. Approximate values of the ratio for these two polymers from results not obtained under Θ conditions are 11.2¹⁷ and 10.6,¹⁴ respectively. In the case of poly(*p*-cyclohexylstyrene), apparently only the result obtained by the approximate methods, a value of the characteristic ratio of 13.7,²¹ is available at the present time.

There is a larger amount of experimental data appropriate for calculating reliable values of the dipole-moment ratio, since the absence of any effect of long-range interactions on $\langle \mu^2 \rangle$ permits the use of dielectric constant measurements on the polymer in any nonpolar solvent. When necessary, such experimental results were corrected to 25° by means of $d \ln \langle \mu^2 \rangle / dT =$

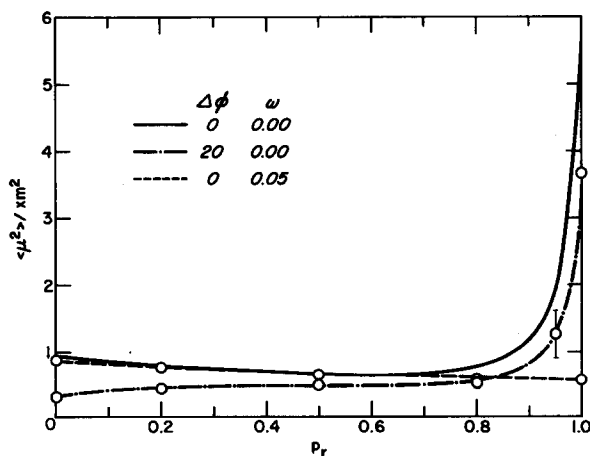


FIG. 9. The effect of $\Delta\phi$ and ω on the dipole-moment ratio of poly(*p*-chlorostyrene) chains having a degree of polymerization of 100.

$-3 \times 10^{-3} \text{ deg}^{-1}$, a value chosen from the entries in Table I. Values of the dipole moment ratio thus obtained are 0.53,³³ 0.55,²³ 0.60,^{34,35} 0.71,^{23,36} 0.74,³⁷ 0.77,²³ and 0.80.^{38,39} The average of these results, 0.68 (± 0.10), is in good agreement with the range 0.80–0.65 calculated for $p_r = 0.2$ –0.5. The most detailed study²³ of the dipole moments of PPCS reports a number of unexpected results which have not yet, however, been verified. In this study, the dipole-moment ratio is reported to be 0.77 and 0.71 when measured in toluene and *p*-xylene, respectively, but 0.55 when measured in isopropylbenzene. Since these solvents are very similar in dielectric constant⁴⁰ and chemical structure, this strong solvent effect is very difficult to understand. The temperature coefficient of $\langle \mu^2 \rangle$ was also reported²³ to be highly unusual in the two solvents, toluene and isopropylbenzene, in which it was determined. These results suggest a value of $d \ln \langle \mu^2 \rangle / dT$ of approximately $-4 \times 10^{-3} \text{ deg}^{-1}$ for the approximate range 10–60°. This value is in good agreement with the value $-5 \times 10^{-3} \text{ deg}^{-1}$ obtained by Stockmayer and co-workers³⁹ from measurements in benzene and in carbon tetrachloride over approximately the same temperature range, and it is in excellent agreement with the range -5 to $-3 \times 10^{-3} \text{ deg}^{-1}$ calculated for this temperature interval and for $p_r = 0.2$ –0.5. Over the approximate temperature range 60–100°, however, a *positive* temperature coefficient of approximately $4 \times 10^{-3} \text{ deg}^{-1}$ is reported,²³ in very poor agreement with the range -2 to $-1 \times 10^{-3} \text{ deg}^{-1}$ predicted by theory. Since the reported²³ marked solvent dependence of the dipole-moment ratio and its highly unusual temperature dependence would seem to be inexplicable in terms of the present theories of chain configuration, further experimental investigations would obviously be of considerable importance.

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