Local Solvent Effects on Configurational Characteristics of Polymer Chains: Poly(*p*-chlorostyrene) in Benzene

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ABSTRACT: The effect of solvent on the configurational characteristics of the polymeric chain is studied for the poly(*p*-chlorostyrene)–benzene system. Among all possible configurations of benzene around the chain unit, two configurations, referred to as the parallel and perpendicular configurations, are found to lead to the lowest energy of interaction. The potential prevailing at the parallel configuration is calculated to be more favorable by 1.2 kcal/mol. Depending on the relative occurrence of these two competing configurations, new energy values are assigned to each rotational isomeric state of the chain structural unit. Configuration-dependent properties such as characteristic ratio, dipole ratio, and their temperature dependence are computed. The reduction in the dipole moment induced by the coupling of benzene with the chlorophenyl group is also included in the calculations. In general, satisfactory agreement with previous experimental measurements is achieved except for the positive temperature coefficient of dipole ratio reported at high temperature.

Introduction

Rotational isomeric state (RIS) theory has proved to be a powerful tool for calculating configuration-dependent properties of polymeric chains.[1-3] During the past two decades, extensive work has been carried out on determining and/or explaining physical properties of macromolecules in terms of the RIS approach and the related matrix generation techniques.[3,4]

In general, rotational isomeric states are identified with the minima of the conformational energy maps. Although higher accuracy may be attained by increasing the number of isomeric states, adoption of a smaller number of rotational isomeric states may equally lead to plausible results.[4,5] Particularly in vinyl chains with large planar substituents, such as poly(methyl methacrylate) and polystyrene, a two-state scheme is sufficient to reproduce the conformational characteristics of the chain.[5-7] In those chains, the gauche–bar ($\bar{g}$) configuration[5] is suppressed due to severe steric overlap between the substituents and the groups bonded to the adjacent α carbon atoms. Accordingly, two states, trans (t) and gauche (g) are considered.

The location and relative weights of the isomeric states are determined from energy considerations between near neighbors along the chain; the evaluated properties are, thus, valid for chains where no perturbation effects due to long-range interactions occur, i.e., for chains under θ conditions. Such chains with only short-range interferences are referred to as ideal or unperturbed chains.[3] In general, good agreement between experiment and theory has been obtained, confirming the hypothesis that the local intramolecular interaction is the main factor governing the conformational statistics of ideal chains. The local polymer–solvent interaction, another short-range effect, may be neglected if no discernible discrimination between conformations occurs, as in the case of symmetric chains. However, in the case of asymmetric chains with bulky side groups, local conformational characteristics are considerably affected by this so-called "specific solvent effect". This situation arises from the fact that the side-group interaction with the solvent molecule differs depending on the configuration of the skeletal bonds. In general, side groups attached to bonds in the gauche (g) state are more readily accessible to favorable interaction with the solvent molecules compared to those belonging to a trans sequence. Consequently, the net effect of solvent molecules is to increase the probability of occurrence of gauche bonds, provided that the side group–solvent interaction is favorable. This effect was incorporated into the conventional RIS model through adoption of a truncation procedure involving an adjustable parameter σ:[6-8] the Lennard-Jones potential between pairs of atoms i and j was assumed to remain constant and equal to its value at the interatomic spacing $r_{ij} = \sigma$, for all $r_{ij} > \sigma$. Clearly, in the absence of solvent–polymer interactions, $\sigma = \infty$. As a rough approximation, Brant and Flory[8] took σ to be the sum of the van der Waals radii of the interacting atoms. In later works,[6,7] trial values such as 3.9, 5, and 7 Å were assigned to σ. Although the energy values were considerably altered due to the introduction of the parameter σ, the shapes of the minima were found to be comparatively insensitive to the value of σ selected.[6,7] Agreement with experiment was achieved upon further adjustments of the newly obtained energy values.

In this work, the polymer–solvent interaction is calculated without recourse to adjustable parameters for the poly(*p*-chlorostyrene) (PPCS)–benzene system. The assumptions and major features of the model used in calculations are described in the second section. In the third section results of numerical calculations for the system under investigation (PPCS–C_6H_6) are presented. The adaptation of the obtained solvent–polymer energy values to the RIS scheme and results from analytical calculations are given in the fourth section. The last section will be reserved for the discussion of the results from the calculations and comparison with related experimental data.

Model

We consider a system of a single vinyl chain comprising n skeletal bonds, or $x = n/2$ structural units, surrounded by N solvent molecules in a coordinate system whose center coincides with an arbitrarily chosen atom of the chain. The chain may be denoted by $(CH_2)_1\cdots(C^{\alpha}HR)_i$-$(CH_2)_{i+1}\cdots(C^{\alpha}HR)_n$, where R indicates the substituted group. The solvent molecules are assumed to be rigid, not necessarily spherically symmetric. The spatial configuration of the jth solvent molecule is, then, specified by $(\mathbf{S}, \alpha, \beta, \gamma)_j$, where $\mathbf{S}$ is the vector from the center of the coordinate system to the jth solvent molecule and α, β, and γ are the three Euler angles representing the orientation of the solvent molecule. Consequently, the set $\{\mathbf{S}, \alpha, \beta, \gamma\}$

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including all $(\mathbf{S}, \alpha, \beta, \gamma)_j$, for $j = 1$–N, fully determines the spatial configuration of the N solvent molecules. On the other hand, with the assumption that valence angles and bond lengths are fixed, the configuration of the polymer is completely specified by the set $\{\phi\} = \{\phi_1, \phi_2, ..., \phi_n\}$, where ϕ_i is the angle of rotation of the ith skeletal bond.

For a given configuration, three terms contribute, additively, to the potential of the system:[9] (i) the intramolecular interaction between various segments of the molecule, which is a function of $\{\phi\}$, (ii) the solvent–polymer interaction, depending on both $\{\phi\}$ and $\{\mathbf{S}, \alpha, \beta, \gamma\}$, and (iii) the solvent–solvent interaction, which is a function of $\{\mathbf{S}, \alpha, \beta, \gamma\}$. The latter has no direct influence on the chain configurational statistics and will be neglected. We shall concentrate mainly on interactions of type (i) and (ii).

