

Dynamic Mechanical Behavior of Polysulfones

C. L. Aitken, J. S. McHattie, and D. R. Paul*

Department of Chemical Engineering and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712

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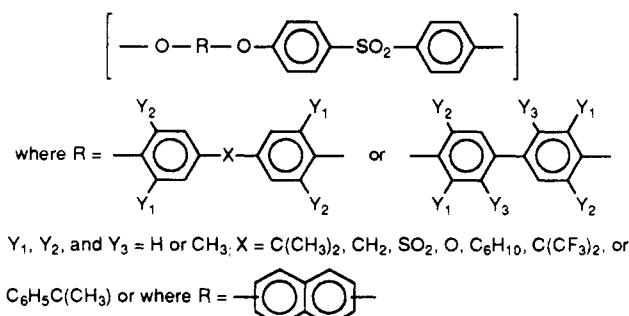
ABSTRACT: The dynamic mechanical properties of a series of polysulfones made from a wide range of bisphenols have been analyzed. The structural variations include 0, 1, 2, or 3 methyl groups per phenyl ring and a wide range of groups connecting the phenyl rings in the bisphenol while the diphenyl sulfone unit was not changed. The symmetry and placement of these modifications and the resulting rigidity affect the T_g and the sub- T_g spectra. Both intramolecular and intermolecular factors contribute to these changes. For these polysulfones, the glass transitions ranged from 150 to 298 °C and the sub- T_g relaxation temperatures ranged from -100 to +200 °C. Substitutions that directly hinder phenylene mobility increase the temperature at which the γ relaxation occurs. The appearance of more than one γ peak for some structures has been interpreted to mean that the extended intramolecular coupling of monomer units proposed for polycarbonates is apparently not a necessary component of the sub- T_g relaxation in these polymers. Differences in the molecular motions of polysulfones and polycarbonates were briefly addressed by molecular modeling. A comparison of selected polysulfones and poly(ether ketones) shows that whatever contribution the sulfone unit makes to the sub- T_g mechanical spectra, carbonyl units make a similar contribution. Intermolecular chain packing or free volume strongly affects the temperature location of the γ relaxation attributed to motions of diphenyl sulfone units.

Introduction

The molecular motions of poly(arylene ethers) and related materials have been characterized over the last 4 decades by a variety of techniques including dielectric relaxation,¹⁻⁴ nuclear magnetic resonance spectroscopy,⁴⁻⁸ and dynamic mechanical analysis.^{1-9,18} The main thrust of previous research has been to characterize the viscoelastic nature of bisphenol A polycarbonate (PC),¹⁻¹⁵ while the polysulfone based on bisphenol A (PSF) has been studied to a lesser extent.¹⁶⁻¹⁸ As part of a continuing investigation on the relationship between gas permeability and polymer structure, the dynamic mechanical behavior of a series of systematically modified polysulfones has been analyzed to probe more thoroughly the local and long-chain motions of these materials.

Like polycarbonates, polysulfones exhibit several temperature regions where relaxation processes occur. Each may be associated with specific molecular processes. An examination of the effects of molecular structural variations on the dynamic mechanical spectra of polysulfones should provide insight about the fundamental nature and origin of these relaxations and any relationship they may have with other physical properties of these materials.

Most of the polysulfones examined here can be described by the following generalized repeat unit:



In other words, all structural variations are made on the bisphenol monomer while the diphenyl sulfone unit remains fixed. We first present an in-depth background section which reviews the relevant literature needed to

interpret the experimental observations described subsequently. The experimental results are organized in a manner that attempts to show the effects on dynamic mechanical behavior of varying certain units while holding others fixed. We frequently reference the observed behavior to the familiar bisphenol A based polysulfone, PSF, which has been studied more extensively and has considerable commercial significance as a material for gas-separation membranes. The gas transport properties of each polysulfone mentioned here are described fully elsewhere.¹⁹⁻²¹ Included in an appendix is an analysis of the dynamic mechanical behavior of some poly(bisketones) and poly(bissulfones). These polymers, synthesized by Mohanty,²² have been examined to compare the effects of ketone versus sulfone groups on sub- T_g relaxations. The gas transport properties of these polymers will also be discussed in a subsequent paper.

