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Conformational Studies on Vinyl Polymers with Sulfur Atoms in the Side Groups

E. Saiz,[†] C. Mijangos,[‡] E. Riande,[*,‡] and D. López[‡]

Departamento de Química Física, Universidad de Alcalá de Henares, 28871 Alcalá de Henares, Madrid, Spain, and Instituto de Ciencia y Tecnología de Polímeros, CSIC, 28006 Madrid, Spain

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ABSTRACT: Mean-square dipole moments, $\langle\mu^2\rangle$, of atactic poly(vinyl phenyl sulfide) (PVPS) $[-CH_2CHS(C_6H_5)-]_x$ were determined from dielectric permittivity measurements carried out in a fraction dissolved in benzene. The conformational analysis of the polymer suggests that both the stereoregularity and the rotational population about the backbone play a relatively minor role in the polarity of the chains. Contrary to what occurs with the unperturbed dimensions, the dipole moment of the polymer is conditioned by the conformational energy governing the incidence of the allowed orientations of the side groups.

Introduction

The conformation-dependent properties of isolated vinyl chains with side groups rigidly linked to the backbone are strongly sensitive to the conformational statistics of the chains.[1-3] This sensitivity may increase as either the length of sequences of meso diads (in which tgtg... conformations are predominant) or the length of sequences of racemic diads (in which ttt... conformations have the lower energy) increases, depending on the structure of the vinyl polymer.[4-6] Thus, theoretical calculations show that the dipole moment ratio of poly(vinyl chloride) (PVC), D_x $(=\langle\mu^2\rangle/x\mu_0^2$, where $\langle\mu^2\rangle$ and $x\mu_0^2$ represent, respectively, the mean-square dipole moment of the chains and that of freely jointed chains), increases from 0.59 for 100% isotactic chains to 4.0 for 100% syndiotactic ones.[5-7] In poly(*p*-chlorostyrene) (PCS), however, the dependence of D_x on the tacticity of the chains follows an opposite trend, because the theoretical values of D_x amount to 5.5 and 0.92 for isotactic and syndiotactic chains, respectively.[4,7] The explanation of this behavior lies in that the relatively small size of the chlorine atom favors the high-polarity tt conformations in racemic diads and hence the high dipole moment of syndiotactic chains.[5,6] On the contrary, disruption of the tt sequences by the effect of the bulkiness of the phenyl group confers low polarity to syndiotactic PCS chains.[4] For isotactic PCS, tg and gt sequences, occasionally interrupted by tt conformations, produce favorable dipolar correlation between successive sequences and, as a result, the polarity of these chains is much higher than that of isotactic PCS. This occurs with other polymers with bulky side groups; for example, the dependence of the polarity of the mean-square dipole moment of poly(vinyl bromide) (PVB)[8] on the stereochemical structure is more like that of PCS than that of its halogenated analog, PVC.

To gain a deeper insight into the relation between structure and properties in chains with polar side groups, a variety of polymers are being analyzed in our laboratories. In this work an experimental study on the dipole moments of poly(vinyl phenyl sulfide) is reported. Special emphasis is devoted to the statistics of the chains, and the theoretical results are compared with those experimentally obtained for the polarity of the chains.

Experimental Section

Poly(vinyl phenyl sulfide) (PVPS) was obtained by radical polymerization of vinyl phenyl sulfide in an ampule at 55 ± 0.5 °C, using AIBN as initiator. The reaction was carried out for 48 h under a nitrogen atmosphere. The polymer was dissolved in THF, precipitated with methanol, and dried at 40 °C in vacuo to constant weight.