An important simplification in the RIS scheme is that the configuration of each bond is determined from the potential of interaction solely between near neighbors along the chain. More precisely, it is sufficient to consider the possible rotations of two consecutive bonds and the groups or atoms attached to them in order to establish the conformational statistical weights. Interactions between elements that are farther apart are neglected in view of the fact that those interactions vanish rapidly as the interactomic spacing increases. Also the excluded volume effect is ignored in ideal chains. Denoting the intramolecular interaction between atoms associated with the ith and $(i + 1)$th skeletal bonds by E_i, we have $E_i = E_i(\phi_i,\phi_{i+1})$.

A similar approach may be applied to polymer–solvent interaction as well. Instead of considering the whole chain with the total of N solvent molecules, the interaction of one structural unit with a solvent molecule, only, may be examined. When it is noted, moreover, that the substituent and not the whole structural unit is the element responsible for changes in interaction with solvent, depending on the conformations of the backbone, calculations may be reduced to the computation of the allowable coupling of the bulky side group–solvent pair as a function of the backbone structure. The solvent molecule is, then, assumed to be fixed at a configuration that engenders the lowest energy of interaction with the substituent, provided that this configuration is not precluded by steric hindrances due to nearest hydrogen and/or carbon atoms on the chain. Considering a single solvent molecule interacting with the side group instead of many solvent molecules surrounding the repeat unit is not expected to bring significant error into calculations, since the main factor responsible for perturbing conformational energy surfaces seems to be the degree of coupling of the solvent molecule under consideration with the bulky side group. In the absence of the side group, for example, in the case of symmetric chains, neglecting the local effect of surrounding dense solvent medium, i.e., treating the chain as an isolated molecule, has proved to be a valid approach.[3,4] The modification introduced by this model aims to include the local solvent effect, as a first-order approximation, into calculations along the lines initiated by Flory and collaborators.

At that point an important simplification may be formulated, as follows: the specific solvent effect is not strong enough to create new rotational isomeric states but perturbs the potential energy of the already existing (in the absence of solvent) isomeric states; i.e., the location of the energy minima are the same, but their magnitudes are changed depending on the solvent–polymer interaction prevailing at that state. Consequently, the most stable conformations are again the isomeric states dictated by short-range intramolecular interactions while their relative probabilities of occurrence are modified by the action of solvent. Treatment of polymer–solvent interaction is greatly simplified by this assumption. Accordingly, it is sufficient to consider, separately, the possible isomeric states of the structural unit and to investigate, for each fixed state, the interaction of the side group and the nearest hydrogen or carbon atoms with the solvent as a function of solvent location and orientation represented by the variables $(\mathbf{S}, \alpha, \beta, \gamma)$. Upon addition of the computed energy values to $E_i(\phi_i,\phi_{i+1})$, where ϕ_i and ϕ_{i+1} are now characteristics of isomeric states, the total potential affecting the local configuration of the chain is obtainable.

Table I
Conformational Energies at 300 K for the Respective Conformations of the Diad[a]

state, ξ	E_ξ, kcal/mol	$\langle E_\xi \rangle$, kcal/mol	$E_{\text{polym-solv}}$, kcal/mol	E_{tot}, kcal/mol
meso, *tt*	0.75	0.91	0.45	1.20
meso, *tg*	1.10	1.17	−0.68	0.42
meso, *gg*	4.35	4.17	−0.68	3.67
racemic, *tt*	0.00	0.00	0.00	0.00
racemic, *tg*	3.45	3.50	−0.68	2.77
racemic, *gg*	2.45	2.48	−0.68	1.77

[a] All values are expressed relative to the racemic, *tt* state.

The application of the above concepts to the PPCS–benzene system will be illustrated in the next section.

PPCS–Benzene System

Short-Range Intramolecular Interaction. Mark and co-workers[10,11] calculated dipole moments of the PPCS chain by making use of the conformational energies of polystyrene (PS) chains and pointing out that para substitution with Cl instead of H has little influence upon the configurational characteristics. Calculations performed in the present work justify their approach: the newly obtained energy maps for PPCS are not reproduced here, as they are very similar to those obtained by Yoon, Sundararajan, and Flory[7] for PS in the absence of solvent. The calculated energies E_ξ, corresponding to the state ξ, for meso and racemic diads[3,5] are presented in the second column of Table I. The energy values in the third column were obtained, for $\sigma = \infty$, by Yoon et al.[7] Results are expressed relative to the racemic, state, the conformation that is subject to the lowest interaction. The reduction of the energy value corresponding to the meso, tt diad of PPCS by 0.15 kcal/mol compared to that of PS arises from the slightly higher attraction of Cl atoms compared to H atoms additioned by a small but favorable electrostatic interaction.

According to the two-state scheme, where the $\bar{g}$ configuration is suppressed, the statistical weight matrices are given by

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \qquad (1)$$

for the pair of bonds flanking the substituted carbon C^α and

$$\mathbf{U}'' = \begin{bmatrix} z_{tt} & z_{tg} \\ z_{gt} & z_{gg} \end{bmatrix} \qquad (2)$$

for the pair of bonds within meso or racemic diads.[6,7] The elements of $\mathbf{U}''$ are the partition functions z_ξ evaluated by the Simpson integration[6,7] of the Boltzmann factors over the conformational domains ξ. In accordance with previous definitions

$$z_\xi = \alpha_\xi \exp\{-\langle E_\xi \rangle / RT\} \qquad (3)$$

where α_ξ is the preexponential factor that is a measure of the relative width of energy minima, T is the absolute temperature, R is the gas constant, and $\langle E_\xi \rangle$ is the average energy value corresponding to state ξ. In agreement with our assumption that the shapes of the minima are unaffected by the solvent effect, the values α_ξ obtained by Yoon et al.[7] will be adopted without modification in our calculations. This assumption is in conformity with the assertion by Yoon, Sundararajan, and Flory[7] that the locations of the minima in conformational energy surfaces are little affected by allowance for solvent–polymer interaction, through the parameter σ. However, the relative occurrence of these stable conformations does depend on the solvent. Thus, $\langle E_\xi \rangle$ values will be calculated rigorously by computing the contribution of the solvent–polymer interaction at each rotational state. Also, experiments carried out with isotactic polystyrene (iPS) gels[12] indicate that both threefold helical and extended conformations are possible, their proportion depending on the type of solvent used to induce crystallization. In general, the perpetuation of the extended conformation, which is characterized by a helix containing 12 monomers in the tt state, is expected to occur if an intramolecular phenyl–phenyl interaction is preferred over a phenyl–solvent interaction. Conversely, the threefold helical conformation, generated by tg sequences where the side groups are accessible to important interaction with solvent, is expected to occur in profusion in solvents leading to favorable interaction with the side group.[12]

