Macromolecules **1982,** *15,* 1587-1593

Conformational Properties of Poly(alkene sulfones)

Marc L. Mansfield[†]

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755.
Received April 12, 1982

ABSTRACT: Semiempirical conformational energy calculations on poly(alkene sulfones), $(\text{-}SO_2CHR_1CHR_2\text{-})_x$, are reported. Grid searches of the configuration space of small molecular weight analogues yield a number of conformations stabilized by electrostatic interactions between neighboring SO_2 groups. The differences produced by changing R_1 and R_2 were examined. Calculations for R_1 an aliphatic chain and for R_2 = H indicate a helical structure with a pitch of about 6–8 Å and with 5–6 repeat units per turn. Such a helix has been recently proposed to explain a number of experimental facts. Calculations for $R_1 = R_2 = CH_3$ indicate chains with a strong preference for trans states at the C–C bond and the above-mentioned helix is not expected to form.

I. Introduction

The alternating copolymers of alkenes with sulfur dioxide, the poly(alkene sulfones), divide into three classes:[1-7] one, $(\text{-}SO_2CHRCH_2\text{-})_x$, with a single side group R per repeat unit; two, $(\text{-}SO_2CR_1R_2CH_2\text{-})_x$, with two side groups on the same carbon; and three, $(\text{-}SO_2CHR_1CHR_2\text{-})_x$, with one side group on each of the two carbons. Groups one and two are dielectrically active in the radio-frequency region (10^3–10^6 Hz), with relaxation times strongly dependent on molecular weight. Groups one and two also exhibit a weaker relaxation in the high-frequency region (>10^7 Hz).[7] These high-frequency relaxations result from local conformational rearrangements, while the low-frequency ones probe global changes in shape.[10] The low-frequency molecular-weight-dependent ones are known in other polymers and most often occur when the total dipole moment is correlated with the end-to-end vector, i.e., when individual dipoles along the chain have a longitudinal, head-to-tail component, thus reflecting the lowest Zimm relaxation time.[8-10] Fawcett, Ivin, and co-workers present evidence that the group three polymers show a strong preference for trans states at the CHR_1–CHR_2 bond.[11,12] Such an arrangement leads to a net dipole moment of zero for the polymer, as may be seen by decomposing the dipole moments along the C–S bonds. They argue that this accounts for the lack of a low-frequency relaxation. The presence of the low-frequency relaxation in classes one and two indicates substantial conformational differences between these and the class three polymers. Particularly difficult to explain is how polymers of groups one and two develop a large longitudinal component of the dipole moment when the SO_2 unit dipole is perpendicular to the backbone. The properties of a series of class one polymers for R = $(CH_2)_xH$ and x between 3 and 18 have been studied in this laboratory.[6,13,14] In the solvents benzene, toluene, cyclohexane, and carbon tetrachloride the dipole moment ratio $\langle \mu^2 \rangle / x\mu_1^2$ increases from less than unity for the shorter side groups to an asymptotic value of about 3 for long side groups. Here μ is the net dipole moment of the polymer molecule, μ_1 is the dipole moment per repeat unit, and x is the number of repeat units. The solubility in these solvents also increases with increasing side-group size. Although a number of questions still remain, it now appears that the unusual properties of the class one and class two polymers outlined above can be explained in terms of helical structures within the chain.[14,15]

An additional class of polymers might also be cited. The properties of a poly(styrene sulfone) have been reported.[5,16] The polymer contains 2.27 styrene residues per SO_2, as opposed to the 1:1 ratio observed for the aliphatic alkenes, with very few single, many double, and some triple styrene moieties between sulfone groups. The dipole moment ratio is about 0.6. In these styrene copolymers, only the high-frequency relaxation is observed.

In this paper we attempt to understand a number of conformational properties of these molecules, including the helical structures mentioned above, using semiempirical conformational energy calculations. Conformational calculations on polysulfones have been performed previously.[11,17] These were limited to chains in gauche and trans states, which is an oversimplification. Molecules assume gauche–trans structures in response to what may be termed steric forces, but in the present molecules we can expect electrostatic interactions between sulfone groups (the dipole moment of the SO_2 group is ca. 4.5 D) to be just as important as steric forces in determining conformational properties. Therefore, in this work, we locate stable conformations of small analogues of the poly(alkene sulfones) through grid searches of the molecular configuration space. Then we argue that the single-side-group polymers $(\text{-}SO_2CHRCH_2\text{-})_x$ with R large have only a limited number of accessible conformations. We then tentatively identify these conformations, using simplifying assumptions about interactions between adjacent side groups. A tendency toward stereospecificity when the side group is large is indicated. A small number of conformations plus the stereospecificity leads to a helical structure. Our calculations also indicate that the C–C bonds are uniquely trans in the class three polymers $(\text{-}SO_2CHR_1CHR_2\text{-})_x$.

The potential functions employed in this work are discussed in section II. In section III we report stable conformations of 1,2-bis(methylsulfonyl)ethane ($CH_3SO_2CH_2CH_2SO_2CH_3$) determined through a grid search of the configuration space of the molecule. In section IV we examine the effects of a single short chain by examining 1,2-bis(methylsulfonyl)propane, -butane, and -pentane ($CH_3SO_2CHRCH_2SO_2CH_3$, R = Me, Et, *n*-Pr). In section V we extend these results to longer side groups and consider the interactions between side groups. In section VI we examine the structure of the helix mentioned above. In section VII we examine stable conformations of 2,3-bis(methylsulfonyl)butane ($(CH_3SO_2CHCH_3)_2$) as an analogue of the two-side-group polymers. In section VIII we summarize the results.