The ^{13}C NMR spectrum of the polymer in deuterated dioxane solution was recorded at 90 °C with a Varian XL 300 MHz spectrometer operating at 75.5 MHz. The resonance peaks corresponding to methine and methylene carbons, appearing in the spectrum from 47.5 to 42 ppm, are not clearly separated; however, by analogy with other vinyl polymers, it is assumed that the 47.5–45.1 region corresponds to the tactic placements of $-CHSC_6H_5-$ carbons, that is, rr, mr, and mm triads, and that of 45.1–42.0 ppm to the methylene carbons. These assumptions have been confirmed by two-dimensional inverse heteronuclear correlation spectroscopy. From this analysis one finds that the fractions of mm, mr, and rr triads are 0.235, 0.495, and 0.270, respectively. The number-average molecular weight of the sample used in this study was 24 000.

The dielectric permittivities ϵ of solutions of PVPS in benzene were measured at 20, 30, 40, and 50 °C with a capacitance bridge (General Radio, Type 1620 A) coupled with a three-terminal cell. Increments in the index of refraction of the solutions, n, with respect to that of the solvent, n_1, at the temperatures of interest were determined with a differential refractometer (Chromatics, Inc.).

Results

Values of the mean-square dipole moment per repeating unit, $\langle\mu^2\rangle/x$, were calculated by the method of Guggenheim and Smith[9]

$$\frac{\langle\mu^2\rangle}{x} = \frac{27k_BTM_0}{4\pi\rho N_A(\epsilon_1+2)^2}\left\{\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right\} \qquad (1)$$

where k_B and N_A represent, respectively, the Boltzmann constant and Avogadro's number, M_0 is the molecular weight of the repeating unit, ρ is the density of the solvent, and w is the weight fraction of polymer in the solution. The term $d\epsilon/dw$ in eq 1 was obtained at each temperature of interest from plots of the permittivity of the solutions against the weight fraction of polymer w in the limit $w \rightarrow 0$. Values of dn/dw were obtained from plots of the increments of the index of refraction against w. The results obtained at several temperatures are shown in the second and third columns of Table 1. In the fourth and fifth columns of this table the values of $\langle\mu^2\rangle/x$ and the dipole

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[†] Universidad de Alcalá de Henares.

[‡] Instituto de Ciencia y Tecnología de Polímeros.

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Table 1. Summary of Dielectric Results for Poly(vinyl phenyl sulfide)

T, °C	$2n_1\,dn/dw$	$d\epsilon/dw$	$\langle\mu^2\rangle/x$, D^2	$\langle\mu^2\rangle/x\mu_0^2$ [a]
20	0.348	2.280	2.349	1.10
30	0.351	2.149	2.310	1.08
40	0.357	2.032	2.272	1.07
50	0.360	1.934	2.260	1.06

[a] A value μ_0 = 1.46 D was used as the dipole moment of the repeating unit to compute the last column of this table. See text for details.

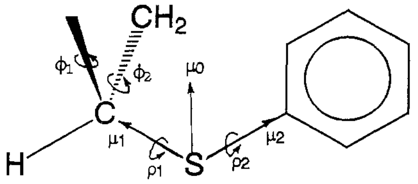

Figure 1. Sketch of the side group of poly(vinyl phenyl sulfide) showing the dipole moments associated with the polar bonds and the rotational angles $\rho_1 = \rho_2 = 0$.

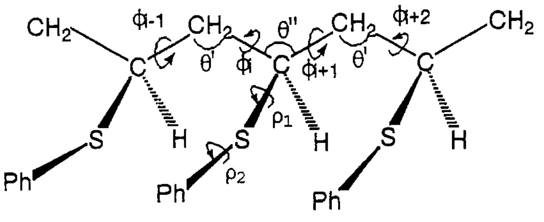

Figure 2. Meso configuration of a segment of poly(vinyl phenyl sulfide) in the *all-trans* conformation.

moment ratio are also given; the uncertainty of these results was estimated to be ±3%.

The dipole moment of PVPS chains exhibits a decreasing temperature dependence. The temperature coefficient, expressed in terms of $d \ln \langle\mu^2\rangle/dT$, amounts to -1.3×10^{-3} K^{-1}.

