Application of the Molecular Simulation Technique To Generate the Structure of an Aromatic Polysulfone System

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ABSTRACT: A model of an amorphous polysulfone, patterned after Udel (Union Carbide Corp.) polysulfone, was generated using a molecular simulation technique. The pair distribution functions obtained for the model structures showed no evidence of long-range order. The properties of these simulated structures are in good agreement with available experimental data. For example, the average density of the calculated structures is 1.17 ± 0.02, a value which compares favorably with an experimental value of 1.24 ± 0.04. The distributions obtained for the torsional angles along the backbone are consistent with model compounds. Contour maps obtained through molecular mechanics show that the conformational distribution of the torsional angles is widest for torsion about the C–S bonds. The calculations indicate that rotational barriers for C–O or C–C bonds are higher than those for C–S bonds and suggest that the mechanism for relaxation in the bulk state may be due to cooperative ring-flip motions associated with rotations about the C–S linkages.

Introduction

For a number of reasons, the amorphous structure of polymeric materials is of great interest. From an application viewpoint, the mechanical and thermal properties of polymers strongly depend on the structure and dynamics of the amorphous state, even for semicrystalline polymers. Because of the availability of numerous characterization techniques for crystalline polymers, their structural parameters are often well-known. The same situation does not exist for amorphous polymers. Usually the best that can be done is to define global chain dimensions, such as the end-to-end distance, radius of gyration, or density derived from scattering methods. Additional information concerning localized structures can be obtained from spectroscopic methods. Even under optimum conditions, detailed structural information or the properties of these structures can be difficult to obtain.

We have recently begun to utilize molecular simulations as a technique complementary to our experimental program to characterize the structures and properties of amorphous polymers. Many previous studies have been carried out using programs developed in various individual laboratories.[1-8] Commercial software, with its greater emphasis on visualization capabilities, is used in this work together with analysis programs developed in our own laboratory. Over the last few years, the marked increase in computing power available to the bench scientist has played a significant role in advancing materials research. The advent of widely available workstations combining high computation speed and superb graphics greatly aids molecular simulation studies for determining geometric parameters, atomic charges, chain flexibility, nature of local relaxation mechanisms, crystalline packing, and a wide variety of elastic properties. With currently available workstations and the associated software, molecular simulation techniques have been widely utilized by molecular biochemists or physicists. These techniques are also now beginning to be exploited in studies of the static or dynamic behavior of synthetic polymers.

In this study, molecular mechanics and molecular dynamics are applied to studies of an amorphous aromatic polysulfone (PSF). Aromatic PSF is an important engineering plastic, possessing excellent thermal stability. Most variants of PSF are completely amorphous with the glassy state encompassing a large temperature range. This study focuses on generation of a model for the amorphous polysulfone as well as on studies of the overall and local structures of this polymer. Rotational isomeric states of individual bonds and energy barriers between various minima in the rotational potential of PSF are calculated, information required for characterization of chain properties. In addition, long-range interactions arising from neighboring chains are approximated by utilizing periodic boundary conditions. Newly developed amorphous building software is used to generate amorphous chains which display properties that agree with experiment. In this study, an analysis of the PSF structure is presented. Other studies regarding thermal and mechanical properties will follow.

Simulation

The monomer repeat unit of aromatic polysulfone, poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene), is shown in Figure 1. The degree of polymerization, *n*, is set at 10. Because of the large monomer size of PSF, the total number of atoms (541) and the resultant contour length of the polymer chain are reasonably large. A commercial material simulation package, POLYGRAF by Molecular Simulations, Inc., is used to generate the polymer chain and amorphous structure. The force field used in calculation of molecular mechanics and molecular dynamics has been published previously.[9]

The bulk amorphous state is simulated by use of periodic boundary conditions. A polymer chain is packed into a unit cell, and the cell is infinitely repeated in a three-dimensional space. The initial density, which is specified in order to generate a model amorphous structure, was 1.20, close to the experimental value of 1.24 ± 0.04.[10] Several structures with an initial density of 1.30 was also considered. The optimum density of the system was calculated using energy minimization molecular mechanics. The conventional method for generation of a polymer chain includes use of a rotational isomeric state (RIS) model. Although rotational barriers of particular segments in PSF have been studied,[11-15] the localized structure of this polymer is not well-defined. The PSF chain is

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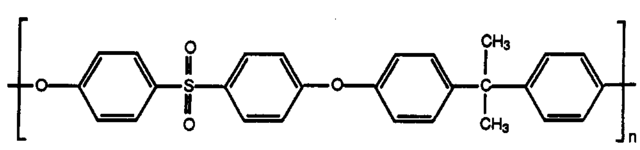

Figure 1. Chemical structure of the aromatic polysulfone chain.