Background

In terms of the commonly used nomenclature, the α relaxation for amorphous polymers corresponds to the onset of large-scale molecular motions associated with the glass to rubber transition. This transition has long been associated with intermolecular barriers to motion and the inherent stiffness of an isolated chain.^{18,23,24} The more rigid the polymer chain, the higher the glass transition temperature, T_g .²⁵ For example, symmetric substitutions of CH_3 groups onto the phenyl rings of polycarbonate¹⁰ and polysulfone²⁶ increase the barriers to phenyl ring rotation and raise the glass transition temperatures of these polymers. Attempts have been made in the literature to correlate the glass transition temperature with a calculated measure of conformational entropy since this should be an indicator of molecular flexibility.²⁷⁻²⁹ Sundararajan reports good success for symmetrically substituted polycarbonates, but the correlation does not hold as well for polycarbonates with replacements for the isopropylidene unit that are unsymmetric.²⁷ The T_g is lower for unsymmetrically substituted materials than the correlation with the calculated partition function or conformational entropy would indicate.

In addition to the example just mentioned, there are other cases reported in the literature where unsymmet-

rical isomers exhibit a marked depression of T_g and specific volume relative to their symmetrical isomers.³⁰⁻³⁷ Light and Seymour³² observed this phenomenon for isophthalate and terephthalate esters. In recent studies of the transport properties of poly(phenolphthalein phthalates), Sheu and Chern found that the glass transition temperatures of the para phenylene isomers are about 50 °C higher than those for the meta form.³⁴ A review of other studies on spatial configuration effects for a variety of polymers suggests that a higher T_g for the para structure is a general phenomenon.³⁴ Min and Paul compared gas transport properties of isotactic, syndiotactic, and atactic poly(methyl methacrylate).³¹ The isotactic form has a higher density and a lower T_g than the syndiotactic material. They suggested that the large difference between the specific volumes of the isotactic and syndiotactic forms is at least partially a result of the quite large difference in glass transition temperatures of the two isomers. Tanaka et al.,³⁷ in a study of polyimide isomers, suggest that the reason for the lower T_g of the meta isomers stems from their higher configurational entropy due to a larger degree of conformational freedom of the main chains than the para-linked polymers. However, this has not yet been proven quantitatively.

The β damping peak of polycarbonates and related materials is often attributed to either nonequilibrium packing defects created by quenching the sample from above the glass transition temperature³⁸ or to orientational stresses introduced during processing.³⁹⁻⁴¹ This peak, which is small and broad for bisphenol A polycarbonate, can be reduced or eliminated by annealing.³⁸⁻⁴¹

While the γ dispersion peak of such materials is often associated with the toughness or impact resistance of glassy polymers,⁴² there is considerable debate in the literature concerning the molecular origin of this relaxation. Yee and Smith¹¹ have given a relatively complete review of previous literature as well as a comprehensive examination of the dynamic mechanical spectra of a wide range of polycarbonates. They conclude that the γ relaxation, which occurs at -100 °C at 1 Hz for bisphenol A polycarbonate, is the result of somewhat synchronous motions of the entire repeat unit with the cooperation of some neighboring units. They further assert that motions of the phenylene rings are the determining factors in this behavior. There is a general consensus among recent authors that all portions of the repeat unit participate in the γ relaxation, but the exact nature of the molecular motions and the degree to which intramolecular and intermolecular factors play a role is still undetermined. It is generally agreed, based on NMR studies, that the phenyl rings in amorphous, aromatic polymers such as PC undergo 180° or π flips.⁶⁻⁸ However, there is still controversy regarding these and other phenylene motions and what influence they have on the γ peak. It has been suggested that the π flips alone are not sufficient to cause the observed mechanical loss since these motions are also seen in very brittle or cross-linked polymers that do not exhibit γ relaxations.¹⁴ It has also been stated that phenylene flips are impossible in *m,m'*-dihydroxyphenyl polycarbonate, yet it still has a sub- T_g peak.¹⁴