II. Potential Functions

In these calculations all bond lengths and bond angles were held fixed at the following values: C–C, 1.54 Å; C–S, 1.80 Å; S–O, 1.44 Å; all bond angles tetrahedral. With these constraints, the conformational energy is a function

---

[†] Present address: Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

0024-9297/82/2215-1587$01.25/0

Table I
Nonbonded Lennard-Jones Parameters Used in Calculations of Conformational Energy

	$10^{-5}d_{ij}$, kcal Å^{12} mol^{-1}	$10^{-2}e_{ij}$, kcal Å^{6} mol^{-1}
CH_3-CH_3	29.02	16.50
CH_3-CH_2	24.08	13.69
CH_3-CH	18.89	10.74
CH_3-S	6.57	4.04
CH_3-O	7.94	7.67
CH_2-CH_2	19.99	11.36
CH_2-CH	15.69	8.92
CH_2-S	5.51	3.38
CH_2-O	6.61	6.39
CH-CH	12.33	7.01
CH-S	4.40	2.70
CH-O	5.22	5.04
S-S	2.18	1.45
S-O	2.01	2.12
O-O	2.15	3.72

Table II
Different Sets of Inherent Barriers and Dielectric Constants Used in Calculations of Conformational Energy

set	V(C-C), kcal/mol	V(C-S), kcal/mol	D
1	0.5	0.5	2.0
2	3.0	3.0	2.0
3	1.5	1.5	2.0
4	1.5	1.5	1.0
5	1.5	1.5	1.5
6	2.0	1.0	2.0

only of the bond rotational angles. In defining bond rotational angles, we have followed the Flory convention,[18] which places trans at 0° and gauche at ±120°. The conformational energy was approximated with Lennard-Jones and coulombic forces between pairs of atoms and with 3-fold "inherent" rotational barriers about each nonterminal bond:

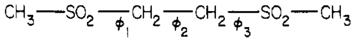
$$U = \sum_j (V_j/2)(1 - \cos 3\varphi_j) + \sum_{j<k} (d_{jk}/r_{jk}^{12} - e_{jk}/r_{jk}^{6} + q_jq_k/Dr_{jk}) \quad (1)$$

We use the "extended-atom" (each CH_n group considered a single unit) Lennard-Jones parameters of Scheraga, Flory, and co-workers[19-23] which appear in Table I. As in the precedent of Fawcett and Ivin,[11,17] only S and O atoms were assigned partial charges (1.10 and −0.55 e, respectively) for the coulombic interaction. These charges were assigned to give the correct dipole moment to the SO_2 unit.

Consistent with the preliminary nature of this study, we have made no effort to justify or adjust the potential energy functions against known properties of small molecules. To compensate for this we examined the effects of changing both the inherent barrier and the dielectric constant. Generally, such alterations affected the energy of conformers without changing their structures. Therefore, we feel we have obtained reasonable structures of the conformers although their energies remain in question.

Six different sets of potential energy parameters were considered by varying the dielectric constant and the inherent barriers. These six sets are summarized in Table II. In all six sets, the Lennard-Jones parameters (Table I) are the same. Some values of inherent barriers that have been employed in the literature are 0, 0.2, and 1.0 kcal/mol for N-C bonds in polypeptides[19] and 2.1[24] and 2.6[25] kcal/mol for C-C bonds in saturated hydrocarbons. We expect the C-S inherent barrier to be less than the C-C barrier because of the increased C-S bond length.[26]

Table III
Minimum-Energy Conformations of 1,2-Bis(methylsulfonyl)ethane[a]



$$CH_3\text{—}SO_2\underset{\phi_1}{\text{—}}CH_2\underset{\phi_2}{\text{—}}CH_2\underset{\phi_3}{\text{—}}SO_2\text{—}CH_3$$

conformation	φ_1	φ_2	φ_3
A	0	0	0
B	−3	−5	109
C	1	67	−106
D	−4	94	−73
E	47	−101	47
F	83	−102	83
G	112	−62	−108
H	112	0	−112
I	114	3	114
J	141	106	141

[a] Angles are in degrees; 0° corresponds to trans.

III. Calculations on 1,2-Bis(methylsulfonyl)ethane: Determination of Conformations

Grid searches of the rotational angle space at intervals of either 3° or 5° were conducted for potential sets 1–4. Minimum-energy structures obtained thereby were further refined with an energy minimization algorithm. These structures as well as all possible gauche–trans sequences were then used as starting points in the energy minimization algorithm to obtain structures for sets 5 and 6. A total of ten unique conformations were located, to which we assign the letters A–J. These findings are summarized in Table III. Only conformations A, B, H, I, and J are gauche–trans sequences. The others exhibit bonds that are nearly eclipsed and are stabilized by coulombic interactions, involving either the close approach of a nonbonded sulfur–oxygen pair or an approximately antiparallel arrangement of two S–O bonds. The values in Table III represent average structures obtained by combining results for all six potential energy surfaces. The rotational angles in most conformations exhibited a variability no greater than about 5° for the different potential energy surfaces, and not all ten conformations appeared as stable minima on each of the six potential surfaces. The complete list of all the minima for each potential energy surface and the associated energies are available as supplementary material.