Theoretical Calculations

Figure 1 shows a sketch of the repeating unit of PVPS which illustrates the direction of its dipole moment μ_0 and the four rotations allowed for each unit (namely ϕ_1, and ϕ_2 over skeletal bonds and ρ_1 and ρ_2 over C$^\alpha$–S and S–C^{ar} bonds on the side group). Figure 2 shows the structure of an isotactic segment of the PVTB chain in the *all-trans* conformation. The *trans* orientation was used as the origin for all the rotation angles; thus, for instance, $\rho_1 = \rho_2 = 0$ for the conformation of the side group shown in Figure 1 and $\phi_{i-1} = \phi_i = \phi_{i+1} = \phi_{i+2} = 0$ in the conformation represented in Figure 2.

The phenyl 2-propyl sulfide (PPS) molecule was used as a model compound for the repeating unit of PVPS. Thus, the geometry of this molecule was optimized with the Sybyl molecular modeling package[10] using the Tripos force field[11] and then its charge distribution was evaluated with the MOPAC program and MINDO procedure,[12,13] obtaining a value of μ_0 = 1.46 D, which is in good agreement with the experimental results reported for this kind of compound.[14] Thus, dipole moments of dimethyl sulfide measured at 25 °C in Cl$_4$C range from 1.45 to 1.56 D, while the values obtained for methyl phenyl sulfide in several solvents at temperatures ranging from 25 to 30 °C lie in the interval 1.29–1.39 D. A value μ_0 = 1.46 D was used throughout this paper as the dipole moment of the repeating unit, for instance to compute the last column in Table 1.

Table 2. Summary of Conformational Magnitudes for Meso and Racemic Diads of the PVTB Chain[a]

conformation	$\langle\phi_1\rangle$	$\langle\phi_2\rangle$	$\langle\theta'\rangle$	$\langle E\rangle$
meso tt	12	18	112.4	0.60
meso tg	12	112	113.0	0.09
meso tḡ	26	225	114.5	2.30
meso gg	85	112	113.7	1.02
meso gḡ	106	225	115.0	3.97
meso ḡḡ	230	270	114.0	5.14
racemic tt	13	11	113.6	0
racemic tg	30	113	115.0	0.46
racemic tḡ	8	231	117.0	5.03
racemic gg	100	102	114.0	0.10
racemic gḡ	88	226	117.0	1.75
racemic ḡḡ	242	241	117.0	9.27

[a] Angles are given in degrees and energies, normalized for the value of tt in both meso and racemic, in kcal/mol.

The optimized geometry of the PPS molecule gives bond lengths of 1.82 and 1.79 Å, respectively, for bonds C$^\alpha$–S and S–C^{ar} and a bond angle C$^\alpha$–S–C^{ar} of 107.4°. With this geometry, both modulus and direction of this dipole can be reproduced by assigning partial charges to C$^\alpha$ (q = 0.1487 e), S (q = −0.2853 e), and the first C^{ar} on the phenyl ring (q = 0.1366 e). Thus the total dipole moment can be written as the sum of two components, $\vec{\mu}_0 = \vec{\mu}_1 + \vec{\mu}_2$, and its orientation depends on the rotational angle ρ_1, but not on ρ_2.

Conformational energies of both meso and racemic diads were computed with Sybyl.[10] A grid search was performed for the conformations of the backbone moving ϕ_1 and ϕ_2 in the range 0–350° with 10° increments and performing a full energy minimization for each conformation of the chain (i.e., for each set of values of ϕ_1 and ϕ_2). Once the approximate location of the isomers of the chain was found, averages of the conformational energies ($\langle E\rangle$), rotational angles ($\langle\phi_1\rangle$ and $\langle\phi_2\rangle$), and backbone angle ($\langle\theta'\rangle$ (C$^\alpha$–CH$_2$–C$^\alpha$ angle)) were computed in areas of ±40° around each isomer.[15,16] The results of this calculation are summarized in Table 2. A value θ'' = 110° was used throughout all the calculations for the backbone CH$_2$–C$^\alpha$–CH$_2$ angle.