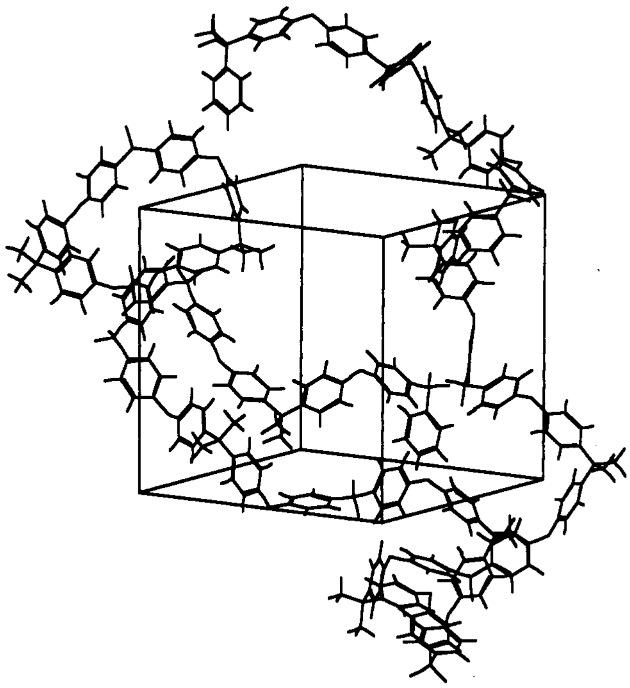

Figure 2. Structure of an amorphous chain generated. The cell is defined to accommodate the overall molecular weight of the polymer chain. The density in this case is 1.17 g/cm^3.

accordingly generated by randomly assigning the backbone torsional angles using a Monte Carlo method. In the process of packing a polymer chain into a defined space with a specified density, the minimum distance allowed for two nonbonded atoms is the sum of the van der Waals radii of the atoms. As monomer units are added to the backbone of the growing chain, the nonbonded distances of the conformation are checked. High-energy conformations, due to overlap of the van der Waals radii, are rejected. A new conformation is then automatically generated and the process repeated. If, after several attempts, the program fails to find an acceptable conformation, it will "back up", delete the previous monomer, and start the process anew. Generation of a polymer chain packed at high density usually requires a downward scaling of the van der Waals radii of the atoms. The van der Waals radii used initially for packing polysulfone were only 30% of their full value and were returned to full value upon completion of packing of the amorphous structure. In order to obtain suitable statistics for further analysis, 10 structures were generated.

The initial structures as generated are usually in a highly energetic state, mainly because of the steric interactions associated with nonbonded van der Waals forces. The total potential energy of the model is then minimized using a conjugated gradient algorithm. To prevent the system from being trapped in a metastable high-energy local minimum requires operation of molecular dynamics at the 300–500 K temperature range. In most cases, molecular mechanics energy minimization and molecular dynamics were alternated for each initial structure. The structure with the lowest energy over many runs was used for further analysis. Generally 5–8 cycles of energy minimization/molecular dynamics are performed for each model structure. The duration of a typical dynamics run is 20 ps. The convergence criteria for each minimization process is a root-mean-square (rms) force of less than 0.1 MPa. Considering the size of the molecules that are being simulated, great effort has been extended to bring each structure to a relatively low energy local minimum. One of the 10 structures obtained in this fashion is shown in Figure 2. Only the central chain and cell are shown. Because of the periodic boundary condition, this central chain and cell is surrounded by 26 similar cells. If a portion of the chain exits the cell, it will reenter the cell from the opposite surface. When the periodic boundary conditions is imposed, the nonbonded interaction is calculated through an Ewald summation.