An alternate approach employs the statistical weight matrices

$$\mathbf{U}_m'' = \begin{bmatrix} w'' & 1/\eta \\ 1/\eta & w/\eta^2 \end{bmatrix} \tag{4}$$

and

$$\mathbf{U}_r'' = \begin{bmatrix} 1 & w'/\eta \\ w'/\eta & 1/\eta^2 \end{bmatrix}$$

for meso and racemic diads, respectively. η denotes the first-order parameter expressing the statistical weight of trans relative to gauche state; w, w', and w'' express the second-order interaction between $CH_2 \cdots CH_2$, $CH_2 \cdots C_6H_5$, and $C_6H_5 \cdots C_6H_5$ pairs, respectively. They are represented in good approximation by[7]

$$w = w' = 1.3 \exp\{-1000/T\} \tag{6}$$

$$w'' = 1.8 \exp\{-E_{w''}/RT\} \tag{7}$$

$$\eta = 0.8 \exp\{-E_\eta/RT\} \tag{8}$$

Substitution of eq 7 and 8 into eq 4 and comparison of eq 4 with eq 2 and 3 identify the energies $E_{w''}$ and E_η as $\langle E_{tt} \rangle$ and $-\langle E_{tg} \rangle$ of the meso diad, respectively. A careful examination of the energy values in Table I reveals the fact that the above two values are the most important variables governing the configurational statistics of PPCS. This is a natural consequence of the low probability of the occurrence of the remaining rotational states (meso, gg; racemic, tg; racemic, gg) associated with their relatively high energy values. Consequently, the correct numerical evaluation of $\langle E_{tt} \rangle_{\text{meso}}$ and $\langle E_{tg} \rangle_{\text{meso}}$ (or alternately E_η and $E_{w''}$) is critically important in the treatment of configuration-dependent properties of PPCS.

In previous work,[7] these values were optimized to achieve best agreement with experiments. The range of optimization was determined with the aid of the adjustable parameter σ, accounting for the local solvent effect. In the present work, the estimation of the energy values will be carried out on the basis of numerical calculations involving solvent–polymer interaction at each rotational state. Various values are reported for the precise location of the minima in conformational energy maps, particularly for the case of the meso, tt diad; Yoon et al. calculated[7] that rotational angles of 22° are required to relieve the severe steric overlap of neighboring side groups. However, in view of the extended conformation X-ray pattern observed by Atkins et al.,[12] Corradini and co-workers proposed[13] a four-atom helix model with successive dihedral angles of the form $(\phi_i, \phi_{i+1}, \phi_{i+2}, \phi_{i+3}) \approx (5°, 15°, 25°, 25°)$. Sundararajan interpreted the same phenomenon on the basis of enlarged tetrahedral angles assigned to skeletal bonds.[14] For the purposes of the present study, geometrical parameters calculated by Yoon et al.[7] approximating the above values will be adopted.

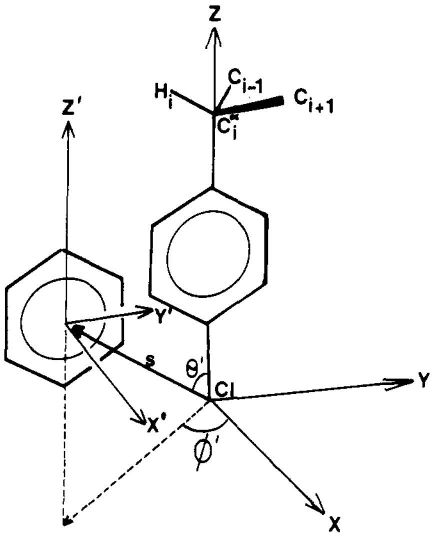

Figure 1. Chlorophenyl group and benzene fixed in the coordinate systems XYZ and $X'Y'Z'$, respectively. Initially, the spatial orientation of the two frames are the same. Benzene assumes various configurations with respect to the chlorophenyl ring by virtue of the mobility of the $X'Y'Z'$ frame.

Local Solvent–Polymer Interaction. In accordance with the above arguments, the interaction of an arbitrary p-chlorostyrene unit with a benzene molecule will be considered. The diad is composed of the $(i + 1)$ and $(i + 2)$th skeletal bonds and the atoms or groups attached therein. We let the para-substituted Cl atom belonging to R_i coincide with the center of the Cartesian coordinate system XYZ, as shown in Figure 1. The chlorophenyl ring lies in the YZ plane. The chlorophenyl ring, the neighbor H_i atom and the $(i + 1)$th skeletal bond joining C_i^α to C_{i+1} are held fixed in coordinate system XYZ. The coordinates of $(H_2)_{i+1}$ and $(CHR)_{i+2}$ will vary depending on the rotational angles ϕ_{i+1} and ϕ_{i+2}.