Since the structures of conformations A–J are only weakly dependent on the parameters given in Table II, the energy of any particular conformation is approximated by

$$E = E_0 + \alpha V_{CC} + \beta V_{CS} + \gamma/D \quad (2)$$

where

$$E_0 = \sum_{j<k} (d_{jk}/r_{jk}^{12} - e_{jk}/r_{jk}^{6}) \quad (3)$$

$$\alpha = 1/2(1 - \cos 3\varphi_2) \quad (4)$$

$$\beta = 1/2(2 - \cos 3\varphi_1 - \cos 3\varphi_3) \quad (5)$$

and

$$\gamma = \sum_{j<k} q_jq_k/r_{jk} \quad (6)$$

The values of E_0, α, β, and γ for conformations A–J are given in Table IV and are expressed relative to the all-trans structure (conformation A). Therefore the values of E_0, α, β, and γ measure the relative contribution to the overall stability of the conformation from van der Waals interactions, from the inherent barrier about the C–C bond, from the inherent barrier about the two C–S bonds, and

Table IV
Relative Contributions of van der Waals Interactions, the C-C Inherent Barrier, the C-S Inherent Barrier, and Coulombic Interactions to the Stability of the Conformations of 1,2-Bis(methylsulfonyl)ethane

conformation	E_0, kcal/mol	α	β	γ, kcal/mol
A	0.00	0.00	0.00	0.00
B	0.20	0.02	0.09	1.97
C	0.03	0.97	0.13	0.72
D	0.96	0.40	0.90	−0.91
E	1.78	0.23	1.78	−2.99
F	1.32	0.21	1.36	1.81
G	0.12	1.00	0.14	1.91
H	0.39	0.00	0.09	2.17
I	0.39	0.01	0.05	4.25
J	2.35	0.13	0.55	5.54

Table V
Some Barriers to Conformational Rearrangement in 1,2-Bis(methylsulfonyl)ethane[a]

$$A \xleftrightarrow[0.73]{1.95} B \qquad D \xleftrightarrow[0.11]{0.01} C \qquad B \xleftrightarrow[1.23]{1.52} H$$

$$C \xleftrightarrow[0.85]{1.52} G \qquad B \xleftrightarrow[1.10]{2.42} I$$

[a] Units are kcal/mol.

from coulombic interactions, respectively. For example, a negative γ for a particular conformation implies that coulombic interactions contribute more to the stability of the conformation than they do to conformatioin A.

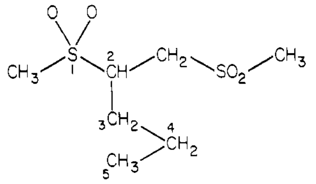
Fawcett and Ivin,[11] interpreting NMR data, report that the related compound $(n\text{-PrSO}_2\text{CH}_2)_2$ favors the trans state about the central C–C bond by about 1.4 kcal/mol. The energies given by eq 2 are consistent with this.

These conformational calculations indicate rather modest barriers to conformational rearrangement. We have shown in Table V several barriers calculated for potential set 1. These may be underestimated because of the modesty of the inherent barriers in potential set 1, but nevertheless they strongly suggest that the classical explanation for the low-frequency molecular-weight-dependent relaxation (that internal barriers are so large that overall rotation of the molecule in a given conformation, rather than conformational rearrangement, is the preferred path for dielectric relaxation[2,4,5,16]) is in error.

We note in Table III that whenever any rotational angles are not trans, φ_1 and φ_3 almost always differ from φ_2 in absolute value. This agrees with the statement made by Fawcett and Ivin,[11,17] within the context of gauche–trans structures, that when the C–C bond assumes the $g^{\pm}$ state, the preferred state for one of its two neighbors is $g^{\mp}$. Such a structure is favored by the electrostatic interactions. The only complete exception to the above rule is structure J, and the large value of γ indicates that this structure is not preferred electrostatically.

IV. Calculations on 1,2-Bis(methylsulfonyl)propane, -butane, and -pentane: Effect of One Side Group on Calculations

The molecules 1,2-bis(methylsulfonyl)propane, -butane, and -pentane, $\text{CH}_3\text{SO}_2\text{CHRCH}_2\text{SO}_2\text{CH}_3$, with R either a methyl, ethyl, or n-propyl group, were studied to probe the effect of the side group R on the conformations in Table III. With the backbone held at each one of the minimum-energy conformations obtained for potentials sets 1–5, we integrated over all internal degrees of freedom of the side group (0, 1, or 2 rotational angles for the methyl, ethyl, and propyl groups, respectively) to calculate a free energy for that conformation (computed at $T = 298$ K). The results obtained for potential sets 1–5 are available as supplementary material. From this calculation we find that most of the conformations drop in energy relative to the all-trans structure. Certain of the B, C, D, E, and G structures drop below or become competitive with the A (all-trans) structure. (We will see below that this is probably only partly true: addition of a short side group seems to stabilize certain conformations relative to the all-trans, but the all-trans remains most stable.) Limiting our attention to the low-energy configurations, we also see that the change in energy as one proceeds from a methyl to an ethyl to a propyl side group is considerably smaller than the change produced with the introduction of the methyl group. Also the change from ethyl to propyl is smaller than the change from methyl to ethyl. This indicates that the interactions between the β and γ carbons of the side group and the atoms of the chain are independent of the conformation of the main chain. It was found in practically every case that the side group had a single preferred conformation. The rotational angle defined by atoms 1–4 in the structure



prefers values of +70° to +90° for the S configuration and of −70° to −90° for the R configuration. The rotational angle 2,3,4,5 prefers to be trans. The ubiquity of this structure probably explains the independence of the interaction between the β and γ carbons and the main-chain atoms on main-chain conformation.

The approach outlined above for studying the effects of the side group has one serious defect. It neglects the possibility that the side group might alter the Table III structures. To examine this, we located minimum-energy structures of 1,2-bis(methylsulfonyl)propane with the energy minimization algorithm. Starting points for the minimization were the structures in Table III plus all possible gauche–trans sequences. The results obtained may be found in the supplementary material. The only significant structural change is the distortion of certain trans bonds to about 20°. The stabilization of conformations relative to the all-trans conformation is once again observed but is not as strong. We have not studied how these energies change with the addition of more atoms to the side group. We will assume in what follows that the first three atoms of the side group maintain the structure given above.

