

# Secondary relaxation processes in bisphenol-A polysulphone

J. R. Fried\* and A. Letton†

Department of Chemical Engineering, and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221-0171, USA

and W. J. Welsh‡

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172, USA  
(Received 8 May 1989; accepted 26 July 1989)

Dynamic mechanical spectra of bisphenol-A polysulphone in torsional deformation have been obtained as a function of frequency and thermal history. Results indicate a major low-temperature  $\gamma$  peak at 166 K and a broad, low-intensity  $\beta$  peak near 352 K at  $10 \text{ rad s}^{-1}$  for quenched samples. Activation energies have been estimated to be 10.7 and  $67.3 \text{ kcal mol}^{-1}$ , respectively. Annealing eliminates the  $\beta$  peak and intensifies the shoulder of the  $\gamma$  peak.

Geometry-optimized CNDO/2 (complete neglect of differential overlap) molecular-orbital calculations for the diphenyl ether and isopropylidene units of polysulphone and use of molecular-mechanical calculations for diphenylsulphone indicate intramolecular conformational energies in the range from 5 to  $10.6 \text{ kcal mol}^{-1}$ . Comparison of these calculated energy barriers to torsional motions with experimentally determined activation energies from dynamic mechanical measurements suggests that phenyl and methyl group rotations in the isopropylidene unit, possibly phenyl ring rotation in the diphenyl sulphone unit, and phenyl group rotations in the diphenyl ether unit may all contribute to the  $\gamma$  transition. The higher-energy  $\beta$  transition is most probably due to intra- or interchain cooperative motions involving motions of several groups along the chain.

(Keywords: relaxation; polysulphone; bisphenol-A polysulphone)

## INTRODUCTION

Relaxational processes of bisphenol-A polysulphone (PSF) have been studied by several investigators using a variety of techniques including dynamic mechanical<sup>1-11</sup> and dielectric<sup>6</sup> measurements taken over a wide frequency range. There is universal support for the presence of a low-temperature ( $\gamma$ ) transition in the range of 163–197 K when data are corrected to 11 Hz. Several investigators have speculated on the nature of molecular motions responsible for this transition. Noting an enhancement of the  $\gamma$  peak with absorbed water, Baccaredda *et al.*<sup>1</sup> have associated this relaxation with the rotational motion of water molecules bound to polar groups along the chain backbone. However, Kurz *et al.*<sup>5</sup> have noted that this transition persists when samples are carefully dried, and suggested that the relaxational process may be associated with chain motions involving the sulphone group, which becomes enhanced through association with bound water.

Chung and Sauer<sup>7</sup> have suggested that the  $\gamma$  peak may contain contributions from two closely associated relaxational processes. The low-temperature process ( $\gamma_1$ ) appears as a peak at 162 K (0.67 Hz) and the high-temperature process ( $\gamma_2$ ) as a shoulder at 204–210 K

(0.61 Hz). Chung and Sauer speculated that motions of the phenylene units of the bisphenol-A and the sulphone moieties may be responsible for the  $\gamma_1$  and  $\gamma_2$  processes, respectively. In consideration of the above speculation and the probable association between the sulphone group and absorbed water, the presence of absorbed water should be expected to increase the magnitude of the  $\gamma_2$  shoulder, which is contrary to the observed behaviour<sup>8,9</sup>. Ting and Cottingham<sup>10</sup> also have noted the presence of a high-temperature shoulder (253 K at  $\sim 1 \text{ Hz}$ ), which they attributed to motions involving the isopropylidene group. In a study of several poly(aryl ethers), Robeson *et al.*<sup>8,9</sup> concluded that the  $\gamma$  process involves rotational motions of only the aryl ether groups and that in the presence of water a second low-temperature process involving the water-SO<sub>2</sub> complex becomes activated<sup>9</sup>.

In addition to the substantial evidence for a low-temperature process possibly consisting of contributions from two or more distinct molecular motions, Rheovibron measurements in our laboratory<sup>11</sup> have indicated the presence of a weak, high-temperature ( $\beta$ ) transition located near 333 K (11 Hz); there is evidence for a similarly located minor peak in the data of Heijboer<sup>2</sup>. The temperature for the  $\beta$  peak is approximately equal to the value of  $0.75 \times T_g$  as proposed by Boyer<sup>12</sup> to be characteristic of the  $\beta$  process in other polymers including bisphenol-A polycarbonate<sup>13-20</sup>. In those studies, the  $\beta$  process was associated with relaxational processes (perhaps involving long-range cooperative motions), which occur in defect regions and can be frozen-in by rapid quenching from the melt. Additional support for

\* To whom correspondence should be addressed

† Present address: Polymer Technology Consortium, Mechanical Engineering Division, Mail Location 3123, Texas A & M University, College Station, Texas 77843-3123, USA

‡ Present address: Department of Chemistry, University of Missouri-St Louis, St Louis, Missouri 63121, USA

the presence of a transition in the intermediate temperature range between the  $\gamma$  transition and glass transition comes from calorimetry<sup>21</sup>, gas chromatography and mechanical property<sup>22</sup> studies.