The benzene molecule is located in a second coordinate system $X'Y'Z'$, whose axes are initially parallel to those of the frame XYZ. We let $\mathbf{S}$ be the vector joining the centers of the two reference frames from XYZ to $X'Y'Z'$. $\mathbf{S}$ is expressed in spherical coordinates in terms of S, θ', and ϕ', where θ' is the angle it makes with the Z axis and ϕ' is the angle its projection on the XY plane makes with the X axis. The benzene molecule lies in the $Y'Z'$ plane, with its center coinciding with that of the coordinate system $X'Y'Z'$. The reference frame XYZ is stationary while the second one, $X'Y'Z'$, may translate or rotate with the benzene molecule fixed in it. The passage from $X'Y'Z'$ to XYZ is done through an appropriate transformation matrix $\mathbf{T}$, involving the Euler angles α, β, and γ. We define α, β, and γ as follows: α denotes an initial right-handed rotation of the system $X'Y'Z'$ about the Z' axis; a subse-

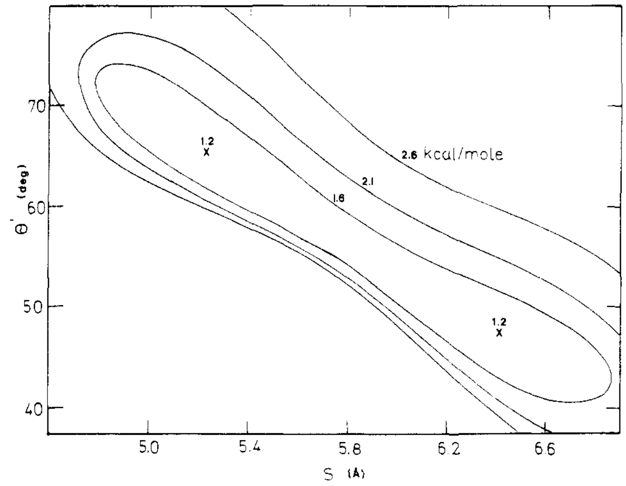

Figure 2. Conformational energy contours as a function of S and θ' for perpendicular configuration of benzene about the meso, *tt* state of the diad. The energy values are expressed relative to the minimum value of the interaction energy of parallel configuration in the meso, *tg* state. (See the caption to Figure 3.)

quent right-handed rotation about the newly obtained x axis by an angle β is followed by another right-handed rotation, by an angle γ about the final z axis. Calculations of interaction energies have shown that only two configurations of the benzene molecule around the chlorophenyl group need be considered. The first configuration, which we refer to as the "parallel configuration", is obtained when the two rings are parallel to each other, characterized by $\phi' = 0$ or π and $\alpha = \beta = \gamma = 0$. The second configuration, called "the perpendicular configuration", takes place when $\phi' = \pm\pi/2$, $\alpha = \pi/2$, and $\beta = \gamma = 0$. In subsequent calculations, the problem is reduced to the determination of the parameters S and θ' that minimizes the energy of interaction. Interactions will be computed with the Lennard-Jones function, $E_{ij} = (a_{ij}/r_{ij}^{12}) - (b_{ij}/r_{ij}^{6})$, for each pair of interacting atoms. Parameters a_{ij} and b_{ij} are assigned in the manner previously described.[3,7,12]

For the Cl atom, the constant b_{ij} was evaluated from the Slater–Kirkwood formula[15] using the atomic polarizability $\alpha = 2.28$ Å^3 taken from Ketelaar,[16] with an effective number of electrons N_e of 12, estimated from the electronic distribution of Cl atom. The van der Waals radius of Cl was taken to be 1.8 Å.[16] The constant a_{ij} was determined, as usual, by mimimizing E_{ij} when r_{ij} is set equal to the sum of the van der Waals radii of the interacting pair.

In agreement with the arguments presented above, we proceed now to the analysis of individual rotational states. We consider, first, the meso, *tt* conformation. The proximity of the consecutive chlorophenyl groups R_i and R_{i+2}, in this conformation, does not allow the access of benzene molecule in between, due to the violation of the van der Waals radii (1.95 Å) of aromatic carbon atoms. Consequently the benzene molecule cannot assume the parallel configuration unless its location is sufficiently distant from the backbone. The latter configuration, where the benzene molecule eventually interacts with two successive side groups of the meso, *tt* diad, was calculated to lead to an energy of interaction of about −1 kcal/mol per chlorophenyl group. Subsequent calculations show that this interaction, though energetically favorable, is not as stable as those considered below. Consequently, no significant change in average energy values and particularly in the evaluated configuration-dependent properties (such as the characteristic ratio, dipole ratio, and their temperature coefficients) is brought about by dismissing this type of parallel alignment of benzene.

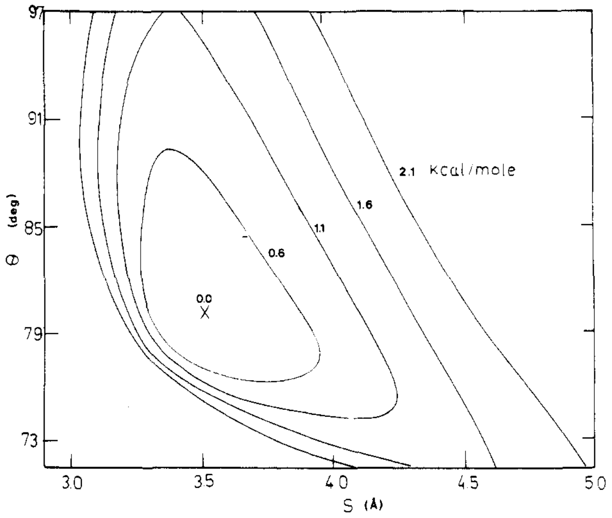

Figure 3. Conformational energy contours for the parallel configuration of benzene about the meso, *tg* state of the diad. The minimum energy at $S = 3.50$ Å and $\theta' = 80°$ is set equal to zero.

As to the perpendicular configuration, the exact location of benzene is determined from the energy contours constructed by varying the parameters S and θ', as shown in Figure 2. Calculations showed that energy maps were similar for the perpendicular configuration regardless of the conformational state of the diad; hence only the map corresponding to meso, *tt* is reproduced in Figure 2. The quoted energy values are representative of the interaction of benzene with $(C^{\alpha}HR)_i$ and are expressed relative to the minimum of the parallel configuration. Two minima corresponding to $(S, \theta') = (5.23$ Å, $65°)$ and $(6.40$ Å, $45°)$ are discernible, with respective absolute energy values $E = -3.39$ and -3.41 kcal/mol. The average value $E = -3.4$ kcal/mol is adopted in subsequent calculations.