V. Effect of Long Side Groups

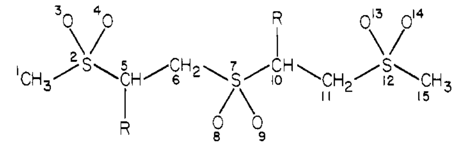
As the size of the side group increases one observes that the conformational properties of the chain level off for side groups 10–15 units long.[6,14] This may imply that the energies of the various conformations change until only one remains Boltzmann accessible. Each additional methylene unit in the side group makes all but one conformation less accessible. A less attractive, alternative explanation is that the relative energies of an entire set of conformations cease to change. The chain with long side groups appears conformationally simpler than the short-side-group chain. In this section we isolate from the list of conformations those that are most likely to accommodate long side groups and also stabilize electrostatic interactions.

It is important to understand the interactions that exist in sections of the chain longer than the single repeat unit.

Table VI
Two-Repeat-Unit Structures Simultaneously Minimizing Side-Group–Main-Chain and Side-Group–Side-Group Interactions

$D^{+*}(R)I^{+}(S)$
$D^{+*}(R)H^{+}(S)$
$D^{+*}(R)B^{+*}(S)$
$D^{+*}(R)G^{-*}(S)$
$C^{+*}(R)I^{+}(S)$
$C^{+*}(R)H^{+}(S)$
$C^{+*}(R)B^{+*}(S)$
$C^{+*}(R)G^{-*}(S)$
$C^{+*}(R)G^{+}(S)$
$C^{+*}(R)C^{-*}(S)$
$D^{+*}(R)C^{-*}(S)$
$D^{+*}(R)B^{+*}(S)$
$D^{+*}(R)G^{+}(S)$
$D^{+*}(R)D^{-*}(S)$
$D^{+}(R)B^{+*}(S)$
$D^{+}(R)G^{-*}(S)$
$D^{+}(R)H^{+}(S)$
$D^{+}(R)G^{+}(S)$
$D^{+}(R)I^{+}(S)$
$C^{+*}(R)I^{-}(R)$
$C^{+*}(R)H^{-}(R)$
$C^{+}(R)I^{+}(S)$
$C^{+}(R)H^{+}(S)$
$C^{+*}(R)B^{-*}(R)$
$C^{+*}(R)G^{+*}(R)$
$C^{+*}(R)D^{-*}(S)$

We now turn our attention to a pair of repeat units, specifically structures of the form



We assume that stable structures of this two-repeat-unit segment can be formed from pairs of single-repeat-unit structures. This requires that interactions between repeat units be sufficiently weak to preserve the structures dictated byt the single-repeat-unit interactions. This assumption is unsupported, but we expect that the longer range interactions can be relaxed by minor variations in the rotational angles since there are so many intervening bonds.

We would like to be able to estimate the interaction between a side group and the main chain, or between two side groups. This interaction would be a potential of mean force felt by the main chain as the side groups sampled their entire configuration space. This potential of mean force would be difficult to calculate. Although the distribution function of atoms in short chains can be determined,[27] it is a rather tedious numerical calculation which would have to be generalized, for example, to the case of two chains of arbitrary initial direction and separation. Such a program goes beyond the preliminary nature of this work. The Abe formalism,[28-30] which treats side chains in the rotational isomeric state model framework, would also be of no help. Since it does not go beyond second-neighbor interactions, it would be incapable of treating the types of interactions we are interested in, e.g., excluded-volume forces between two side groups.

Our approach is as follows. We define four physical points associated with the two-repeat-unit structure: Point P_1, the average position of the first repeat unit (atoms 1–9); point P_2, the average position of the second repeat unit (atoms 7–15); points P_3 and P_4, the positions of the third atom in each of the two side groups when the first three side-group atoms assume the preferred conformation given above. Now we assume that the side-group–monomer interactions are characterized by the distances $|P_1 - P_4|$ and $|P_2 - P_3|$ and that the side-group–side-group interactions are characterized by $|P_3 - P_4|$. We tabulate these distances for all possible pairs of conformations considered in the 1,2-bis(methylsulfonyl)pentane calculations including both *S* and *R* configurations and potential sets 1–5, a few thousand possibilities for each potential set. Of all these structures, we isolate those that simultaneously give large values of the three distances $|P_1 - P_4|$, $|P_2 - P_3|$, and $|P_3 - P_4|$. Keeping only structures for which all three distances are in the 75th percentile leads to about 25 structures in all. For example, we list in Table VI the structures obtained for the set 1 conformations. Each structure in Table VI has a mirror image counterpart, which is not shown.

Table VII
Two-Repeat-Unit Structures Simultaneously Minimizing Side-Group–Main-Chain and Side-Group–Side-Group Interactions That Can Be Incorporated into Chains

$C^{+*}(R)C^{-*}(S)$
$C^{+*}(R)D^{-*}(S)$
$D^{+*}(R)D^{-*}(S)$
$D^{+*}(R)E^{+}(S)$
$D^{+*}(R)C^{-*}(S)$
$D^{+*}(R)D^{-*}(S)$
$E^{-}(R)D^{-*}(S)$
$E^{-}(R)E^{+}(S)$

Mirror Images

$C^{-*}(S)C^{+*}(R)$
$C^{-*}(S)D^{+*}(R)$
$D^{-*}(S)D^{+*}(R)$
$D^{-*}(S)E^{-}(R)$
$D^{-*}(S)C^{+*}(R)$
$D^{-*}(S)D^{+*}(R)$
$E^{+}(S)D^{+*}(R)$
$E^{+}(S)E^{-}(R)$

In Table VI and the remainder of the paper the notation for each conformation has been altered to account for the symmetries that are broken when the side group is added. The superscripts + or – indicate that the signs of the three rotational angles as they appear in Table III should be either retained or reversed. The superscript asterisk indicates that the order of the three rotational angles should be reversed. The *S* and *R* are the usual notation for absolute configuration at the chiral carbon.