Table I
Cell Parameters (Å and deg) Containing One Amorphous Polysulfone Chain

$a = 18.39 \pm 0.51$	$\alpha = 89.88 \pm 1.22$
$b = 18.43 \pm 0.30$	$\beta = 90.21 \pm 1.74$
$c = 18.50 \pm 0.27$	$\gamma = 89.97 \pm 0.70$

The advantage of the Ewald summation for calculating nonbonded interactions has been considered. In our study, we have also used potential terms with a cutoff at 9 Å for the model PSF structures. The energies thus obtained are consistently higher, by approximately 50–80 kcal/mol, than those calculated by the Ewald summation method as long-range attractive interactions cannot be properly accounted for using potentials with a cutoff. The cohesive energy densities calculated without Ewald summation are significantly lower than experimental values. Our results, combined with previous simulation studies,[2] suggest the need for incorporation of the "tail correction" in order to obtain high accuracy.

As shown in Figure 1, this aromatic polysulfone has many polar groups along the backbone. To simulate a model chain correctly, specific interactions between these polar groups must be taken into account accurately. The conventional method is to calculate the partial charges on each atom and include Coulombic electrostatic interactions. Two methods were used to calculate partial charges for each atom.[16,17] The structures generated including such interactions were not satisfactory. The cohesive energy calculated was much lower than the experimental value if electrostatic interactions were included. For this particular polymer, structural calculation without charges is a more reasonable approach, since nonbonded energy parameters in the force field have taken some of the electrostatic interactions into account.[9]

Results and Discussion

The simulated PSF structure is shown schematically in Figure 2. Structural parameters are presented in Table I. Values obtained indicate that the structure is isotropic in nature as the parameters exhibit negligible deviation from a totally symmetric *cell*. The average density of the 10 structures generated is 1.17 ± 0.02 g/cm^3, in comparison to the experimental value of 1.24 ± 0.04 g/cm^3. For the structures generated using an initial density of 1.30, the ultimate density obtained is also 1.17–1.18 g/cm^3. Depending on chemical substitution and thermal history, the PSF density has been observed to differ significantly. The components of the internal stress tensor are defined as the first derivatives of the potential energy per unit volume with respect to strain

$$\sigma_{ij} = \frac{1}{V}\frac{\partial U}{\partial \epsilon_{ij}} \qquad (1)$$

where U is the potential energy, ϵ_{ij} is the component of the

Table II
Internal Stress Tensor of One Model Polysulfone (MPa)

	x	y	z
x	0.06 ± 0.21		
y	-0.06 ± 0.16	0.10 ± 0.16	
z	-0.05 ± 0.20	-0.09 ± 0.10	-0.09 ± 0.11

strain tensor, and V is the volume of the system. For a state at equilibrium, with no external force, the potential energy is at a minimum. The first derivative of the potential energy, the internal stress tensor, should vanish and may be calculated by summing the forces acting between every pair of atoms

$$\sigma_{ij} = \frac{1}{2V}\sum (r_i^k F_j^{kl} + r_i^l F_j^{lk}) = \frac{1}{2V}\sum (r_i^k - r_i^l) F_j^{kl} \quad (2)$$

where r_i^k is the ith coordinate of atom k and F_j^{kl} is the jth component of the interaction force between the kth and lth atoms. A large value would indicate net stress on the system, with positive values indicating tension and negative values indicating compression. For all optimized structures, the internal stress components were nearly zero, deviating at most by 0.10 MPa from zero as shown in Table II. This indicates that each structure is relaxed and stress free, as anticipated for an equilibrium structure.

The characteristic ratio, defined as

$$C_n = \frac{1}{nl^2}\langle r^2 \rangle_0 \quad (3)$$

can be used to characterize chain flexibility. In this expression, n is the number of structural units, l is the effective length of each structural unit, and $\langle r^2 \rangle_0$ is the unperturbed square of the end-to-end distance.[18] For the most flexible chain, i.e., that most gaussian-like, $C_n = 1.00$. For PSF, there are effectively two types of bonds, O–C_6H_4–S (5.82 Å) or O–C_6H_4–C (5.76 Å). For calculation of the characteristic ratio, the value of l used is 5.79 Å, the average of the two. Each model polymer chain contains 40 bonds. The average end-to-end distance measured for the 10 simulated structures was 48.2 ± 23.7 Å. The root-mean-square end-to-end distance, $(\langle r^2 \rangle)^{1/2}$, was 53.20 Å, and the average chain length was 231.6 Å. The calculated characteristic ratio was 2.11, compared to 1.79 calculated for polycarbonate.[19–21] Characteristic ratios of most polymers are typically in the 4–10 range.[18] The characteristic ratio obtained for PSF indicates this polymer to be coil-like.