We consider, now, the meso, *tg* conformation. Both parallel and perpendicular configurations are accessible to benzene. The geometrical parameters corresponding to the perpendicular configuration are already known. The parallel configuration will be treated as follows: suppose the benzene molecule is placed at the same height as the chlorophenyl group R_i, at a distance corresponding to the lowest energy of interaction. Under this configuration, the hydrogen atom that is closest to the skeletal bonds of the diad is subject to severe steric repulsion from H_{i+2} and C_{i+2} as their respective separations exceeds the sum of the van der Waals radii. Consequently the benzene molecule is expected to be pushed slightly away from the backbone, keeping however its parallel configuration with respect to the chlorophenyl group. These predictions are confirmed by calculations; the geometrical parameters leading to the most favorable interaction are found to be $(S, \theta') = (3.50$ Å, $80°)$ as shown in Figure 3. At that state, $E = -4.55$ kcal/mol.[17] This value includes the interaction of $(C^{\alpha}H)_{i+2}$ with benzene, in addition to that of R_i. If we consider, now, the coupling of benzene with R_{i+2}, instead of R_i for the same diad (meso, tg), the interaction with $(CH_2)_{i+1}$ comes into play. Similar calculations yield $E = -4.68$ kcal/mol at $S = 3.60$ Å and $\theta' = 74°$. On the basis of the above explanations the average value $E = -4.62$ kcal/mol may be accepted to be representative of the benzene–chlorophenyl interaction in parallel configuration. In Figures 2 and 3 all energy values are expressed relative to this minimum.

As stated in the preceding section the chain statistics are little affected by the polymer–solvent energy values corresponding to meso; *gg*, racemic; *tg*, and racemic; *gg* states, due to the relatively high intramolecular interaction caused by these conformations. Consequently the exact evaluation of the solvent–polymer interaction in those states is immaterial, inasmuch as their relative probabilities are substantially smaller than unity. Besides, the degree of exposure of the chlorophenyl group to benzene, in those states, is almost the same as that of meso, *tg* state. Accordingly, the already calculated energy values in meso, *tg* for the two competing conformations, the perpendicular and the parallel one, are equally applicable to those states.

The parallel configuration for the racemic diad with *tt* conformation deserves special attention. Suppose, for instance, the benzene molecule assumes its parallel configuration with respect to R_i. At a first glance, no factor apart from H_{i+2} may appear to be limiting the access of benzene to that configuration. But if the adjacent $(i + 3)$th skeletal bond is in *t* state, a strong steric overlap between benzene and the $(C^{\alpha}HR)_{i+4}$ group is created, which precludes the occurrence of the parallel configuration. This type of second-order interaction between benzene in parallel configuration and $C^{\alpha}HR$ groups adjacent to the diad was eliminated when at least one of the bonds of the diad was in *g* state. But in the case of the racemic, *tt* diad, the state of the adjoining bonds, $(i - 1)$ and $(i + 3)$ has to be considered. From eq 1 the conditional probability of occurrence of a *tt* state for a pair of bonds flanking an α carbon, given that one of them is in the *t* state, is calculated to be 0.62 by similarity transformation.[3] By making use of that value, we can conclude that the parallel configuration is precluded with about 60% a priori probability. Otherwise, the two configurations (parallel and perpendicular) are probable, in conformity with their respective Boltzmann factors.

On the basis of the above computations, average energy values for the solvent–polymer interaction are assigned to each state. For cases where both parallel and perpendicular configurations are possible, average values are obtained by weighting with the respective Boltzmann factors. The calculated values, normalized to the racemic, *tt* state, are listed in the fourth column of Table I. The fifth column is obtained by summing the values in the second and fourth columns and gives the total energy of interaction governing local statistics.

Calculation of Configuration-Dependent Properties

Characteristic Ratio. The characteristic ratio, $C_n = \langle r^2 \rangle_0 / nl^2$ was calculated according to conventional matrix generation techniques.[3,4] For vinyl chains, the unperturbed mean-square length of the chain vector, $\langle r^2 \rangle_0$, is computed from

$$\langle r^2 \rangle_0 = Z^{-1} \mathcal{G}_0 \{ \prod_{k=1}^{x-1} \mathcal{U}' \mathcal{G}_k \} \mathcal{G}_x \tag{9}$$

where Z is the configurational partition function given by

$$Z = \mathbf{U}_0 \{ \prod_{k=1}^{x-1} \mathbf{U}_k' \mathbf{U}_k'' \} \mathbf{U}_x \tag{10}$$

and, adopting procedures previously described,[7,12] the generator matrices $\mathcal{U}'$ and $\mathcal{G}_k$ are defined by

$$\mathcal{U}' = \mathbf{U}' \otimes \mathbf{E}_5 \tag{11}$$

$$\mathcal{G}_k = \begin{bmatrix} \mathbf{G}_t & \mathbf{0} \\ \mathbf{0} & \mathbf{G}_g' \end{bmatrix} (\mathbf{U}_k'' \otimes \mathbf{E}_5) \begin{bmatrix} \mathbf{G}_t'' & \mathbf{0} \\ \mathbf{0} & \mathbf{G}_g'' \end{bmatrix} \tag{12}$$

where $\mathbf{E}_5$ is the identity of order five, $\otimes$ denotes the direct product, and $\mathbf{G}'$ and $\mathbf{G}''$ are the generator matrices for the first and second bond, respectively, of the *k*th diad. Depending on the stereochemical structure of the *k*th diad, either $\mathbf{U}_m''$ or $\mathbf{U}_r''$ are used for $\mathbf{U}_k''$ in eq 10 and 12. The elements of $\mathbf{U}_k''$ are calculated from the total energy values given in the fifth column of Table I by using either eq 4–8 or the more rigorous procedure utilizing eq 2 and 3. Both approaches lead to almost equivalent results for $\mathbf{U}''$, as expected. The terminal matrices $\mathcal{G}_0$, $\mathcal{G}_k$, $\mathbf{U}_0$, and $\mathbf{U}_x$ retain their previous definitions.[7]