Almost without exception, the structures isolated in this way have opposite chiralities at the two chiral carbons. In other words, the polymer can best accommodate large side groups if the side groups alternate in absolute configuration. Stereospecificity could arise when steric hindrance stabilizes the proper transition state during polymerization, particularly for long side groups. No experimental evidence about the tacticity of the large-side-group polymers is available. NMR spectra would probably show many crowded peaks and would not be an accurate probe of the tacticity.[31] The short-side-group polymers are atactic.[16] The steric forces probably are not sufficient to force stereospecificity unless the side groups are long.

We can still eliminate many of the two-repeat-unit structures arrived at in this way. We only accept units appearing both on the right and on the left of the pairs in Table VI, since in the chain the left unit of one pair is the right unit of the next pair. When this is done for the structures from both the 1,2-bis(methylsulfonyl)ethane and -propane calculations for potential sets 1–5, we limit the list to those shown in Table VII. The E conformation appears as a minimum-energy conformation in only two of the six potential energy surfaces for 1,2-bis(methylsulfonyl)ethane and not at all for 1,2-bis(methylsulfonyl)propane, so we omit from Table VII all but the C and D conformations. (In the helix calculations described below, we also find that the helices built up with E conformations exhibit excessive steric overlap, thus providing additional justification for removing them.) In addition, $D^{+*}(R)$ or $D^{-*}(S)$ occurs only for set 6 in the 1,2-bis(methylsulfonyl)propane potential surfaces. However, the C and D conformations are very similar, differing by rotations of 20–30° about several bonds. So, although D seems inappropriate, we will retain it for reasons to become apparent later. The true conformation assumed by the polymer may prove to be some hybrid of the C and D forms. We conclude that the polymer with long side groups prefers a stereospecific helix where each repeat unit assumes structures resembling the C* or D* conformations.

We recognize that the approach in this section is far from a precise treatment of the side-group interactions.

Table VIII
Parameters of a Number of Different Helices[a]

φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	$z_{2\pi}$	θ	$m_{2\pi}$	$\mu_{2\pi}$	μ_R	A
−100.9	66.7	1.0	100.9	−66.7	−1.0	0.00	138.4	5.20	0.00	0.00	0.00
−112.1	66.5	0.6	112.1	−66.5	−0.6	0.00	140.0	5.14	0.00	0.00	0.00
−108.2	65.5	0.9	108.2	−65.5	−0.9	0.00	139.3	5.17	0.00	0.00	0.00
−111.1	64.5	1.4	111.1	−64.5	−1.4	0.00	138.5	5.20	0.00	0.00	0.00
−100.9	66.7	1.0	69.5	−87.8	7.6	5.47	152.0	4.74	2.62	0.55	0.48
−104.6	67.9	1.1	74.2	−90.9	3.2	5.85	150.1	4.80	3.17	0.66	0.54
−103.2	68.5	1.4	71.9	−93.9	2.4	6.22	150.3	4.79	3.42	0.71	0.55
−108.2	65.5	0.9	78.9	−89.6	−2.9	6.39	146.1	4.93	3.71	0.75	0.58
−112.1	66.5	0.6	82.4	−97.7	−9.8	7.46	144.1	5.00	5.04	1.01	0.68
−111.1	64.5	1.4	95.1	−95.4	−28.0	8.16	123.8	5.81	6.37	1.10	0.78

[a] The first six columns give the sequence of bond rotational angles that generate the helix. Columns 7-12 give, respectively, the quantities $z_{2\pi}$, θ, $m_{2\pi}$, $\mu_{2\pi}$, μ_R, and A, which are defined in the text. Here, the unit of length is the angstrom, the unit of dipole moment is the debye, and angles are given in degrees.

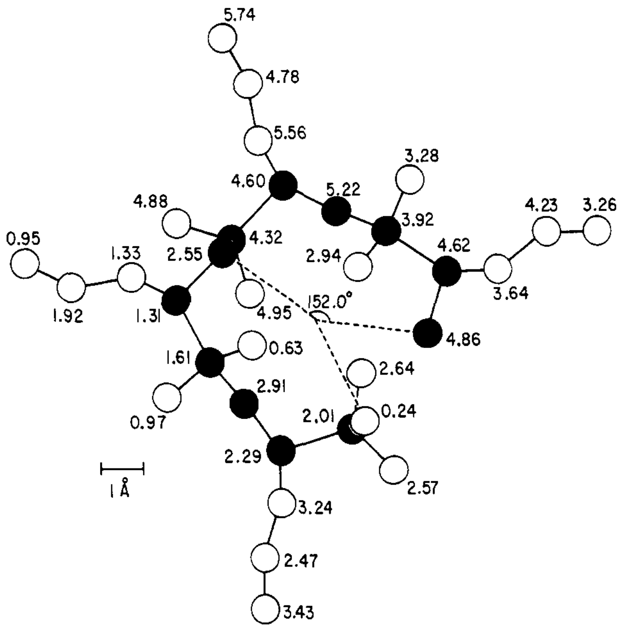


Figure 1. Four repeat units of the fifth helix listed in Table VIII.

We only adopt it as a heuristic calculation, which, with some luck, will yield the preferred conformation of the long-side-group polymers. As will become apparent below, the conformation obtained in this fashion seems consistent with present experimental fact but additional work will, of course, be necessary before if can be accepted.