The fundamental difference between crystalline and amorphous states is the existence of long-range order in the former and absence of long-range order in the latter. Long-range order may be most conveniently described by the pair distribution function. A complete characterization of an amorphous polymer such as PSF, which possesses many different atoms, requires a complete set of pair distribution functions. Only the total pair distribution function, $g(r)$, is considered. The function $g(r)$ is defined as the probability of finding any two atoms at a distance r apart in the simulated structure relative to the expected probability calculated for a completely homogeneous phase with random atoms.[22] In the simulated structure, $g(r)$ can be calculated using the expression[23]

$$g(r) = \frac{\rho_r}{\rho} = \frac{N_r V}{N(4\pi r^2)\,\mathrm{d}r} \quad (4)$$

where ρ_r is the number of atoms in the volume element, ρ is the overall number density, N_r is number of atoms inside the shell, N is the total number of atoms in the system, and V is the defined volume.

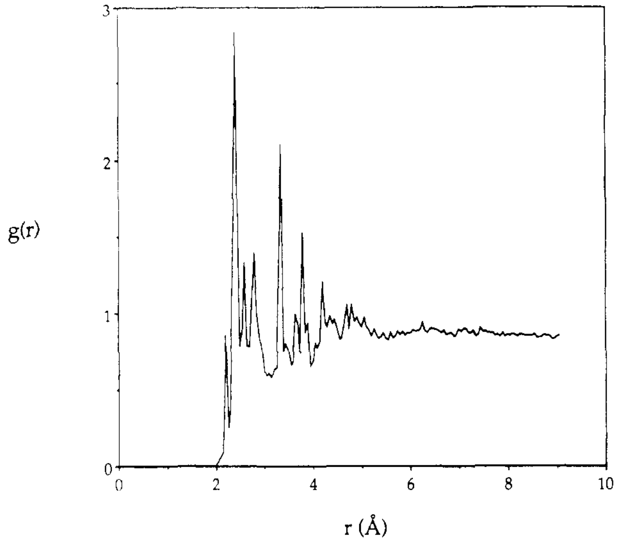

Figure 3. Pair distribution function found for a model amorphous polysulfone.

Table III
Energy Decomposition of One Model Polysulfone Chain (kcal/mol)

	bulk	single chain
bonds	111.7 ± 2.5	112.8 ± 0.5
angles	96.7 ± 5.1	68.3 ± 3.4
torsions	64.0 ± 8.3	42.7 ± 1.2
inversions	4.6 ± 0.9	1.2 ± 0.2
van der Waals	274.8 ± 9.0	585.6 ± 8.4
total	551.8 ± 16.7	810.5 ± 9.3

The calculated pair distribution function for simulated PSF is shown in Figure 3. The value of $g(r)$ in the range $r < 2$ Å is not plotted. $g(r)$ is zero for $r < 1$ Å. Between 1 and 1.75 Å, $g(r)$ exhibits spikes associated with specific atomic placements within covalent bonds. For example, at ~1.0 Å, $g(r)$ equals 11 as all C–H bonds are calculated to be ~1.08 Å. Another sharp spike in $g(r)$ is associated with the interatomic C–C bonds of phenyl rings. The difference between the small-molecule liquid and disordered polymer is that short-range order in polymers is dominated by specific fixed distances associated with backbone atoms. The pair distribution function clearly demonstrates the amorphous nature of the simulated PSF structure, i.e., complete absence of long-range order. Another feature of note is the absence of sharp spikes in $g(r)$ for interatomic distances in the range 5.4–6.0 Å. Distances between atoms x and y separated by a phenyl ring, x–C_6H_4–y, along the polymer chain are expected in this region. Absence of any peak indicates that the effect of connectivity disappears at a relatively short distance, ~5 Å. The Fourier transform of $g(r)$ is $S(r)$, the structure factor, which can be measured by the scattering method. If order does not exist in $g(r)$, it cannot be observed by any experimental method. Without independent measurements, it is difficult to conclude the existence of order in the range of 5–6 Å.