The elements of the statistical weight matrices for the pair of bonds C$^\alpha$–CH$_2$–C$^\alpha$ within a diad in both the meso and racemic orientations can be obtained as Boltzmann exponentials of their corresponding energies given in Table 2. Thus, the values obtained at 20 °C are

$$\mathbf{U}_m'' = \begin{bmatrix} 1.000 & 2.400 & 0.054 \\ 2.400 & 0.486 & 0.003 \\ 0.054 & 0.003 & 0.000 \end{bmatrix}$$

$$\mathbf{U}_r'' = \begin{bmatrix} 1.000 & 0.454 & 0.000 \\ 0.454 & 0.842 & 0.050 \\ 0.000 & 0.050 & 0.000 \end{bmatrix} \qquad (2)$$

while the interdiad matrix for the pair of bonds CH$_2$–C$^\alpha$–CH$_2$ is

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \qquad (3)$$

The statistical model represented by eqs 2 and 3 gives a good account of the conformational characteristics of the polymer main chain. However, in the evaluation of these matrices, the rotations ρ_1 and ρ_2 of the side groups have been taken into account only in the energy minimization for each conformation of the skeleton. But since the dipole moment of the repeating unit lies in the side group and its orientation (and therefore the possible reinforcement or cancellations of contributions from successive diads along the main chain) depends on the rotation ρ_1, this parameter deserves closer attention.

A very simple procedure for incorporating the rotational parameter ρ_1 into the scheme of calculation, which has been used before in polymers having flexible side groups,[17] consists in assuming that the side group of each repeating unit may adopt several orientations with a priori probabilities that are independent of the conformation of that particular diad within the chain. Thus, the chain is generated with standard procedures of the matrix multiplication scheme,[1,18] and every time that a new diad is going to be incorporated into the growing polymer, it is decided which one among its allowed orientations should be used.

An estimation of the number, location, and a priori probabilities of the allowed orientations for the ρ_1 angle could be obtained by computing the energy of the PPS molecule, which closely reproduces the first-order interactions for the side group of each repeating unit. This calculation was performed with Sybyl[10] moving ρ_1 from 0 to 170° with increments of 10° and minimizing the energy of each orientation thus obtained with respect to all other geometrical parameters, including the ρ_2 rotation. The results indicate that the preferred orientations are $\rho_1 \approx 0$ (*trans* orientation) and $\rho_1 \approx 180°$ (*cis* orientation), which is ca. $E_c \approx 0.5$ kcal/mol above *trans*. Thus, representing by γ the Boltzmann factor $\exp(-E_c/RT)$, the probabilities of the *trans* and *cis* orientations of the side group would be $p_t = 1/(1 + \gamma)$ and $p_c = \gamma/(1 + \gamma)$.

Mean-square dipole moments of the polymer, $\langle \mu^2 \rangle$, were computed by generating chains containing $x = 200$ repeating units with a Bernouillian distribution of meso and racemic centers. Each time that a new diad was incorporated into the chain, i.e., each time that a new matrix had to be annexed to the serial product, a random number within the range [0,1] was generated to decide whether the *trans* (whose dipole moment in the reference frame[1] attached to skeletal bond C^{α}–CH_2 is given by the vector $\mu_0 = 0.834, -1.192, 0.134$ D) or the *cis* (having $\mu_0 = -0.213, 0.305, 1.413$ D) orientation should be used. All the results shown below are averages over 200 chains independently generated according to this procedure. Such a large sample ensures a good random distribution of *trans*/*cis* orientations of the side group as well as meso/racemic centers on the main chain. In fact, typical differences between predetermined values of p_c and w_m and the actual results of the simulation were ca. 1%. The results of $\langle \mu^2 \rangle$ thus obtained were converted into dipole ratios D_x. In a similar way, the number of repeating units per chain ($x = 200$) is large enough to ensure that the asymptotic limit of D_x for $x \to \infty$ has been reached; the difference in the values of D_x computed for $x = 200$ and extrapolations to $x \to \infty$ are smaller than 2%; consequently, all the results presented below were obtained with $x = 200$.