VI. The Helix

It is not difficult to show that polymers in which the rotational angles repeat periodically assume helix structures and that any dipole moment associated with the structure lies parallel to the helix axis for sufficiently long helices.[32] Various helix parameters were calculated[32] for several $C^{+*}(R)C^{-*}(S)$ and $C^{+*}(R)D^{-*}(S)$ sequences, with the results shown in Table VIII. In addition to these ...CCC... and ...CDCD... sequences, several higher order sequences, e.g., ...CCDCCD... etc., were examined. The parameters calculated include $z_{2\pi}$, the pitch of the helix, or displacement along the helix axis per turn; θ, the angle through which the helix rotates for every pair of repeat units; $m_{2\pi}$, the number of repeat units per turn of the helix; $\mu_{2\pi}$, the component of the dipole moment along the helix axis per turn of the helix; μ_R, the component of the dipole moment along the helix axis per repeat unit; and A, the component of the dipole moment along the helix axis per unit length. Figures 1 and 2 show projections of four repeat units for each of two different helices onto a plane perpendicular to the helix axis. Figure 1 is the (−100.9, 66.7, 1.0, 69.5, −87.8, 7.6) helix obtained by pairing structures from the set 1 1,2-bis(methylsulfonyl)ethane calculations. Figure 2 is the (−111.1, 64.5, 1.4, 95.1, −95.4, −28.0) helix obtained from structures from the set 1,2-bis(methylsulfonyl)propane calculations. The backbone atoms are shown in black. Beside each atom is shown its distance behind the plane of projection. Note that the side groups radiate out from the helix. Zero-pitch helices result if the second three bonds are exact mirror images of the first three bonds and therefore cannot be accepted. This is the motivation of retaining the D* conformations. For the same reason, the higher order sequences such as ...CCDCCD... also had intolerably small pitches. We therefore believe that the ...CDCD... helix represented in Figures 1 and 2 and by the last six entries of Table VIII best represents the structure of the polymer.

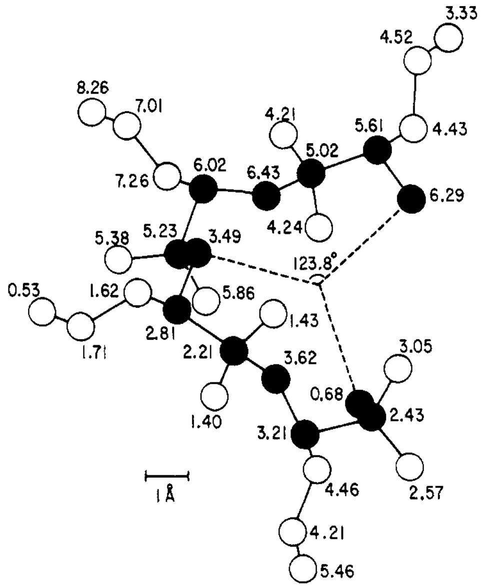


Figure 2. Four repeat units of the last helix listed in Table VIII.

The last six entries of Table VIII show a correlation between the rotational angle of the sixth bond and the values θ, $z_{2\pi}$, and $\mu_{2\pi}$. Figures 1 and 2 represent the two extremes obtained by varying the sixth rotational angle. The extreme represented by Figure 2 could be a more accurate picture of the polymer conformation for the following reasons: First, that particular value of the sixth rotational angle is expected, on the basis of calculations described in section IV (consult supplementary material), in the presence of the side group. Second, the side groups are seen in Figures 1 and 2 not to protrude horizontally, relative to the helix axis, but to alternate up and down. Interference between side groups on adjacent turns of the helix would tend to force an even number (i.e., 6) of repeat units, rather than an odd number (i.e., 5). Third, the large value of the pitch minimizes interference between turns of the helix and offers good accessibility to solvent molecules. In any case, small changes in rotational angles generate large changes in the overall helix structure, and the longer range forces arising from interactions not considered explicitly here can probably be relaxed with minor adjustments of the rotational angles. It is premature to insist on exactly C and D structures, but we believe that helices something like these can be expected.

If, as a result of rather long sequences of helices, there is no appreciable transverse dipole moment, and only a small number of repeat units not in helical sections, then we expect direct proportionality between the total dipole moment and the end-to-end vector: $\mu = Ar$, with A given by the final column of Table VIII. The proportionality constant can also be estimated experimentally, $A = \langle\mu^2\rangle^{1/2}/\langle r^2\rangle^{1/2}$. Using experimental values[6] of these two root-mean-square means (both in the perturbed state; $\langle r^2\rangle$ computed from intrinsic viscoscity data) gives $A = 0.30$, 0.48, and 0.50 D/Å for polymers with side groups of 3, 6, and 14 carbons, respectively. The two latter values of A are in good agreement with the values shown in Table VIII, consistent with our prediction that the helix structure will dominate when the side group is long enough.

Now assume that the polymer exists as sequences of helical sections. Suppose each section contains m repeat units and occurs with frequency n_m. Let μ_R be the dipole moment per monomer and g the mean projection of the helix axis of one section on the succeeding section. Then we obtain[18]

$$\langle\mu^2\rangle = K\sum_m n_m(m\mu_R)^2 \tag{7}$$

where $K = (1 + g)/(1 - g)$ is of order unity. Now the number of monomers $x = \sum_m mn_m$, so that

$$\langle\mu^2\rangle/x = K\bar{m}_w\mu_R^2 \tag{8}$$

where $\bar{m}_w = \sum m^2n_m/\sum mn_m$ is the weight-average number of repeat units in a helical section. Taking $\mu_R = 0.7$ D (consistent with Table VIII and independent studies[15]) and previously measured[6,14] values of $\langle\mu^2\rangle$ yields $\bar{m}_w = 8$, 37, 62, and 110 for side groups containing 3, 4, 6, and 14 carbon atoms, respectively and for $K = 1$. If we further assume that the helical sequences obey the "most probable distribution"[33] (accurate only if a monomer has a probability p of being in a helical sequence independent of the state of all other monomers) and that $K = 1$, then[15,33]

$$\langle\mu^2\rangle/x = \mu_R^2(1 + p)/(1 - p) \tag{9}$$

and

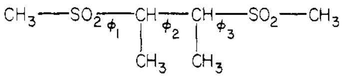
$$\bar{m}_n = (1 - p)^{-1} \tag{10}$$

for $\bar{m}_n$ the number-average number of repeat units in a helical section. This yields $p = 0.78$, 0.95, 0.97, and 0.98 and $\bar{m}_n = 5$, 19, 31, and 55 for side groups containing 3, 4, 6, and 14 carbon atoms. A similar value of p (about 0.96) has been given independently by Fawcett and Fee[15] for four carbons in the side group.