The present work is an attempt to understand better the nature of sub- $T_g$  relaxational processes in PSF. Torsional dynamic mechanical spectra for PSF samples with controlled thermal history are presented and assignments for molecular motions are made by use of geometry-optimized CNDO/2 (complete neglect of differential overlap) molecular-orbital (MO) and molecular-mechanics (MM) calculations of model compounds as described below.

## QUANTUM-MECHANICAL AND MOLECULAR-MECHANICS CALCULATIONS

Quantum-mechanical calculations of conformational energies were based on application of the CNDO/2 molecular-orbital technique<sup>23</sup>, which incorporates an iterative scheme for achieving direct geometry optimization<sup>24,25</sup>. This optimization was based upon the gradient of the potential energy function, the computations of which were made more efficient in terms of computer time by exploiting symmetry aspects. Specifically, the number of coordinates defining the molecular geometry were reduced by the use of symmetry coordinates, in which case non-totally symmetric coordinates may be ignored since the gradient, a totally symmetric function, vanishes for all such coordinates. Differentiation of the CNDO/2 total molecular energy expression with respect to each of the totally symmetric symmetry coordinates led to the analytically defined elements of the gradient of the potential energy function. The optimization cycle was repeated until the absolute value of each gradient element became less than a specified threshold value. In practice, a convergence criterion of  $0.1 \text{ eV } \text{Å}^{-1}$  was found to be acceptable. The electronic energy calculated by CNDO/2 is very sensitive to changes in the nuclear coordinates of the molecule. Consequently, for the self-consistent field (SCF) electron energy iteration, the convergence criterion, taken as self-consistency between two successive calculations, was set to an extremely small value ( $10^{-9} \text{ eV}$ ) compared with that typically used ( $10^{-5} \text{ eV}$ ) in non-optimized CNDO/2 calculations<sup>25</sup>. The conformational energy associated with a given conformation was taken as the difference in CNDO/2 total energy between that conformation and the conformation associated with the lowest energy. In most cases, the CNDO/2 energies were calculated for torsional angles varied in increments of  $10^\circ$  to  $20^\circ$ .

In the case of the diphenylsulphone segment, the presence of the sulphur atom precluded use of the present CNDO/2 technique for geometry optimization. Instead, empirical molecular-mechanics (MM) calculations were carried out, extending the work of an earlier study<sup>26</sup>. In the MM studies, the relative conformational energy was taken as a sum of contributions from a van der Waals term and an intrinsic torsional term<sup>27</sup>. The van der Waals term consisted of the familiar expression:

$$E_{\text{vdw}} = \sum_{i < j} a_{ij} \exp(-b_{ij}d_{ij}) - c_{ij}/d_{ij} \quad (1)$$

in which  $d_{ij}$  is the interaction distance between atom  $i$  and atom  $j$  and  $a_{ij}$ ,  $b_{ij}$  and  $c_{ij}$  are empirical parameters

assuming standard values given in the literature<sup>26,28</sup>. The form of the two-fold symmetric intrinsic bond torsional term is given as<sup>26,28</sup>:

$$E_{\text{tor}} = (E_{\text{tor}}^\circ/2)[1 - \cos(2\phi)] \quad (2)$$

where  $E_{\text{tor}}^\circ$  is the intrinsic barrier height for the rotating bond and  $\phi$  is the torsional angle, with  $\phi = 0^\circ$  taken as the conformation in which the phenylenes and the  $\text{C}_{\text{Ar}}\text{-S-C}_{\text{Ar}}$  group are coplanar. Based on results of an earlier study<sup>26</sup>, the value assigned to  $E_{\text{tor}}^\circ$  was varied from 0 to  $1.0 \text{ kcal mol}^{-1}$  but was found to bear a negligible influence on the results. The calculations permitted deformation of the  $\text{C}_{\text{Ar}}\text{-SO}_2\text{-C}_{\text{Ar}}$  bond angle away from the initial value of  $100^\circ$ , while the  $\text{C}_{\text{Ar}}\text{-SO}_2$  bond length was held fixed at  $1.84 \text{ Å}$ . Other structural parameters within the moiety were held fixed at standard values.

For all calculations, the polymer repeat unit was investigated using model compounds; for example, the isopropylidene segment was represented by dimethyldiphenylmethane,  $\text{C}(\text{CH}_3)_2(\text{Ph})_2$ . In this case, four separate torsional rotations of consequence are possible about the central carbon atom. These are two  $\text{C-CH}_3$  rotations and two  $\text{C-phenylene}$  rotations. For the present analysis, the two phenylene group rotations were considered to be decoupled from the methyl group rotations. This decoupling was justified on the basis of preliminary calculations and on the construction of molecular models indicating that significant interactions between a methyl group and a phenylene group occur only when the phenylene group is in a high-energy and therefore low-probability conformation.