Some exploratory calculations were performed to check the variation of D_x with the parameters used in the calculation. They proved that D_x is rather insensitive to the conformational characteristics of the main chain. Thus, variations of 5° in the backbone angle θ', of 10° in the torsion angles defining the location of rotational isomers, or 0.5 kcal/mol in their relative energies produce modifications of ca. 4–5% in the results of D_x.

As far as the value of D_x is concerned, the most important conformational parameter is the energy E_c governing the incidence of the two orientations allowed for the side group. Figure 3 shows the values of D_x computed at 20 °C for meso, racemic, and heterotactic chains as function of E_c from $E_c = -1$ kcal/mol (i.e., *cis* orientation preferred) to $E_c = 1$ kcal/mol (i.e., *trans* being the dominant orientation). As this figure indicates, the isotactic chains are the most sensitive to this parameter, although in all cases, the value of D_x increases by more than twice when E_c changes from -1 to 1 kcal/mol. Values of $D_x \approx 1.1$ for $w_m \approx 0.5$ close to the experimental results summarized in Table 1 are found for $E_c \approx 0.5$ kcal/mol, which is close to the estimation of this parameter obtained by the analysis of the conformational energies of the PPS molecule.

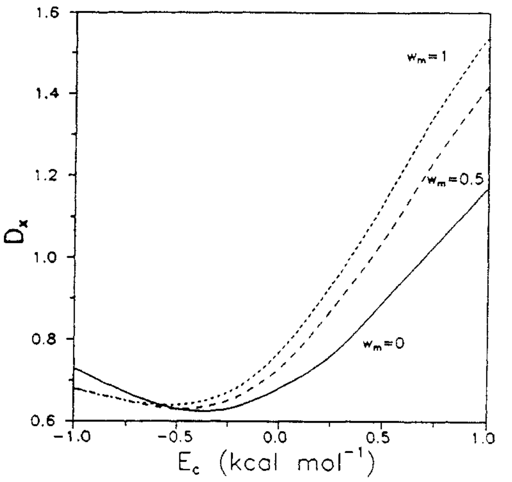

Figure 3. Dependence of the dipole moment ratio on the conformational energy associated with the CH–S bond of the side group.

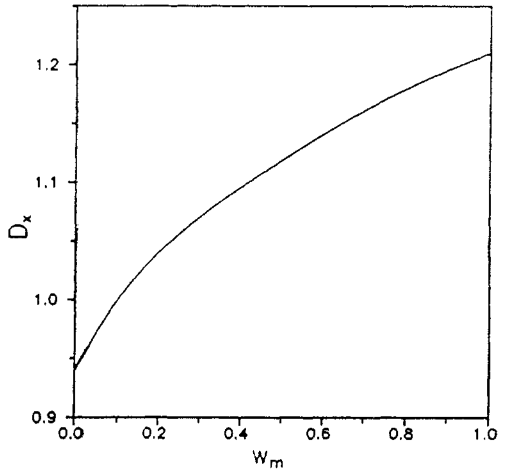

Figure 4. Variation of the dipole moment ratio with the tacticity of the chain.

Figure 4 illustrates the variation of D_x with the tacticity of the chain computed at 20 °C with $E_c = 0.6$ kcal/mol and indicates that D_x increases by roughly 20% from pure syndiotactic to perfectly isotactic chains. In particular, a value of $D_x = 1.12$ is obtained for the heterotactic chain having $w_m = 0.5$, in excellent agreement with the experimental result of Table 1.