Table III presents various contributions to the overall potential energy of PSF. Both the single-chain approximation and the bulk state have been considered. It is evident that valence angles and torsional angles are somewhat distorted in both states so as to produce more favorable packing of PSF chains. The slight increase in intramolecular terms is more than compensated by the decrease in the intermolecular terms. The energy difference between a chain in bulk versus a single chain is defined as the cohesive energy of the system. The Hilde-

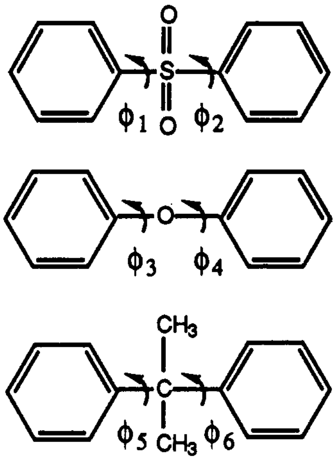

Figure 4. Definition of the structural parameters used in rotational potential contour calculation.

brand solubility parameter, δ, is defined as the square root of the cohesive energy density. These expressions are

$$E_{\mathrm{coh}} = E_{\mathrm{single}} - E_{\mathrm{bulk}} \tag{5}$$

$$\delta = (E_{\mathrm{coh}}/V_{\mathrm{m}})^{1/2}\ (\mathrm{cal/cm^3})^{1/2} \tag{6}$$

where E_{coh} is the cohesive energy, E_{single} is the total energy of a single chain, E_{bulk} is the energy of the simulated bulk state, and V_{m} is the molar volume of the system. The solubility parameter calculated for the PSF chain is 8.29 $(\mathrm{cal/cm^3})^{1/2}$. If the cohesive energy density is defined as that also associated with nonbonded interactions, δ is calculated to be 9.08 $(\mathrm{cal/cm^3})^{1/2}$.

Calculation and characterization of the torsional angle distribution of the structure are important. The potential energy contours provide not only chain conformation but also the pathway for chain relaxation. Torsional angles along the backbone are defined in Figure 4. Torsional angle calculations are conducted at 10° intervals. For energy minimization, one pair of torsional angles is held stationary and the remainder allowed to relax. The torsional contribution is determined by the rotational term with some contributions from both bond stretching and valence angle bending terms added to the nonbonded interactions. Since the torsional force field is expressed in terms of the hybridization states of backbone atoms, contributions from nonbonded interactions are also included. Overall potential energy contours are shown in Figures 5–7. The local minima are located near (±70, ±70) and (±110, ±110) for the torsional angle about C–S, (±90, ±90) for C–O rotations, and (±50, ±50) for C–C rotations as shown. It is difficult to test the accuracy of these proposed localized PSF structures. Optical anisotropy calculated for the chain, not available for the model PSF chain, perhaps is the definitive parameter characteristic of the localized potential.[14]

The actual torsional angle distributions calculated for the 10 model structures are shown in Figures 8–10. The distribution of C–S rotational angles, shown in Figure 8, is very broad, spreading over a large area for many values of ϕ_1 and ϕ_2. A number of chain conformations can exist between the four clusters (consisting of two minima) observed. Distribution of C–O rotational angles, shown in Figure 9, is also relatively broad but more localized, being confined to four narrow areas. The C–C torsional angle distribution is even more confined about the PSF backbone than the other two sets of torsional angles. If the barrier height between the various regions is lower than 3 kcal/mol, there can be a finite population of chain conformations containing some torsional angles not necessarily at the minima. Confined structures can, of course, exist when the barrier is higher than 3 kcal/mol. Clearly the torsional angle distribution of the simulated amorphous PSF structures agrees well with model structures. The C–S bonds are the most flexible, the C–C bonds are the most rigid, and the C–O bonds are intermediate. In the simulation procedure, the amorphous bulk structure is generated by randomly assigning the initial torsional

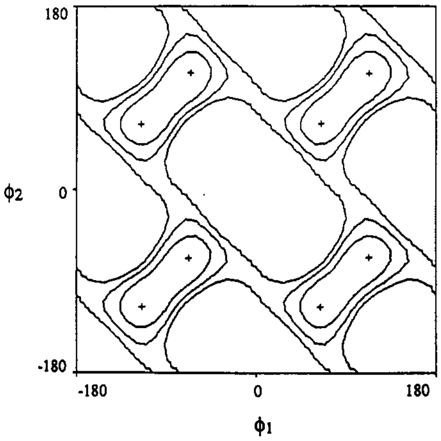

Figure 5. Calculated potential contour of backbone rotations ϕ_1 and ϕ_2. Pluses indicate local minima. The increment is 0.5 kcal/mol.