## EXPERIMENTAL

Polysulphone (P-1700) was obtained as additive-free pellets through the courtesy of Dr Lloyd M. Robeson of Union Carbide. Reduced viscosity ( $0.2 \text{ g/100 ml}$ ) in chloroform at  $25^\circ\text{C}$  was reported to be 0.48. The number-average molecular weight determined by g.p.c. using polystyrene calibration in tetrahydrofuran (THF) was 41 580. The pellets were dried at  $100^\circ\text{C}$  in vacuum for at least 24 h prior to compression moulding in the form of  $3 \times 3 \times 0.040$  inch sheets as described elsewhere<sup>29</sup>. Three groups of samples were prepared with different thermal histories, as described in Table 1. Samples for torsional dynamic mechanical testing were cut from these moulded films into  $0.5 \times 2.0$  inch strips by means of a Tensilkut model 10-13 milling machine.

Dynamic mechanical spectra were obtained by use of a Rheometrics Dynamic Spectrometer (RDS-7700) operating in the forced torsion mode. Two dynamic mechanical experiments were run on separate specimens:

**Table 1** Thermal history of moulded sample

Sample no.	Moulding temperature ( $^\circ\text{C}$ )	Cooling conditions
1A	220	Ice-water quench
1B	250	Ice-water quench
1C	280	Ice-water quench
1D	300	Ice-water quench
2A	250	Slow cool
2B	270	Slow cool
2C	320	Slow cool
3A	280	Annealed at $180^\circ\text{C}$ , 10 h

isochronal (constant-frequency) temperature sweeps and isothermal frequency sweeps at several temperatures. Isochronal measurements over a temperature range from  $-150$  to  $220^\circ\text{C}$  were obtained at a heating rate of  $4^\circ\text{C min}^{-1}$  and at a frequency of  $10 \text{ rad s}^{-1}$ . Data were collected at a sampling interval of  $0.5 \text{ min}$ . Isothermal measurements were made over a frequency range from  $0.1$  to  $100 \text{ rad s}^{-1}$ . Frequencies were selected to be equally spaced on a logarithmic scale with five data points per decade. Temperatures were chosen to be  $20^\circ\text{C}$  above and below the temperature of the secondary and primary loss peak maxima as determined in previous runs. Strains used during these experiments ranged from  $0.04$  to  $1.0\%$ ;  $1\%$  strain was used for measurements in the glass transition region. Thermal soak periods lasting  $3 \text{ min}$  were employed between temperature changes.

RESULTS

Dynamic mechanical measurements

Dynamic moduli of a representative PSF sample are plotted as a function of temperature in Figure 1. Results of torsional testing of samples with different thermal histories are shown in Figure 2. In all cases, there is clear evidence for a major secondary relaxation with a peak maximum located near  $-107^\circ\text{C}$  ( $166 \text{ K}$ ) and for a glass transition ( $\alpha$  peak) near  $188^\circ\text{C}$  ( $461 \text{ K}$ ) at  $10 \text{ rad s}^{-1}$ . Slow cooling or short-time annealing had no apparent effect on the location of the major peak maxima. As shown by the Arrhenius plot in Figure 3, our assignments for the

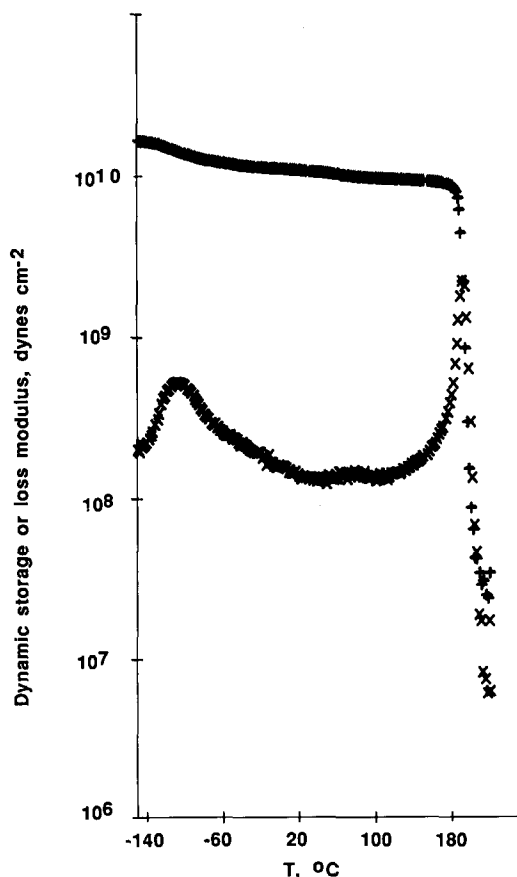


Figure 1 Plots of dynamic storage modulus  $G'$  (+) and loss modulus  $G''$  (x) as functions of temperature at  $10 \text{ rad s}^{-1}$  ( $\sim 1.6 \text{ Hz}$ ) for a polysulphone torsion bar that had been quenched from  $280^\circ\text{C}$  (sample 1C)