The generator matrix $\mathbf{G}$ for bond j is given by

$$\mathbf{G} = \begin{bmatrix} 1 & 2\mathbf{l}^T\mathbf{T} & \mathbf{l}^2 \\ \mathbf{0} & \mathbf{T} & \mathbf{l} \\ 0 & \mathbf{0} & 1 \end{bmatrix}_j \tag{13}$$

where $\mathbf{l}_j$ and $\mathbf{l}_j^T$ are the bond vector and its transpose, respectively, $\mathbf{T}_j$ is the transformation relating the coordinate system for bond $(j + 1)$ to that for bond j.[3] Following prescriptions assigned for the bond-based coordinate system,[5] the generator matrices for meso and racemic diads are

$$\begin{aligned} \mathbf{G}_m' &= \mathbf{G}(\mathbf{T}^{*\prime}) \\ \mathbf{G}_r' &= \mathbf{G}(\mathbf{T}') \\ \mathbf{G}_m' &= \mathbf{G}(\mathbf{T}^{*\prime\prime}) \\ \mathbf{G}_r' &= \mathbf{G}(\mathbf{T}^{*\prime\prime}) \end{aligned} \tag{14}$$

where $\mathbf{T}$ is the conventional transformation matrix operating between two right-handed coordinates[3] and $\mathbf{T}^* = \mathbf{T}$ diag (1, 1, −1).[3,5] The primes indicate the pair of bonds on which the transformation matrices operate. The averaged rotational angles listed in Table I of ref 11, together with the supplemental angles $\theta' = 66$ and $\theta'' = 68$, were used in the transformation matrices.

Monte Carlo chains of $x = 100$ units with Bernoullian distribution of meso and racemic diads were generated. The atactic chain is expected[7,11] to fall within the range $0.3 < w_m < 0.5$, where w_m is the fraction of meso diads within the chain. The characteristic ratios computed for $w_m = 0.3$ and 0.5 at 300 K are $C_\infty = 11.59$ and 8.71, respectively; the corresponding temperature coefficients are found to be $d \ln C_\infty / dT = -0.68 \times 10^{-3}$ deg^{-1} and -0.84×10^{-3} deg^{-1}, respectively.

Dipole Moment Ratios. The dipole moment ratio is defined as $D_\infty \equiv \lim_{x \to \infty} \langle \mu_x^2 \rangle / (x \mu_0^2)$, where $\langle \mu_x^2 \rangle$ is the mean-squared dipole moment of the chain and μ_0 is the dipole of the structural unit. The computation of $\langle \mu_x^2 \rangle$ is analogous to that of $\langle r^2 \rangle_0$. It is sufficient to replace the bond vector $\mathbf{l}_j$ in $\mathbf{G}'$ by μ_j, where μ_j is the dipole moment vector attached to R_{j-1} but expressed in the *j*th reference frame. Due to the absence of a polar group fixed in the frame of the successive bond, the generator matrix $\mathbf{G}''$ is used with the zero vector replacing the bond vector. The computed dipole ratio is a dimensionless quantity, independent of μ_0. However, it is strongly dependent on the orientation of μ_j.

In addition to the specific solvent effect influencing local conformational statistics, dipole induction associated with the polarizability of benzene was considered as another factor affecting the experimentally observed $\langle \mu_x^2 \rangle$. The dipole moment induced by a charge e on a polarizable bond with polarizability tensor α is[18]

$$\mu^* = e \alpha \mathbf{S} / S^3 \tag{15}$$

where $\mathbf{S}$ is the vector pointing from the charge to the center of the bond. The total induced moment corresponding to a given state was evaluated by assigning partial charges to the Cl and C atoms of the C–Cl bond and summing the vectors μ^* resulting from the electrostatic interaction with each of the C–C and C–H bonds of benzene. The bond polarizability tensors were taken from

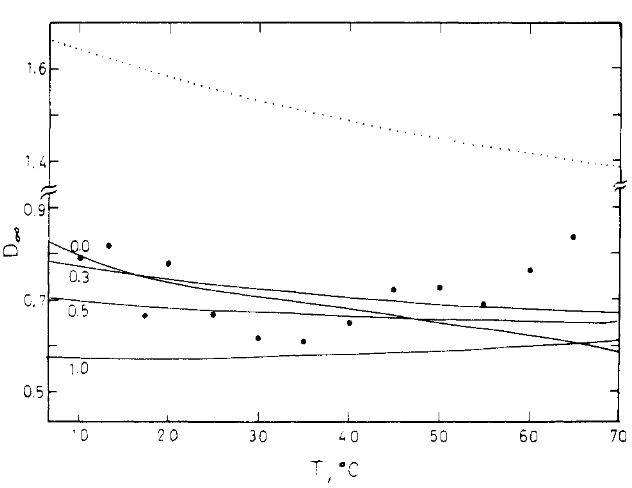

Figure 4. Dependence of D_∞ on temperature. Each curve is labeled by w_m, the fraction of meso diads. The upper dotted line is computed with energy values in the second column of Table I, i.e., not including the solvent effect. The solid points are the experimental data from ref 35.

Denbigh.[19] From symmetry considerations, induced dipoles in other directions than the z axis of the XYZ frame vanish. The fractional decrease μ^*/μ_0 in the dipole of the structural unit were computed to be equal to 0.04 and 0.16 for perpendicular and parallel configurations, respectively. The resulting μ_j values, corresponding to each state ξ, were evaluated by using the Boltzmann weighting factors.

The computed D_∞ values are shown in Figure 4 as a function of temperature for various stereochemical compositions. At 300 K, $D_\infty = 0.73$ for atactic chains with $w_m = 0.3$ and 0.68 for $w_m = 0.5$. The respective temperature coefficients, d ln D_∞/dT, are -2.05×10^{-3} and -0.93×10^{-3} deg^{-1}.