The calculated value of the temperature coefficient of D_x is negative, in good agreement with experiment. Thus, a value $D_x = 1.06$ is obtained at 50 °C for $w_m = 0.5$ using $E_c = 0.6$ kcal/mol, i.e., a decrease of 5% with respect to the value obtained at 20 °C.

Discussion

As indicated above, the conformational characteristics of the main chain of PVPS play a minor role on the polarity of the polymer. Instead, the most important parameter for this magnitude is the energy E_c governing the incidence of the two allowed orientations of the side groups and, thus, the reinforcement or cancellation of contributions from different units along the chain. A set of values for all the parameters obtained by conformational analysis of model compounds is able to reproduce the experimental results of both the dipole moment of the chain and its temperature coefficient.

The critical interpretation of the mean-square dipole moments of PVPS suggests that the dependence of $\langle \mu^2 \rangle$ on the stereoregularity of the chains may decrease whenever the polar side groups have a high degree of freedom with respect to the main chain. In this case the polarity of the polymer depends not only on the flexibility of the side group but also on the orientation of the dipoles in consecutive diads. Actually, conformational studies carried out on phenyl-halogenated esters of poly(acrylic acid)[17] have shown that the dipole moment ratio of the chains is strongly dependent on both the location of the halogen atom on the phenyl group and the relative states of the carbonyl groups in two consecutive diads. Thus, the value of D_x changes from 0.54 for poly(*m*-chlorophenyl acrylate) (POCPA) to 1.1 for poly(*o*-chlorophenyl acrylate) (POCPA).

The sensitivity of the mean-square dipole moment of the chains to both the conformations of the backbone and the stereochemistry of the chains is found to be a minor one, if it is compared with this dependence for other conformation-dependent properties such as the unperturbed dimensions. The values of the conformational energies indicated in Table 2 suggest that tt and tg conformations in meso diads differ little in energy so that helicoidal tgtg... sequences and planar tt... conformations are disrupted by t$\bar{g}$ and g$\bar{g}$ conformations in isotactic chains. As a consequence, it is expected that the characteristic ratio C_∞ ($= \langle r^2 \rangle_0 / nl^2$, where $\langle r^2 \rangle_0$ is the unperturbed mean-square end-to-end distance and nl^2 is the value of this quantity for a freely jointed chain) is relatively small for isotactic PVPS chains. Contrary to what occurs for isotactic diads, $\bar{g}$ conformations are forbidden for syndiotactic diads; since high spatial extension conformations (tt, tg, and gg) are totally predominant, it is expected that syndiotactic chains have a high characteristic ratio. These assumptions are confirmed in Figure 5, which shows that the value of C_∞, calculated by using the statistics described above, decreases from 13.7 to 5.2 when the isotactic replacement changes from 0 to 1; this variation is only from ca. 0.94 to ca. 1.21 for the dipole moment ratio. This behavior contrasts with what occurs in the situations in which the bond or group dipoles are rigidly linked to the main chain. In these cases dipole moments are much more sensitive to structure than the unperturbed dimensions owing to the fact that skeletal bonds change much more in polarity than they do in length.[19]

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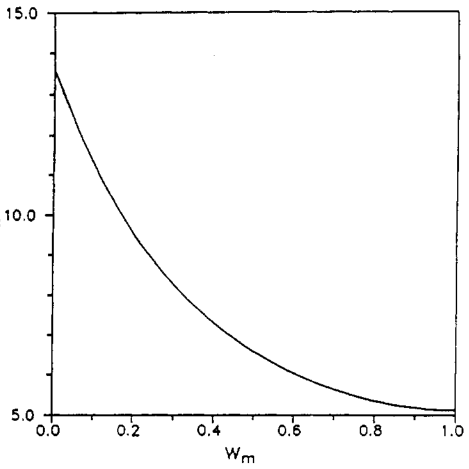

Figure 5. Changes in the characteristic ratio with the tacticity of poly(vinyl phenyl sulfide).

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