Several other theories on the mechanism of the sub- T_g relaxations in polycarbonate have been proposed. Jones⁴³ proposed that the γ dispersion involves a conformational interchange between neighboring carbonate groups from cis-trans to trans-trans conformational states. The interchange is envisioned as the diffusion of the cis-trans conformation down the length of a primarily trans-trans polymer chain accompanied by a codiffusing volume

fluctuation. The conformational change is also accompanied by π flips of the adjacent phenylene rings. Vadarajan and Boyer⁴⁴ interpreted the γ relaxation in PC as the superposition of three component peaks, γ_1 , γ_2 , and γ_3 , corresponding to phenylene, coupled phenylene-carbonate, and carbonate motions, respectively. They observed that exposure to methylene chloride reduced the intensity of the γ_3 relaxation while the γ_1 peak remained unchanged. They ascribe this effect to specific interaction between methylene chloride and the carbonate group. Earlier dielectric relaxation work by Allen et al.⁴⁵ tends to support the notion of superimposed component peaks. They found that the temperature location of the γ peak maximum in PC and PSF was higher for wet samples than for dry samples. They also found that the intensity of the peak increased with increasing water content. These observations were rationalized in terms of a specific interaction of water with the polar carbonate or sulfone unit that is said to intensify its contribution to the γ peak while the other component parts remain unaffected. Robeson¹⁸ et al. also found the dynamic mechanical behavior of a number of polysulfones to be sensitive to the presence of water. They ascribed the γ relaxation to motions of a water-sulfone complex and motions about the aryl ether bonds. The γ relaxation in poly(arylene ethers) without the sulfone unit was unaffected by water.¹⁸ However, this relaxation cannot be solely due to the polar complex since there is still a peak at approximately -100 °C for polymers such as poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) that do not have either carbonyl or sulfone components.¹³

Assuming that the γ peak is a composite of several different molecular motions, the broadness and proximity of the relaxations indicate a relative insensitivity to the identity of the mobile groups present in the polymer backbone. Structural modifications that may have a significant effect on the glass transition temperature often leave the γ relaxation temperature unchanged.¹¹ A major exception is the introduction of substituents onto backbone phenylene rings. Replacement of the phenylene hydrogens with methyl or halogen groups results in large changes in the secondary relaxation behavior of the polymer.¹¹ Both intramolecular and intermolecular arguments for these shifts have been given in the literature.

Quantum mechanical calculations by Bendler⁴⁶ for diphenylpropane indicate that rotation of one phenyl ring causes at least partial rotation of the adjacent ring across the isopropylidene group. Space-filling molecular models show that some degree of intramolecular cooperation must occur for these motions to be possible. Ratto et al.⁴⁷ studied the motions of chlorine-substituted polycarbonate rings using ¹³C NMR. They found that the rotational motions of the substituted and unsubstituted rings in an asymmetric monochlorinated polycarbonate are similar, but not identical, and substantially slower than those in bisphenol A polycarbonate. This suggests that the phenylene motions in the chlorinated polymer are strongly coupled, although not necessarily synchronous.

There is some evidence that these intramolecular considerations are the primary barriers to the γ relaxation. Densification of the polymer by annealing has been shown to be ineffective in changing the γ temperature.^{38-41,48} The addition of antiplasticizers, on the other hand, can be used to depress or even eliminate this relaxation.⁴⁹ Through the use of small-angle X-ray scattering and ²H NMR, Fischer et al.⁵⁰ rationalized these observations in terms of local free volume fluctuations. They suggested that annealing only eliminates large defects without affecting the local free volume fluctuations. Antiplasticizing ad-

ditives, on the other hand, decrease free volume fluctuations by depressing molecular mobility and, thus, have a large effect on the γ relaxation. Experimentally it is observed that sub- T_g annealing has only a small effect on free volume while antiplasticizers can have a large effect.⁴⁹⁻⁵³ These arguments tend to favor small-amplitude reorientational motions, that need not be intermolecularly cooperative, as the origin of the γ dispersion.