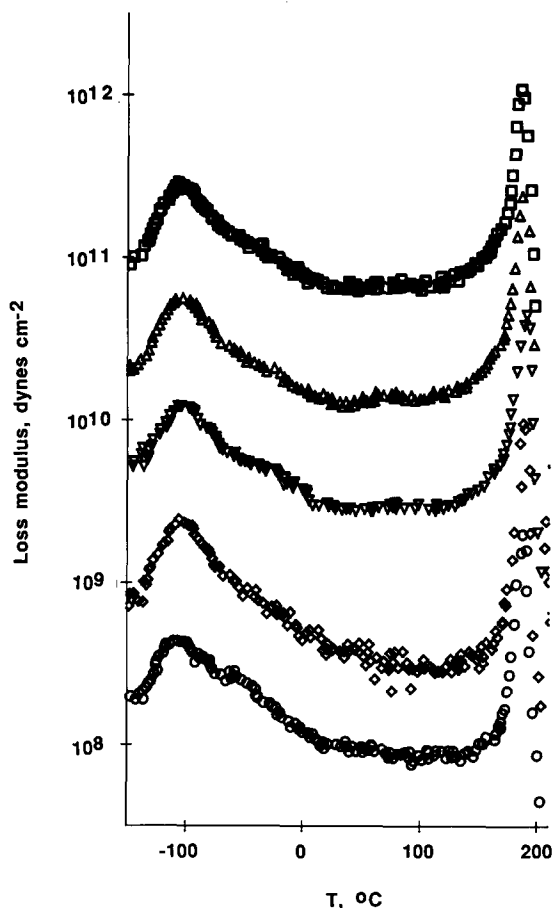


Figure 2 Plot of dynamic loss modulus  $G''$  versus temperature at  $10 \text{ rad s}^{-1}$  for samples with five different thermal histories. Curves have been arbitrarily shifted along the ordinate for ease of comparison. From top to bottom, thermal histories are: 1C, 1B, 1A, 2C and 3A

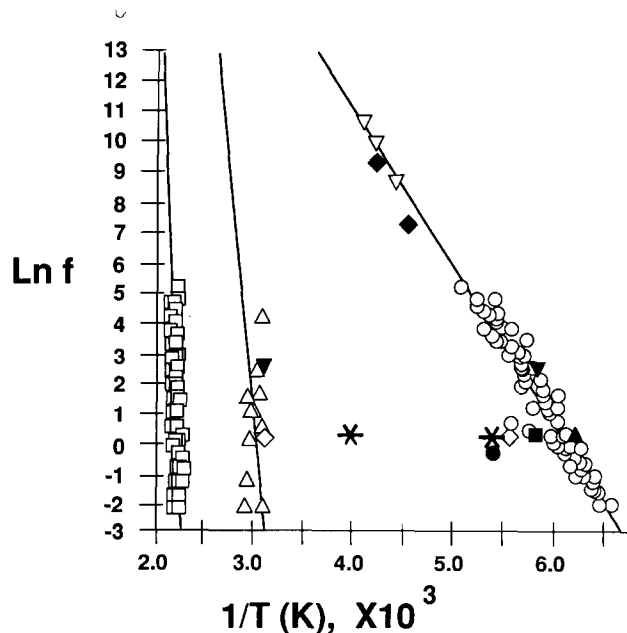


Figure 3 Arrhenius plot of frequency ( $\text{rad s}^{-1}$ ) versus  $1/T_{\text{max}}$  for the  $\alpha$  ( $\square$ ),  $\beta$  ( $\triangle$ ) and  $\gamma$  ( $\circ$ ) transitions of polysulphone. Literature data: ( $\nabla$ ) electrostatic, Baccaredda *et al.*<sup>1</sup>; ( $\diamond$ ) torsion pendulum, Heijboer<sup>2</sup>; ( $\blacksquare$ ) torsion pendulum, Robeson *et al.*<sup>8</sup>; ( $\triangle$ ) torsion pendulum, Kurz *et al.*<sup>5</sup>; ( $\nabla$ ) Rheovibron, Fried and Kalkanoglu<sup>11</sup>; ( $\blacklozenge$ ) dielectric, Allen *et al.*<sup>6</sup>; ( $\bullet$ ) inverted torsion pendulum, Chung and Sauer<sup>7</sup>; ( $*$ ) torsion pendulum, Ting and Cottingham<sup>10</sup>

main  $\gamma$  peak are in good agreement with the majority of previous studies and yield an activation energy of  $10.7 \pm 1.1 \text{ kcal mol}^{-1}$  ( $\pm 95\%$  confidence limits) for data obtained from frequency scans of four separate torsion bars. By comparison, activation energies of 10.5 (ref. 7), 12 (ref. 1) and  $16.6 \text{ kcal mol}^{-1}$  (ref. 6) have been reported in previous studies. For the  $\alpha$  transition, an apparent activation energy of  $219.7 \pm 55.2 \text{ kcal mol}^{-1}$  (four samples) was obtained, the large relative error being due to the small temperature shifts over the frequency range from 0.1 to  $100 \text{ rad s}^{-1}$ .