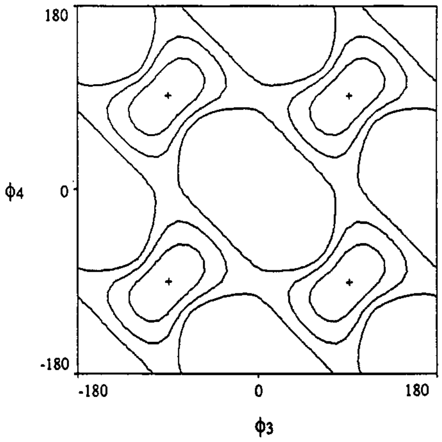

Figure 6. Calculated potential contour of backbone rotations ϕ_3 and ϕ_4. Pluses indicate local minima. The increment is 1.5 kcal/mol.

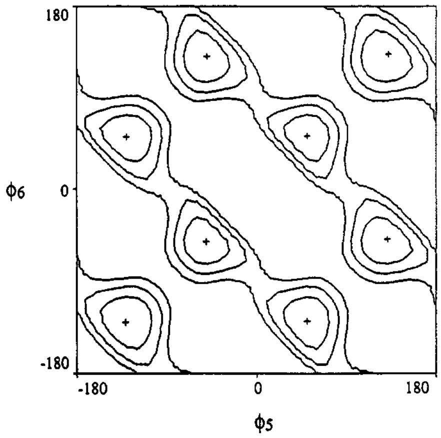

Figure 7. Calculated potential contour of backbone rotations ϕ_5 and ϕ_6. Pluses indicate local minima. The increment is 1.5 kcal/mol.

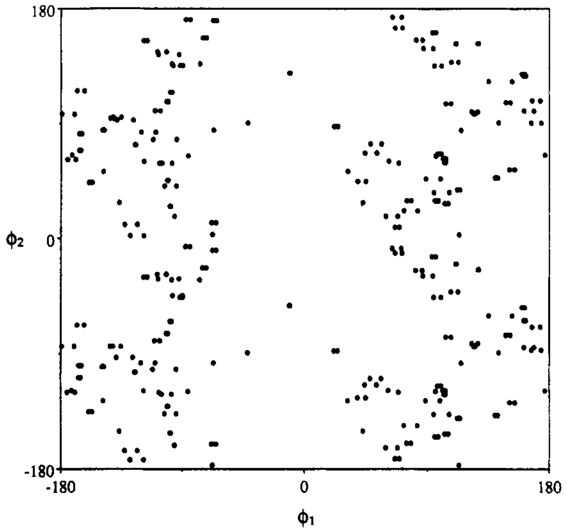

Figure 8. Distribution of backbone rotations ϕ_1 and ϕ_2 of model polysulfone.

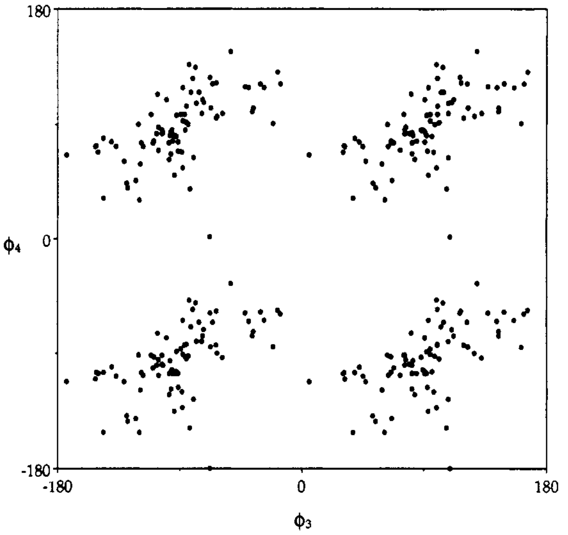

Figure 9. Distribution of backbone rotations ϕ_3 and ϕ_4 of model polysulfone.