Comparison with Experiments and Discussion

The perturbation of the conformational structure of the chain molecule due to local solvent effect, is investigated in the present study. A rigorous approach should consider the interaction of all solvent molecules with polymeric chains in a constrained volume.[9] The statistical mechanical theory developed by Chandler and Pratt[20] for describing conformational structures of nonrigid molecules dissolved in liquid solvents was applied[21] to n-butane in various solvents to show that the local packing of solvent and solute species exerts an appreciable influence on the configurational characteristics of n-butane, the latter being viewed as a small-chain molecule. Their calculations lead to the conclusion that the solvent medium produces significant shifts in the configurational equilibrium of n-butane from that found in the gas phase, while the location of the energy minima remain unchanged.[21] In contrast to the treatment of Chandler et al.[20,21] calculations by Flory and collaborators show that the local solvent effect is inconsequential on chain properties. Although their approach suitably represents the behavior of symmetric chains, the agreement with experiment is not equally successful for vinyl chains. A correction to the latter system is attempted in this study by considering a single solvent molecule interacting with a repeat unit. The method constitutes an analogy to the treatment of the solvent as a very dilute gas without any environmental constraints. The model is simple as it does not treat the difficult problem of surrounding the chain with a dense fluid. But the fact that the calculated configuration-dependent properties exhibit good agreement with experiments (see below), justifies the choice of this model as a first-order approximation.

In the presence of solvent, the conformational potential prevailing at the *tg* state of the meso diad is reduced by an amount equal to 0.68 kcal/mol while that of *tt* state bears an increase of 0.45 kcal/mol. Consequently the meso, *tg* (or *gt*) state is rendered more favorable compared to the *tt* state by the action of the solvents. This result is in agreement with experimental studies by Sundararajan et al.[12] on the gelation of iPS: it was found that with aromatic solvents both extended (*tt*) and threefold helical (*tg*) conformations, but exclusively the latter, were formed. This was rationalized on the basis of accessibility of the phenyl groups for interaction with the solvent and the compatibility of the interacting pair. These qualitative predictions are now quantitatively confirmed by the present study. The total change in the difference between the energies corresponding to these two states is equal to 1.13 kcal/mol. It is interesting to note that this increase in the energy of the meso, *tt* state relative to *tg* is very close to that calculated by Yoon et al.[7] for PS (1.1 kcal/mol) through the use of the parameter $\sigma = 5$ Å that best reproduces experimental findings. As to the racemic diad, the probability of conformations possessing *g* bonds is slightly increased, but the *tt* state still dominates the local statistics as being the most favorable conformation, in agreement with the previous results[7] obtained for PS with the aid of adjustable parameters.

In general, solvent molecules of a size commensurate with that of the substituent will be participating in the solvent–polymer interaction. The "specific" effect depending on the type of solvent is estimated to be relatively insensitive to the choice of the solvent, provided that no special interaction such as a strong ionic or polar interaction occurs. Then, the size and shape of the substituent and not the solvent appears to be the main factor influencing the polymer–solvent potential that is associated with their degree of coupling. No such effect is discernible in the absence of bulky side groups. These predictions are confirmed with the measurements carried out by Izumi and Miyake.[22] The characteristic ratio of atactic PPCS in 11 θ solvents was found to vary from 9.88 to 10.85 depending on the specific solvent effect, as was pointed out by these authors. This is a rather narrow range compared to the value $C_\infty \approx 16$ obtainable in the absence of solvent using the energy values listed in the second column of Table I. Since our computation procedure does not involve any long-range interference, the obtained results are expected to be representative of the unperturbed dimensions of the chain. In fact, the value $C_\infty = 10.15$ for $w_m = 0.4$ falls within the experimentally observed range. Also, this value is in good agreement with the average value 10.6 deduced by Mark[10] from various experimental studies.[23-26] As to the temperature dependence, both positive and negative temperature coefficients d ln C_∞/dT are reported,[22] depending on the type of the solvent. The same is true for PS, whose behavior is very similar to that of PPCS. Orofino and Ciferri observed[27] a small positive temperature coefficient while Kuwahara and co-workers[28] reported a negative value. Our calculations yield a negative value of the same order of magnitude as those calculated for PS.[7]

A large amount of experimental data has been published on dipole moment measurements of PPCS.[29-33] Since the dipole moments of chains with dipoles perpendicular to the contour are accepted to be insensitive to excluded volume effects,[38] various solvents regardless of the Θ conditions were used in those investigations. The magnitude $\langle \mu_x^2 \rangle / x$ reported in those studies exhibits, however, considerable scatter. This feature was interpreted, first by Burshtein and Stepanova,[31] as being attributed to the solvent quality, the latter varying with both the type of the solvent and the temperature. The sensitivity of the dipole moment to the solvent was later confirmed by subsequent works.[32-37] Though some deviations in the observed data may be attributed to differing stereochemical compositions, the specific solvent effect affecting local backbone conformation seems to be an important source of disparity among the observed values, as pointed out by Tonelli and Belfiore.[35] Accordingly, the D_∞ values computed in the present work have to be compared with the results from experiments carried out with benzene.[32,37] In Figure 4 solid points refer to experimental data obtained by Aras and Baysal[37] for atactic PPCS in benzene. The experimental points are seen to lie about the region corresponding to the atactic chain ($0.3 < w_m < 0.5$), except for the high-temperature regime. In particular, the value $D_\infty = 0.67$ reported[32,37] for the atactic chain at 25 °C is in excellent agreement with the value 0.68 computed for $w_m = 0.5$ at 300 K. The theory developed in the present work predicts a negative, almost constant slope for $\mathrm{d}\ln\langle\mu_x^2\rangle/\mathrm{d}T$. This prediction, however, disagrees with the slope inversion experimentally observed in the vicinity of 35 °C. The same phenomenon was also observed experimentally in other polymer–solvent systems.[31,37,39]

The syndiotactic chain exhibits the highest temperature dependence, in agreement with earlier studies.[10,11] However, the magnitude of the dipole ratio of the syndiotactic chain is higher compared to that of isotactic chain, in contradiction with previous predictions.[10,11] As Saiz, Mark, and Flory pointed out,[11] the contribution to dipole moment per unit of preferred conformation in the isotactic chain (*tg* or *gt*) is smaller than that for the syndiotactic chain ($\mu_0/3$ vs. $\mu_0/3^{1/2}$), and, in addition, the average sequence length is smaller in isotactic chains. But Saiz et al.[11] argued that, in spite of these properties, the mean-squared moments for isotactic chains are still larger due to positive correlations between successive sequences compared to the adverse correlations existing in the syndiotactic chains. The present study, however, does not support the last argument. In general, no significant dependence on tacticity is observable from Figure 4. Further experimental works would be of interest for testing the validity of these theoretical predictions.