The spectra also show evidence for the presence of a high-temperature shoulder on the  $\gamma$  peak as has been suggested by Chung and Sauer<sup>7</sup> and by Ting and Cottingham<sup>10</sup>. This shoulder appears to intensify with annealing, as shown in Figure 4.

In the case of the quenched samples (the top three spectra in Figure 2), there appears to be a very weak, broad ( $\beta$ ) peak near  $79^\circ\text{C}$  (352 K). This assignment is in good agreement with our earlier Rheovibron results<sup>11</sup> and with the data of Heijboer<sup>2</sup>; however, the torsional  $\beta$  peak is weaker than measured in the dynamic tensile mode of the Rheovibron. Because of the breadth of this transition, temperature assignment is difficult; activation energy is estimated to be  $67.3 \pm 35.7 \text{ kcal mol}^{-1}$  ( $\pm 95\%$  confidence limits). As shown by Figure 2, annealing or slow cooling appears to eliminate this transition.

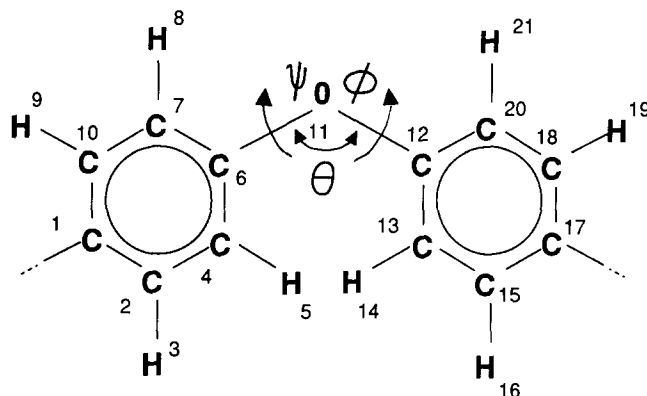
#### CNDO/2 and MM calculations

Selected values of the CNDO/2 energies and corresponding optimized geometries for some of the more significant conformations in the diphenyl ether moiety of PSF are listed in Table 2. Designations of atom sites and

**Table 2** Selected results of CNDO/2 conformational calculations for the diphenyl ether segment

$\phi, \psi$ (deg)	0, 0	40, 40	90, 90
$\Delta E^a$ (kcal mol <sup>-1</sup> )	0	-8.44	-6.51
Bond length (Å)			
O(11)-C(6)	1.42	1.40	1.40
C(12)-O(11)	1.42	1.40	1.40
Bond angle (deg)			
C(6)-O(11)-C(12)	126.5	116.8	113.6
Interatomic distance (Å)			
H(14)···H(5)	1.69	2.66	2.57

<sup>a</sup> Conformational energy relative to the  $0^\circ, 0^\circ$  conformation

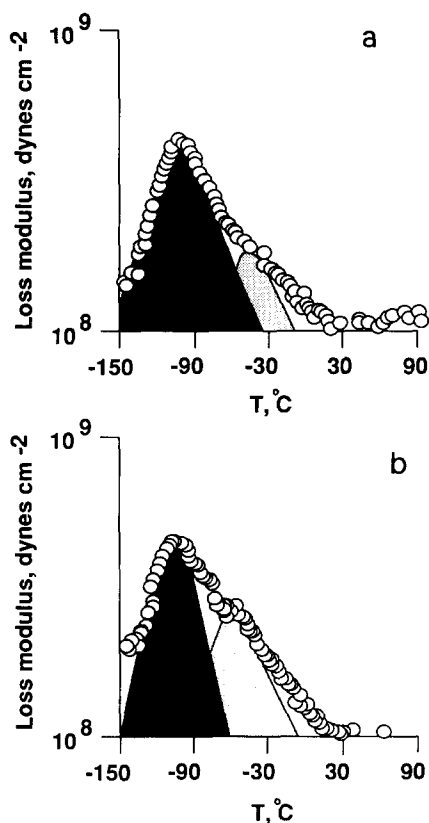


**Figure 5** The diphenyl ether segment of the polysulphone chain. Angles of rotation around the C-O bond are designated as  $\phi$  and  $\psi$ , while  $\theta$  is the C-O-C bond angle