We would not, on the basis of these calculations, have predicted such a great stability for the helix in the shorter-side-group polymers, since these calculations (see section IV) indicate that structure A (all-trans) is the preferred conformation. It may well be that an additional source of stabilization is the head-to-tail arrangement of the dipole moments associated with each turn of the helix.

Decay of correlation in the helix direction could result from thermal population of less stable conformations, fluctuations in the bond rotational angles[34,35] of monomers in the helix, and from left-hand–right-hand reversals caused by reversals in tacticity. The monomers at which the tacticity reversals occurred would probably be forced into some other conformation and lead to some unknown correlation in the directions of the two helix sections on either side. Note that the tacticity reversals will not reverse the direction of the dipole moment relative to the helix axis (dipole moment vectors and displacement vectors transform the same under coordinate system inversions), so that the polymer will continue to build up dipole moment.

Table IX
Minimum-Energy Conformations of (*R*,*S*)-2,3-Bis(methylsulfonyl)butane for Two Different Potential Energy Sets[a]



$$CH_3\text{—}SO_2\overset{\phi_1}{\text{—}}\underset{\displaystyle CH_3}{CH}\overset{\phi_2}{\text{—}}\underset{\displaystyle CH_3}{CH}\overset{\phi_3}{\text{—}}SO_2\text{—}CH_3$$

	set	φ_1	φ_2	φ_3	energy
A⁺(R,S)	6	12.9	0.0	−12.9	0.00
	3	12.3	0.0	−12.3	0.00
B⁺(R,S)	6	10.8	−2.3	90.3	1.13
	3	9.9	−2.8	91.2	1.29
B⁻(R,S)	6	14.6	2.3	−131.8	1.23
	3	14.0	2.5	−131.1	1.24
H⁺(R,S)	6	133.4	0.0	−133.4	1.28
	3	132.8	0.0	−132.8	1.29
H⁻(R,S)	6	−91.2	0.0	91.2	1.36
	3	−92.2	0.0	92.2	1.71
I⁻(R,S)	6	−91.4	0.8	−133.7	2.30
	3	−92.3	0.9	−133.0	2.48
	6	−20.6	101.6	49.8	6.42
	3	−19.7	101.1	48.1	6.79
D⁺(R,S)	6	−21.2	101.3	−64.3	7.04
	3	−20.3	100.8	−65.0	7.45
	6	−17.7	100.2	164.0	9.48
	3	−17.0	99.6	162.3	9.76

[a] Energies shown are relative to all-trans and in units of kcal/mol.

The helix structure provides excellent solvation of the side groups by thrusting them outward from the molecule. This fact, along with increased shielding of the SO_2 groups by long side groups, is consistent with the increase in solubility in the nonpolar solvents as the side groups grow.

As for poly(styrene sulfone), the lack of a regular repeat unit completely destroys the possibility of helix formation. The dipole moment is once again modest,[5] and no longitudinal component is built up.

VII. Calculations on 2,3-Bis(methylsulfonyl)butane: Effect of Two Side Groups on Conformations

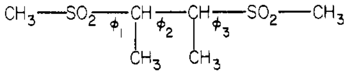
Minimum-energy conformations of 2,3-bis(methylsulfonyl)butane ($(CH_3SO_2CHCH_3)_2$) for both potential sets 3 and 6 were obtained by energy minimization from the structures in Table III and all possible gauche–trans sequences. Results for each diastereomer of this molecule are shown in Tables IX and X, respectively. Only the lower energy conformations have been displayed. As can be seen, the C–C bond is almost always trans, consistent with the results of Fawcett and Ivin.[11,12]

VIII. Summary

A. Conformational Properties. These calculations have elucidated the conformational properties of two different classes of poly(alkene sulfones): namely, those with a single side group and those with two short side groups on adjacent carbons. The following predictions can be made about both classes.

A helix of about 5 or 6 repeat units per turn and a pitch of about 6–8 Å resembling Figures 1 or 2 is the favored

Table X
Minimum-Energy Conformations of (*R*,*R*)-2,3-Bis(methylsulfonyl)butane for Two Different Potential Energy Sets[a]



$CH_3—SO_2 \overset{\phi_1}{—} CH(CH_3) \overset{\phi_2}{—} CH(CH_3) \overset{\phi_3}{—} SO_2—CH_3$

	set	φ_1	φ_2	φ_3	energy
A^+(R,R)	6	−18.7	−2.7	−18.7	0.00
	3	−17.7	−2.5	−17.7	0.00
B^-(R,R)	6	−17.7	−0.8	−132.5	2.10
	3	−16.6	−0.5	−131.8	2.04
B^+(R,R)	6	−19.4	−2.1	94.2	3.15
	3	−18.3	−1.9	94.9	3.24
I^-(R,R)	6	−133.4	−0.1	−133.4	3.22
	3	−132.6	0.2	−132.6	3.12
D^+(R,R)	6	18.0	116.3	−88.4	3.52
	3	17.7	116.4	−88.6	3.67
H^-(R,R)	6	−131.9	0.5	95.6	4.27
	3	−131.1	0.9	96.4	4.28
J^+(R,R)	6	139.9	117.8	139.9	4.45
	3	139.7	117.9	139.7	4.49
E^-(R,R)	6	−56.6	114.4	−56.6	4.59
	3	−56.4	114.3	−56.4	5.36

[a] Energies shown are relative to all-trans and in units of kcal/mol.

conformation for those polymers with a single side group. This helix is stabilized by short-range electrostatic interactions (between adjacent SO_2 groups), by side-group interference and solvation, and, apparently, by longer range electrostatic interactions between separate turns of the helix. For longer side groups, steric forces may produce stereospecificity during polymerization, which would lead to further preference of the helix. As the helix becomes more important, the SO_2 dipoles become more strongly correlated and the net dipole moment of the molecule grows. For the longest side groups the primary sources of static flexibility may be helix reversals caused by tacticity reversals or fluctuations in the shape of the helix caused by fluctuations in rotational angles.

