MOLECULAR FLEXIBILITY IN THE SHORT-SIDE-CHAIN
PERFLUOROSULFONIC ACID MEMBRANE

S. J. Paddison\textsuperscript{a} and J. A. Elliott\textsuperscript{b}

\textsuperscript{a} Department of Chemistry & Materials Science, University of Alabama in Huntsville, 301 Sparkman Dr., Huntsville, Alabama 35899, USA
\textsuperscript{b} Department of Materials Science & Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK

We present a comparative theoretical study of the differences in rotational degrees of freedom of the various C–C, C–O, C–S, and S–O bonds in oligomeric sequences of the short-side-chain (SSC) perfluorosulfonic acid (PFSA) membrane for the purposes of understanding the flexibility of pendant side chain and the ability of the sulfonic acid group to aggregate in the polymer. Potential energy profiles were determined at the B3LYP/6-31G** level in the \text{CF}_3\text{CF}–\text(O(\text{CF}_2)_2\text{SO}_3\text{H})–(\text{CF}_2)–\text{CF}–\text(O(\text{CF}_2)_2\text{SO}_3\text{H})\text{CF}_3 two pendant side chain fragment of the PFSA polymer. The rotational barrier of the \text{CF}_2–\text{CF}_2 bonds along the backbone was found to be nearly 7.0 kcal/mol and is the energy difference between the staggered trans and planar cis conformations. Furthermore, the calculations revealed that the stiffest portion of the side chain is near its attachment to the backbone, with the CF–O and O–CF\textsubscript{2} barriers of 9.1 and 8.0 kcal/mol, respectively. The most flexible portion of the side chain is the carbon-sulfur bond with a barrier of only 2.1 kcal/mol.

INTRODUCTION

With absorption of water, state-of-the-art proton exchange membranes (PEMs) exhibit a morphology where the hydrophobic backbone is phase-separated from nanodimensioned domains containing not only the water but fixed anions (the conjugate bases) and hydrated protons. These materials, however, only possess sufficiently high proton conductivities necessary to function efficiently as electrolytes for fuel cells when fully hydrated (1). As the PEM fuel cell is anticipated to offer the potential of considerable energy savings, energy security, and improvement in air quality through a wide range of modular power applications (2), there is substantial need for the development PEMs which permit operation of the fuel cell at temperatures above 100°C and with little or no humidification. The route to successful development of novel high-performance materials hinges on a fundamental, molecular-based understanding of how membrane morphology and chemical composition determine the transport of both protons and water (3).

The current understanding of the properties and function of the available perfluorinated sulfonic acid (PFSAs) functionalized ionomers has recently been reviewed by several authors (4-10). These electrolytes are two-phase systems, containing water dispersed as a second phase in a principally amorphous polymeric primary phase (11,12). The water solvates the acidic groups of the polymer and promotes mobility of the protons via both structural diffusion (13) (\textit{i.e.} Grotthuss-type “hopping” of the protons through
the hydrogen-bonded network of water molecules) and vehicular motion (i.e. coupled proton-water transport of hydronium ions) (14). In both transport mechanisms, the presence of water is critical in the formation of hydrated protons (i.e. as Zundel, H$_3$O$_2^+$, or Eigen, H$_2$O$_4^+$, cations) and mobility of the protons (15).

Extensive molecular modeling (16-31) of the acidic functional groups, polymeric fragments, proton diffusion, and dielectric properties of the confined water in various PEMs has suggested that critical ingredients of proton conduction in hydrated PEMs include: complexity; connectivity, and cooperativity; and that the chemical and physical processes need to be examined across diverse length and time scales. The complexity of proton conduction encompasses dissociation of the proton from the acidic site, subsequent transfer of the proton to the aqueous medium, separation of the hydrated proton from the conjugate base (e.g. the sulfonate anion), and finally diffusion of the proton in the confined water within the polymeric matrix. The connectivity involves not only hydrogen bonding of the water to the protogenic groups but also greater length scales including connection of the water domains with in the polymeric matrix. Cooperative effects include the amphotericity of the protogenic groups and also the flexibility of the side chains and or backbone. Undoubtedly, the route to a highly conductive membrane will be tailoring a material that possesses these ingredients working in a synergistic fashion.