bond angles are shown in Figure 5. A broad minimum energy region was found for  $\phi = 90^\circ \pm 55^\circ$ ,  $\psi = 90^\circ \pm 55^\circ$  (within a  $180^\circ$  conformational energy space) with an absolute minimum located at  $\phi = 40^\circ$ ,  $\psi = 40^\circ$  corresponding to a 'propeller' conformation. These results agree with earlier MM calculations and X-ray crystallographic analysis of poly(phenylene oxide)<sup>26</sup>. This broad energy well indicates a considerable degree of conformational flexibility about these bonds. These low-energy conformations were an average  $8.4 \text{ kcal mol}^{-1}$  lower in energy than the least preferred conformation, located at  $\phi = 0^\circ$ ,  $\psi = 0^\circ$  (the coplanar conformation). Analysis of the optimized geometries provides a basis for the large energy barrier at the coplanar (i.e.  $\phi = \psi = 0^\circ$ ) conformation. First, the severe steric repulsion found for conformations near or at  $\phi = 0^\circ$ ,  $\psi = 0^\circ$  are relieved considerably at the more energetically preferred conformations. For example, the interaction distance for the critical H···H conformation, e.g. H(5)···H(14) in Figure 5, increases from  $1.69 \text{ Å}$  at  $\phi = 0^\circ$ ,  $\psi = 0^\circ$  to  $2.66 \text{ Å}$  at  $\phi = 40^\circ$ ,  $\psi = 40^\circ$  compared with the normal van der Waals distance of about  $2.40 \text{ Å}$ . Similar results are obtained for the isopropylidene and sulphone units.

The second aspect more specific to the diphenyl ether group is the wide variation in the value of the Ph-O-Ph bond angle with variations in  $\phi$  and  $\psi$ . Specifically, the bond angle ranged from a maximum of  $126.5^\circ$  at  $\phi = 0^\circ$ ,  $\psi = 0^\circ$  to a minimum of  $113.5^\circ$  at  $\phi = 90^\circ$ ,  $\psi = 90^\circ$ . These extreme values span a range of  $13^\circ$ , thus emphasizing the considerable degree of steric congestion arising in the coplanar conformation, which is partially relieved by expansion of the C-O-C bond angle.

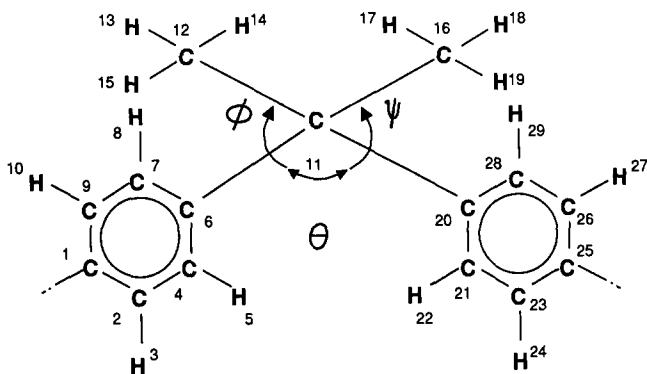
Energies were calculated for the isopropylidene moiety (Figure 6) as a function of rotation of the two phenylene groups while the two methyl groups were held fixed.



**Figure 4** Plot of dynamic loss modulus  $G''$  versus temperature for polysulphone: (a) quenched from  $280^\circ\text{C}$  (sample 1C); (b) annealed (sample 3A)

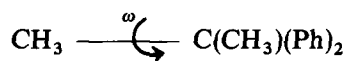
**Table 3** Results of CNDO/2 conformational calculations for the isopropylene group

$\omega', \omega''$ (deg)	0, 0	0, 0	0, 0	0, 0	0, 20	0, 50	0, 60
$\phi', \psi$ (deg)	0, 0	45, 45	90, 90	45, 45	45, 45	45, 45	45, 45
$\Delta E$ (kcal mol <sup>-1</sup> )	0	-10.1	-7.7	-3.6	-11.1	-15.0	-15.4
Bond length (Å)							
C(20)-C(11)	1.49	1.49	1.49	1.49	1.48	1.48	1.48
Bond angle (Å)							
C(6)-C(11)-C(20)	123.5	112.9	107.4	114.2	112.9	113.1	113.0
Interatomic distance (Å)							
H(22)···H(5)	1.40	3.22	2.78	1.51	3.19	3.15	3.11

**Figure 6** The isopropylidene group of the polysulphone chain. Rotational and bond angles are as identified in Figure 5

Selected results of the CNDO/2 calculations are summarized in Table 3. As in the case of the diphenyl ether group, a broad region of low energy was found at  $\phi = 90 \pm 50^\circ$ ,  $\psi = 90 \pm 50^\circ$  with an absolute minimum energy located at  $\phi = 45^\circ$ ,  $\psi = 45^\circ$ . These results are also consistent with earlier MM calculations for related systems<sup>26</sup>. The least preferred conformation was again found to be the coplanar one ( $\phi = 0^\circ$ ,  $\psi = 0^\circ$ ) with an energy 10.1 kcal mol<sup>-1</sup> above the preferred conformation. Deformation of the Ph-C(CH<sub>3</sub>)<sub>2</sub>-Ph bond angle is significant, ranging from 123.5° at  $\phi = 0^\circ$ ,  $\psi = 0^\circ$  to 107.3° at  $\phi = 90^\circ$ ,  $\psi = 90^\circ$ . Both the diphenyl ether and isopropylidene moieties thus indicate comparable degrees of rotational flexibility and maximum barriers to torsional rotation.