When two short side groups are present on adjacent carbons, the C–C bonds of the backbone favor trans highly, and the net dipole moment is much smaller (but nonvanishing; see below). This conclusion has already been reached by Fawcett and Ivin.[11,17]

B. Dynamical Properties. On the basis of experimental results[14,15] and supported by these calculations, the evidence seems compelling that the low-frequency molecular-weight-dependent dielectric relaxation observed in the single-side-group polymers is not a result of tumbling of the molecule in a more or less unchanging conformation, as had once been thought, but is due to the lowest Zimm mode of a more dynamically flexible molecule. The lowest Zimm mode is rendered dielectrically active through the formation of a helix and a resulting dipole moment along the helix axis. Even the molecules with very long side groups, to which we now ascribe very little static flexibility, can display a great deal of dynamic flexibility due to fluctuations in rotational angles.[34,35] Indeed, it has been pointed out that only such motions dominate in the lower Zimm modes.[36] Additional types of motions may, of course, be possible, especially for shorter side groups, including the motion of individual segments shuttling in and out of helical conformation.

When two side groups are present on adjacent carbons, the C–C bonds can better favor trans, the helix does not form, so there is no longitudinal dipole moment, and a low-frequency relaxation is neither expected nor observed. A high-frequency relaxation is present,[6,7] indicating that the C–C bonds are not all strictly trans (trans states at all C–C bonds will precisely cancel any net dipole moment[11]). Thermal population of nontrans conformations, fluctuations of the C–C rotational angles about their potential minima,[34] and the possibility that these minima are not exactly 0° probably explain this. The absence of the helix in poly(styrene sulfone) is also adequate to explain the dielectric relaxation of these polymers.

Acknowledgment. The author thanks Professor Walter H. Stockmayer for a number of helpful suggestions and conversations. This work was supported by the National Science Foundation under Grants DMR76-22987 and DMR79-13227 of the Polymers Program, Division of Materials Research, and Grant No. CHE-8000910.

Supplementary Material Available: Tables giving additional results of conformational calculations (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Bates, T. W.; Ivin, K. J.; Williams, G. *Trans. Faraday Soc.* **1967**, *63*, 1964.
(2) Bates, T. W.; Ivin, K. J.; Williams, G. *Trans. Faraday Soc.* **1967**, *63*, 1976.
(3) Fawcett, A. H.; Ivin, K. J. *Polymer* **1972**, *13*, 439.
(4) Stockmayer, W. H.; Jones, A. A.; Treadwell, T. L. *Macromolecules* **1977**, *10*, 762.
(5) Stockmayer, W. H.; Matsuo, K.; Guest, J. A.; Westphal, W. B. *Makromol. Chem.* **1979**, *180*, 281.
(6) Matsuo, K.; Stockmayer, W. H., to be submitted.
(7) Mashimo, S.; Matsuo, K.; Cole, R. H.; Winsor, P., IV; Stockmayer, W. H., to be submitted.
(8) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(9) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.
(10) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(11) Fawcett, A. H.; Ivin, K. *J. Polymer* **1975**, *16*, 569.
(12) Fawcett, A. H.; Heatley, F.; Ivin, K. J.; Stewart, C. D.; Watt, P. *Macromolecules* **1977**, *10*, 765.
(13) Herlihy, E. M. A. Thesis, Dartmouth College, 1977.
(14) Matsuo, K.; Mansfield, M. L.; Stockmayer, W. H. *Macromolecules* **1982**, *15*, 935.
(15) Fawcett, A. H.; Fee, S. *Macromolecules* **1982**, *15*, 933.
(16) Cais, R. E.; Bovey, F. A. *Macromolecules* **1977**, *10*, 757.
(17) Fawcett, A. H.; Ivin, K. J. *Polymer* **1975**, *16*, 573.
(18) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(19) Scheraga, H. A. *Adv. Phys. Org. Chem.* **1968**, *6*, 103.
(20) Brant, D. A.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 2791.
(21) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1965**, *42*, 2209.
(22) Brant, D. A.; Miller, W. G.; Flory, P. J. *J. Mol. Biol.* **1967**, *23*, 47.
(23) Gibson, K. D.; Scheraga, H. A. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 420.
(24) Shieh, C.-F.; McNally, D.; Boyd, R. H. *Tetrahedron* **1969**, *25*, 3653.
(25) Hägele, P. C.; Pechold, W. *Kolloid Z. Z. Polym.* **1970**, *241*, 977.
(26) Boyd, R. H., personal communication, 1979.
(27) Freire, J. J.; Rodrigo, M. M. *J. Chem. Phys.* **1980**, *72*, 6376 and references cited therein.
(28) Abe, A. *J. Am. Chem. Soc.* **1968**, *90*, 2205.
(29) Abe, A. *Polym. J.* **1970**, *1*, 232.
(30) Abe, A. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 54*, 135.
(31) Bovey, F. A., personal communication to W. H. Stockmayer, 1980.
(32) Mansfield, M. L. Ph.D. Thesis, Dartmouth College, 1980.
(33) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(34) Mansfield, M. L. *J. Chem. Phys.* **1980**, *72*, 3923.
(35) Olsen, W. K. *Macromolecules* **1980**, *13*, 721.
(36) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979; pp 168ff.