Several different strategies have been mounted to improve proton conduction in PEMs (5,32) and these include: alternative fluids to replace the function of water in the membrane (e.g. phosphoric acid and polybenzimidazole (33,34), phosphonic acid (35), and imidazole (36,37)); the addition of inorganic particles in ionomers to facilitate proton conduction along the inorganic interface and retain water in the membrane at elevated temperatures (6) (e.g. silica, heteropolyacids, etc.); and modification of specific molecular features of existing PFSAs (i.e. the protogenic group, backbone and/or side chain chemistry, etc). With respect to the latter, scientists at DuPont (38) recently reported the synthesis and fuel cell testing of a PEM similar to Nafion but with a partially fluorinated backbone and a di(tetrafluoroethylene) ether sulfonic acid side chain (i.e. –CF$_2$CF$_2$OCF$_2$CF$_2$SO$_3$H) that exhibited higher proton conductivity than Nafion. The Fuel Cell Components group at 3M (39) also recently reported the synthesis and characterization of a PFSA membrane possessing improved conductivity with the same PTFE backbone as Nafion, but with the shorter –O(CF$_2$)$_4$SO$_3$H side chain. Enhancement of proton conductivity had been observed earlier in ionomers with a PTFE backbone and pendant short-side-chain (i.e. –O(CF$_2$)$_4$SO$_3$H) (40-43) first synthesized by the Dow Chemical Company. Although this PEM has a similar morphology to Nafion as suggested by SAXS and SANS experiments (41-43), significantly higher proton conductivity than Nafion at low to intermediate water contents (44-46), and a current density as much as three times greater than Nafion at 0.5 V in an operating fuel cell (47), it did not see widespread application in fuel cells or even further characterization due to the substantially more difficult synthesis route as developed by Dow (43). Recently, however, Solexis has developed a much simpler route for the synthesis of the ionomer and have reported superior performance when compared to Nafion (48). As discussed earlier, the improved conductance in this SSC PFSA is not currently understood, certainly not on a molecular basis; and is therefore the provocation for the present investigation.

In earlier studies (49,50) we sought to understand: (i) primary hydration of the sulfonic acid groups; (ii) the hydrogen bonding network of the ‘chemical’ water molecules connecting neighboring pendant side chains (i.e. those sequential on the same backbone chain); (iii) the role of the side chain in facilitating proton dissociation in
fragments of the SSC ionomers with varying degrees of side-chain separation; and (iv) the effects of conformational changes in the PTFE backbone on hydration and proton transfer. In the present work, we investigate the flexibility of the CF$_3$CF(–O(CF$_2$)$_7$SO$_3$H)–(CF$_2$)$_7$–CF(–O(CF$_2$)$_2$SO$_3$H)CF$_3$ oligomeric fragment (without water) through computation of the rotational barriers of the backbone and all bonds along the length of one of the side chains.

**METHOD**

*Ab initio* self-consistent field (SCF) molecular orbital calculations were performed using the GAUSSIAN 03 suite of programs (51) on Linux/MPI Beowulf clusters consisting of Intel Itanium 2 1.3 and 1.5 GHz dual and quad processor nodes. Full optimizations were undertaken by conjugate gradient methods (52) without symmetry constraints using Hartree-Fock theory with the 6-31G(d,p) split valence basis set (53) from initial structures with the fluorocarbon backbone and side chains in various configurations and orientations. The resulting equilibrium structures were then further refined using density functional theory with Becke’s 3 parameter functional (B3LYP) (54-56), initially with the same 6-31G(d,p) basis set and finally with the slightly larger 6-311G** (57). The effects of diffuse functions on the minimum energy structures were assessed and only minor differences in the structural parameters accompanied with a systematic difference in the total electronic energy was observed. Potential energy profiles were computed in the polymeric fragment displaying the lowest energy at the B3LYP/6-31G(d,p) level by systematically rotating about each of the bonds along one of the side chains and the carbon-carbon bonds along the backbone. Only the dihedral angle of the bond was constrained and optimization was performed over all other degrees of freedom of the molecular fragment. We remark, in passing, on the difficulty of obtaining a smooth potential energy surface, despite rotating the bond through only 5° increments, seemingly due to the side chain being caught in slightly higher energy configurations.