With the two isopropylidene rings held fixed in their preferred  $\phi = 45^\circ$ ,  $\psi = 45^\circ$  conformation, CNDO/2 energies were computed as a function of rotation of the two methyl groups. The torsional bonds of interest here are of the type:



In the initial calculations, one methyl group was rotated in increments of 20° while the other methyl group and two phenylene rings were held in their energetically preferred conformations. The minimum and maximum calculated energies were found at the staggered ( $\omega = 60^\circ$ , 180°, 300°) and eclipsed ( $\omega = 0^\circ$ , 120°, 270°) conformations, respectively, with an energy difference of 5.3 kcal mol<sup>-1</sup> (see Table 4). Additional calculations were performed for the case where the other methyl group was rotated to maximize the barrier to rotation. In this case, a barrier of 9.8 kcal mol<sup>-1</sup> was found. This would suggest that the barrier to methyl group rotation in the isopropylidene moiety falls in the range from 5 to 10 kcal mol<sup>-1</sup>.

Direct CNDO/2 calculations of the remaining diphenylsulphone moiety were precluded due to the

**Table 4** CNDO/2 conformational energy calculations for methyl group rotation<sup>a</sup>

$\omega', \omega''$ (deg)	$\Delta E^b$ (kcal mol <sup>-1</sup> )
0, 0	0
0, 30	0.97
0, 60	7.28
0, 90	0.60
30, 90	-1.15
60, 90	-2.51
90, 90	-1.20

<sup>a</sup> Case in which  $\phi$  and  $\psi$  are held at 45° and -45°, respectively (i.e. most strained case)

<sup>b</sup> Relative to the energy calculated for the  $\omega' = 0^\circ$ ,  $\omega'' = 0^\circ$  conformation

**Table 5** CNDO/2 calculated energy barriers to torsional rotation

Group	$\Delta E$ (kcal mol <sup>-1</sup> )
Diphenyl ether	8.4
Isopropylidene	
phenyl rotation	10.1
methyl rotation	5, 10 <sup>a</sup>
Diphenylsulphone	10.6

<sup>a</sup> The lower value corresponds to the case for methyl group rotation with second methyl group and both phenylene rings in their preferred conformations; the higher value is obtained for the case in which both methyl groups are free to rotate with the phenylene rings in their preferred conformations

presence of the sulphur atom. Instead, MM calculations that allowed deformation of the Ph-SO<sub>2</sub>-Ph bond angle while the C-SO<sub>2</sub> bond length remained fixed were performed. In this case, the minimum and maximum energy conformations were obtained at  $\phi = 90 \pm 30^\circ$ ,  $\psi = 90 \pm 30^\circ$  and  $\phi = 0^\circ$ ,  $\psi = 0^\circ$ , respectively. The maximum energy difference was 10.6 kcal mol<sup>-1</sup>. Again, a considerable degree of deformation of the Ph-SO<sub>2</sub>-Ph bond angle was found, ranging from an average of 100° for the preferred conformation to 116° for the coplanar conformation. These results are in qualitative agreement with earlier studies, which did not consider bond deformation explicitly<sup>26</sup>.

## DISCUSSION AND CONCLUSIONS

A listing of the calculated energy barriers to rotation within each chemical subunit is given in Table 5. Comparison with experimentally determined activation energies suggests that the  $\gamma$  transition may contain contributions from phenyl and methyl group rotations of the isopropylidene unit, possibly phenyl group rotations in the diphenylsulphone unit and phenyl group rotations in the diphenyl ether moiety. The high activation energy (67.3 kcal mol<sup>-1</sup>) of the  $\beta$  relaxation cannot be assigned

to any single set of torsional motions based on energy barrier calculations but most probably involves some intra- or interchain cooperative motion of several segments. Rapid cooling freezes-in this higher-energy conformational state. Upon heating of the non-equilibrium glass, conformations are then able to obtain lower energy states. This change in conformational energy results in the weak  $\beta$  transition observed in the case of quenched samples.

As noted in the dynamic mechanical spectra (Figure 4), there is evidence for at least two separate transitions in the  $\gamma$  region. Annealing intensifies the higher-temperature shoulder or  $\gamma_2$  transition. It is possible that the  $\gamma_2$  relaxation is associated with the rotation of the methyl groups in the isopropylidene unit. Space-filling model studies of the PSF high-energy conformations suggest a possible coupling of the methyl group rotations with the phenyl group rotation. A similar coupling has been suggested by Schaefer *et al.*<sup>30</sup> for the isopropylidene unit of bisphenol-A polycarbonate. In the high-energy conformation, interfering hydrogens in the phenyl rings of the isopropylidene segment, H(8) and H(29) in Figure 6, sterically hinder the methyl groups from rotating. During annealing, the isopropylidene group achieves a lower-energy conformation. In so doing, the hydrogens that previously prevented methyl group rotation are no longer in a position to sterically hinder the rotation of the methyl groups. Further studies are required to investigate the effect of long-term annealing on the  $\gamma$  transition and its relation to impact properties.