Registry No. PPCS, 24991-47-7; C_6H_6, 71-43-2.

References and Notes

(1) Volkenstein, M. V. *Configurational Statistics of Polymeric Chains*; translation from the Russian edition (1959) Timasheff, M. J., Timasheff, S. N.; Interscience: New York, 1963.
(2) Birshtein, T. M.; Ptitsyn, O. M. *Conformations of Macromolecules*; translation from the Russian edition (1964) Timasheff, M. J., Timasheff, S. N.; Interscience: New York, 1966.
(3) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(4) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(5) Flory, P. J.; Sundararajan, P. R.; Debolt, L. C. *J. Am. Chem. Soc.* **1974**, *96*, 5015. Fujiwara, Y.; Flory, P. J. *Macromolecules* **1970**, *3*, 280. Flory, P. J.; Fujiwara, Y. *Macromolecules* **1969**, *2*, 315.
(6) Yoon, D. Y.; Suter, U. W.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 784. Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 756.
(7) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(8) Brant, D. A.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 2791.
(9) Lifson, S.; Oppenheim, L. J. *J. Chem. Phys.* **1960**, *33*, 109.
(10) Mark, J. E. *J. Chem. Phys.* **1972**, *56*, 458.
(11) Saiz, E.; Mark, J. E.; Flory, P. J. *Macromolecules* **1977**, *10*, 967.
(12) Atkins, E. D. T.; Isaac, D. H.; Miyasaka, K. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 211. Sundararajan, P. R.; Tyrer, N. J.; Bluhm, T. L. *Macromolecules* **1982**, *15*, 286. Sundararajan, P. R.; Tyrer, N. J. *Macromolecules* **1982**, *15*, 1004.
(13) Corradini, P.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Eur. Polym. J.* **1979**, *16*, 1089.
(14) Sundararajan, P. R. *Macromolecules* **1979**, *12*, 575.
(15) Pitzer, K. S. In *Advances in Chemical Physics*; Prigogine, I. Ed.; Interscience: New York, 1959; Vol. 2, p 59.
(16) Ketelaar, J. *Chemical Constitution*; Elsevier: New York, 1958.
(17) Repeating the calculations with $\beta = \pm\pi/2$, $\gamma \neq 0$, so as to investigate the possible occurrence of a more stable configuration slightly deviating from the parallel configuration yielded $E = -4.58$ kcal/mol at $\gamma = \pm 1°$ with $S = 3.50$ Å and $\theta' = 80°$.
(18) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: New York, 1952.
(19) Denbigh, K. G. *Trans. Faraday Soc.* **1940**, *36*, 936.
(20) Chandler, D.; Pratt, L. R. *J. Chem. Phys.* **1976**, *65*, 2925. Chandler, D.; Pratt, L. R. *J. Chem. Phys.* **1977**, *66*, 147.
(21) Pratt, L. R.; Hsu, C. S.; Chandler, D. *J. Chem. Phys.* **1978**, *68*, 4202.
(22) Izumi, Y.; Miyake, Y. *Polym. J. (Tokyo)* **1973**, *4*, 205.
(23) Kurata, M.; Stockmayer, W. H. *Adv. Polym. Sci.* **1963**, *3*, 196.
(24) Kuwahara, K.; Ogino, K.; Kasai, A.; Ueno, S.; Kaneko, M. *J. Polym. Sci., Part A* **1965**, *3*, 985.
(25) Mohite, R. B.; Gundiah, S.; Kapur, S. L. *Makromol. Chem.* **1968**, *116*, 280.
(26) Noguchi, Y.; Aoki, A.; Tanaka, G.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2651.
(27) Orofino, T. A.; Ciferri, A. *J. Phys. Chem.* **1964**, *68*, 3136. Orofino, T. A. *J. Chem. Phys.* **1966**, *45*, 4310.
(28) Kuwahara, N.; Saeki, S.; Konno, S.; Kaneko, M. *Polymer* **1974**, *15*, 66.
(29) Debye, P.; Bueche, F. *J. Chem. Phys.* **1951**, *19*, 589.
(30) Kotera, A.; Suzuki, K.; Matsumura, K.; Shima, M.; Joko, E. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 750.
(31) Burshtein, L. L.; Stepanova, T. P. *Vyoskomol. Soedin., Ser. A* **1969**, *11*, 2885.
(32) Baysal, B.; Lowry, B. A.; Yu, H.; Stockmayer, W. H. In *Dielectric Properties of Polymers*; Karasz, F. E., Ed.; Plenum: New York, 1972.
(33) Yamaguchi, N.; Sato, M.; Ogawa, E.; Shima, M. *Polymer* **1981**, *22*, 1464.
(34) Mashimo, S.; Nozaki, R.; Work, R. N. *J. Chem. Phys.* **1982**, *77*, 2663. Yoshihara, M.; Work, R. N. *Ibid.* **1982**, *76*, 5174.
(35) Tonelli, A. E.; Belfiore, L. A. *Macromolecules* **1983**, *16*, 1740.
(36) Blasco, F.; Riande, E. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 835.
(37) Aras, L.; Baysal, B. M. *Macromolecules* **1985**, *18*, 1693.
(38) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(39) Masegosa, R. M.; Hernandez-Fuentes, I.; Ojalvo, E. A.; Saiz, E. *Macromolecules* **1979**, *12*, 862.