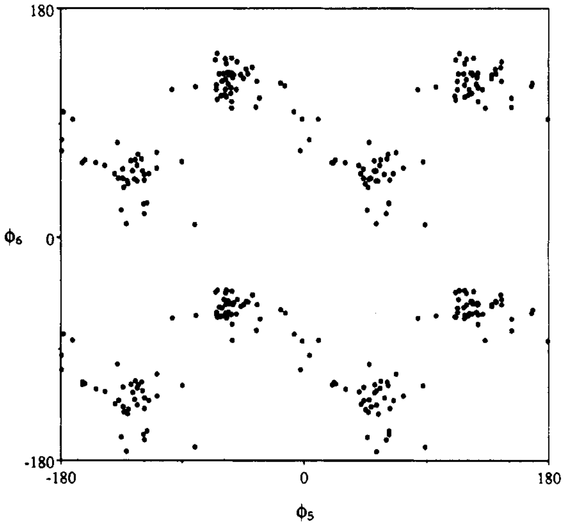

Figure 10. Distribution of backbone rotations ϕ_5 and ϕ_6 of model polysulfone.

angles. The molecular mechanics and energy minimization process have produced model structures with reasonable properties. Even if the torsional potential is not exactly defined, making application of rotational isomeric state models difficult, a reasonable chain structure can nevertheless be obtained.

Comparison of the contour plots in Figures 5–7 reveals that the most flexible segment is associated with the C–S bond. Barriers to rotation about the backbone ϕ_1 and ϕ_2 are considerably lower than those corresponding to ϕ_3, ϕ_4, ϕ_5, or ϕ_6. The backbone permits ϕ_1, or ϕ_2, to change independently with a maximum barrier height of about 1.5 kcal/mol. In contrast, a simultaneous change of the barrier for ϕ_3 or ϕ_4 would entail a much larger barrier height of 4.5 kcal/mol or much lower chain flexibility for this portion of the backbone. For PSF the C–S bond (1.71 Å) is much longer than C–O (1.37 Å). To rotate about the backbone, the valence angles would be distorted around C–O–C linkages. Because of the longer C–S bonds, the intermolecular interactions would be much lower, principally due to nonbonded intermolecular interactions.

Torsions about the C–C bond require the most energy. The contour is similar to that obtained for polycarbonate. Rotational barriers for PSF are higher than those found for polycarbonate.[19-21] In comparison to C–S or C–O, C–C linkages are the least flexible portion of PSF backbones. Little possibility exists for the simultaneous change of ϕ_5 or ϕ_6. Changes in chain conformation from one minimum to another usually involve ring flips. As mentioned earlier, C–S or C–O linkages permit independent ith or $(i + 1)$th rotations. For C–C, however, rotations about the ith and $(i + 1)$th bonds are strongly correlated and must occur simultaneously in order for ring flip to occur. To follow the lowest energy path, in ith and $(i + 1)$th units, the angles ϕ_5 to ϕ_6 must change in the opposite sense: one increasing and the other decreasing.

The minimum rotational barriers around the C–S linkages are similar in magnitude to thermal energy at room temperature (~0.9 kcal/mol). Ring-flip motions should thus occur relatively easily. Actual ring flip involves more than two adjacent bonds. For example, the flip of a phenyl ring with a C–S bond at one end and a C–O bond at the other requires that these two bonds rotate simultaneously. Each would be correlated to another of the same type. A direct calculation of the time required for the transition going from one conformation to another would be difficult to carry out because of the extremely long computation time that would be required.

Conclusions

By use of a molecular simulation technique, an equilibrium, stress-free, amorphous aromatic polysulfone chain has been generated. This structure does not exhibit evidence of long-range order in pair distribution function. The density of the bulk state agrees well with the experimental value. The cohesive energy density and its contributions have been calculated. Potential contour maps for the model chains have also been calculated. The torsional angle distribution measured from the amorphous structure is consistent with the calculated potential contour maps. The C–S linkages are the most flexible, the C–C linkages are the least flexible, and the C–O linkages are intermediate. Chain relaxation is found to occur by ring flips in certain sections of the backbone. Such motion is essentially forbidden around C–C linkages. This study demonstrates that molecular simulation is an effective tool for studies of the structure of amorphous polymers, even those with a complex monomeric structure such as aromatic polysulfone.

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