#### ACKNOWLEDGEMENTS

Partial support of this work under AFOSR-82-0301 (JRF) and the Hermann Schneider Research Laboratory of the University of Cincinnati is gratefully appreciated. In addition, one of us (AL) wishes to extend appreciation to NSF for Minority Graduate Fellowship support. The assistance of Drs I. Goldfarb and C.-Y. Lee and Mr J. Henes in providing use of their facilities at the Polymer Branch of the Materials Laboratory of Wright-Patterson AFB is gratefully acknowledged.

#### REFERENCES

- 1 Baccaredda, M., Butta, E., Frosini, V. and de Petris, S. *J. Polym. Sci., Polym. Phys. Edn.* 1967, **5**, 1296
- 2 Heijboer, J. *Br. Polym. J.* 1969, **1**, 3
- 3 Robeson, L. M. and Faucher, J. A. *J. Polym. Sci., Polym. Lett. Edn.* 1969, **7**, 35
- 4 Robeson, L. M. *Polym. Eng. Sci.* 1969, **9**, 277
- 5 Kurz, J. E., Woodbrey, J. C. and Ohta, M. J. *J. Polym. Sci., Polym. Phys. Edn.* 1970, **8**, 1169
- 6 Allen, G., McAinsh, J. and Jeffs, G. M. *Polymer* 1971, **18**, 85
- 7 Chung, C. I. and Sauer, J. A. *J. Polym. Sci., Polym. Phys. Edn.* 1971, **9**, 1097
- 8 Robeson, L. M., Farnham, A. G. and McGrath, J. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1975, **16**(1), 476
- 9 Robeson, L. M., Farnham, A. G. and McGrath, J. E. in 'Molecular Basis of Transitions and Relaxations', (Ed. D. J. Meier), Gordon & Breach, New York, 1978, pp. 405-25
- 10 Ting, R. Y. and Cottingham, R. L. in 'Rheology', (Eds. G. Astarita, G. Marrucci and L. Nicolais), Plenum Press, New York, 1980, Vol. 3, pp. 349-54
- 11 Fried, J. R. and Kalkanoglu, H. *J. Polym. Sci., Polym. Lett. Edn.* 1982, **20**, 381
- 12 Boyer, R. F. *Polymer* 1976, **17**, 996
- 13 Heijboer, J. *J. Polym. Sci., Polym. Symp. Edn.* 1968, **16**, 3755
- 14 Kunori, T. and Geil, P. H. *J. Macromol. Sci., Phys.* 1980, **18**, 93
- 15 Yee, A. F. and Smith, S. A. *Macromolecules* 1981, **14**, 54
- 16 Watts, D. C. and Perry, E. P. *Polymer* 1978, **19**, 249
- 17 Illers, K. H. and Breuer, H. *J. Colloid Sci.* 1963, **18**, 1
- 18 Frank, W. and Stuart, H. A. *Kolloid Z. Z. Polym.* 1968, **225**, 1
- 19 Frank, W., Goddar, H. and Stuart, H. A. *J. Polym. Sci., Polym. Lett. Edn.* 1967, **5**, 711
- 20 Varadarajan, K. and Boyer, R. F. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 141
- 21 Filiski, F. E. and Raghava, R. S. *J. Macromol. Sci. Phys.* 1976, **12**, 317
- 22 Dangayach, K. C. B. and Bonner, D. C. *J. Polym. Sci., Polym. Lett. Edn.* 1978, **16**, 443
- 23 Pople, J. A. and Beveridge, D. L. 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970
- 24 Jaffe, H. H. CNDO/S and CNDO/2 (FORTRAN IV), *Quantum Chem. Program Exch.* 1977, 315
- 25 Kondo, H., Jaffe, H. H., Lee, H. Y. and Welsh, W. J. *J. Comput. Chem.* 1984, **5**, 84
- 26 Welsh, W. J., Bhaumik, D. and Mark, J. E. *J. Macromol. Sci., Phys. (B)* 1981, **20**, 59 and references therein
- 27 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley-Interscience, New York, 1969
- 28 Welsh, W. J., Bhaumik, D. and Mark, J. E. *Macromolecules* 1981, **14**, 947 and references therein
- 29 Letton, A., Ph.D. Dissertation, University of Cincinnati, 1984
- 30 Schaefer, J., Stejskal, E. O., McKay, R. A. and Dixon, W. T. *Macromolecules* 1984, **7**, 1479