**RESULTS AND DISCUSSION**

In a previous investigation (49) we obtained minimum energy structures for fragments of the SSC PFSA polymer with three distinct separations of the pendant side chains: 5, 7, and 9 CF$_2$ groups. For the present investigation of assessing the flexibility of the side chains and backbone, we selected the polymeric fragment with 7 difluoromethylene units along the backbone and the global minimum energy structure is displayed in Figure 1. As discussed in our earlier work (49), the fully optimized structure shows the side chains well separated from each other and the carbon atoms along the backbone in a staggered *trans* configuration ($\angle$(C–C–C–C) $\approx$ 162°). The reasons for the staggered minimum energy conformation in perfluoroalkanes are discussed in detail by Jang *et al.* (58), but it is thought mainly to be due to electrostatic repulsions between fluorine atoms caused by relative polarity of the C–F bond. A potential energy surface, according to the procedure described in the Method section, was determined by rotating one of the C–C bonds midway between the side chains at 5° increments from the minimum energy structure (at $\angle$ CF$_2$–CF$_2$–CF$_2$–CF$_2$ = 162.5°) and is plotted in Figure 1. The barrier is a substantial 6.9 kcal/mol ($\angle$ $\approx$ 2.5°) and corresponds to a rotation that re-orientates the 1 and 4 (in the dihedral angle) carbons to a *cis* configuration. The other two significant maximums in the potential energy surface occur with barriers of approximately 3.8 kcal/mol and are due to rotation that eclipses the C-F bonds.
Potential energy profiles were determined for the point of attachment of the side chain to the perfluoro- backbone at the B3LYP/6-31G** level, including the FC–O and O– CF₂ bonds and are displayed in Figure 2. It has generally been believed that the ether linkages in the side chains provide flexibility and conformational freedom of the side chains. A prior (18) first principles investigation by one of the authors revealed that the rotational barrier of the outermost ether linkage in the Nafion side chain was about 4.6 kcal/mol. Examination of the surfaces in Figure 2, however, indicate that the barriers of the (sole) ether linkage of this SSC to the backbone is substantially greater with barriers of approximately 9.1 and 6.7 kcal/mol for the FC–O and O–CF₂ bonds, respectively. We do point out that both surfaces are quite “rough” and at some points appear to be disjointed. These results are likely due to the inability of the minimization scheme (52) to locate a global minimum for the side chain (i.e. it becoming entangled as the dihedral angle is constrained) and are despite a very substantial effort to “smooth out” the surface by performing numerous scans of the angle beginning from different points on the surface. It is also important to note that despite these significant barriers for the complete rotation of the side chain at its attachment to the backbone, there is a significant portion of the surface less than 4 kcal/mol higher than the global minimum. This does suggest...
that there is substantial conformational freedom and flexibility of the side chain even at its attachment to the backbone, but significant barrier for complete rotation.

Potential energy surfaces were also computed for the carbon-carbon and carbon-sulfur bonds along the side chain and are plotted in Figure 3. Although the magnitude of the rotational barriers are slightly different at 3.9 and 2.1 kcal/mol for the F$_2$C−CF$_2$ and F$_2$C−S bonds, respectively, their profiles are quite similar showing approximately a 3-fold degeneracy to the barriers and minima. These barriers occur when rotation of the chain results in eclipsing of either the C−F bonds with neighboring C−F bonds or the C−F bonds with the S−O bonds. Both of these surfaces are somewhat smoother than those obtained for the bonds involving the ether oxygen (Figure 2) and were much easier to obtain. The potential energy surface for rotation about the carbon-sulfur bond significantly smaller than that reported previously by one of the authors (16) for triflic acid where the barrier was determined to be approximately 3.4 kcal/mol, but this may be due to the fact that calculations were performed at the MP2/6-31G* level.

Finally, a similar potential energy profile was determined for the sulfur-oxygen (protonated) bond at the B3LYP/6-31G** level and is shown in Figure 4. There are two physically equivalent minima on this surface and two distinctly different maxima; the greatest at nearly 4.8 kcal/mol is due to a rotation that eclipses the O−H bond with the S−C bond. The lower barrier of about 2 kcal/mol is due to a rotation that points the acid-
ic proton away from the side chain (a difference of 180° from the greater barrier). Previous molecular modeling of triflic acid (16) indicated that with the inclusion of electrostatic solvation (with a dielectric constant of 77.4 for the continuum) this lower barrier was reduced by nearly 1 kcal/mol. Clearly the presence of water will affect the rotational barrier of this bond to the greatest extent (when compared to the other bonds examined in this study) due to the terminal part of chain being the site of interaction with the water.

CONCLUSIONS

We conducted a computational first principles based study of the flexibility of both the backbone and side chain in a ‘dry’ two side chain fragment of the SSC perfluorosulfonic acid (PFSA) membrane through determination of rotational potential surfaces. Potential energy profiles determined at the B3LYP/6-31G** level indicate that the backbone is relatively stiff, with a barrier of nearly 7.0 kcal/mol corresponding to the energy difference between the staggered trans and planar cis conformations of the carbon atoms. Furthermore, the calculations revealed that the stiffest portion of the side chain is near its attachment to the backbone with the CF−O and O−CF2 barriers of 9.1 and 8.0 kcal/mol, respectively. The most flexible portion of the side chain occurs at the point of attachment of the sulfonic acid group where the rotational barrier of the carbon-sulfur bond was determined to be only 2.1 kcal/mol.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Engineering and Physical Sciences Research Council (EPSRC) of the UK, and SJP thanks the University of Alabama Huntsville for financial support in the purchase of one of the Beowulf clusters used in this work.

REFERENCES