A most convincing observation in favor of intramolecular arguments is that blends of PC and tetramethylbisphenol A polycarbonate (TMPC) exhibit separate γ peaks. The magnitudes of the relaxations are a function of composition, but the peak temperatures essentially are not.⁵⁰ Random copolymers of the same composition, however, show three γ relaxations, including peaks at the relaxation temperatures of pure TMPC and PC and a broad peak that spans the range between the T_g 's of the two homopolymers.¹⁵ In this system, the effect of neighboring rings is only felt when the rings are on the same backbone chain, demonstrating the effect of intramolecular cooperation. In addition, a suppression of the upper T_g was observed in blends of PC with PMMA⁵ and in the copolymers of PC and TMPC¹⁵ due to coupling of the motions. The extent of intramolecular cooperation has recently been studied by examining how sub- T_g transitions are affected by monomer sequence length in PC-TMPC copolymers.¹⁴ Jho and Yee¹⁴ synthesized a series of copolymers having a 1/1 mole ratio of the two units that ranged from an alternating copolymer to multiblock copolymers with 6 or 9 repeat units per block segment. They concluded that several repeat units are required in order for the individual γ peaks of the homopolymers to appear due to the intramolecularly cooperative nature of the γ relaxation.

Intermolecular considerations may also play a significant role in the nature of the γ relaxation. Despite its apparent insensitivity to densification by annealing, Ito et al.⁵⁴ showed that the dielectric γ relaxation in drawn films of PC decreased with draw ratio and in general followed an inverse relationship with density. Perhaps the densification caused by annealing is not enough to show this effect, or, using the arguments of Fischer⁵⁰ given above, annealing only eliminates the large packing defects that are unrelated to the γ temperature. In any case, these results show that intermolecular factors can affect the γ relaxation. In a series of substituted poly(phenylene oxides), Eisenberg and Cayrol^{13,55} found that polymers with asymmetrically substituted rings do not exhibit the transition associated with phenylene oscillations seen in the symmetric polymers. The asymmetric materials have lower free volumes, and the absence of the transition was attributed to an intermolecular packing effect. Calculations by Schaefer and Stejskal⁸ for isolated chains suggest that the phenylene rings in both PC and PPO should be nearly free rotating. Experimentally, however, ¹³C NMR shows that PPO rings execute only small-amplitude ring motions while PC undergoes primarily ring flips. Apparently, interaction of the rings in PPO with neighboring chains prevents the π flips seen in PC. Finally, large polar substituents, like chlorine, on the methyl carbons of the isopropylidene unit in PC shift the γ relaxation to a much higher temperature while substitution of large nonpolar groups for the isopropylidene tends to have little effect.¹¹ The polarity and polarizability of the chlorine atoms may increase intermolecular interactions and, thus, caused the observed shift in the γ peak. Clearly, intermolecular as well as intramolecular factors determine relaxation behavior and a complete explanation of the origins of the γ

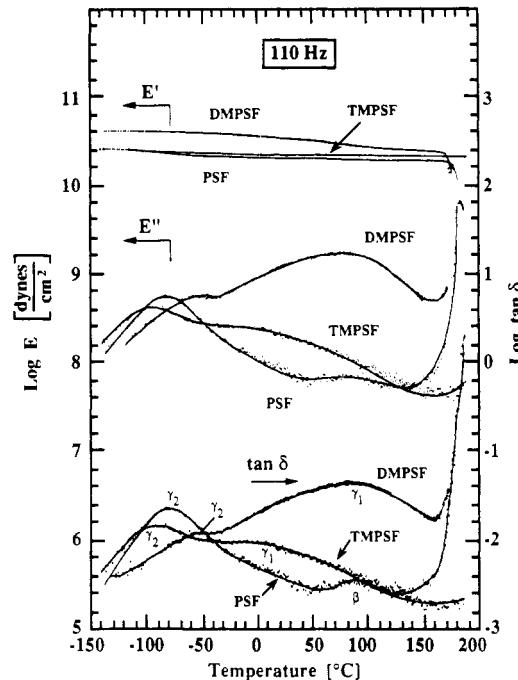


Figure 1. Dynamic mechanical properties at 110 Hz for PSF, DMPSF, and TMPSF.

relaxation should necessarily be consistent with both considerations.

Experimental Section

The polysulfones employed in this study were synthesized in our laboratories by procedures described elsewhere.⁵⁶ Dense films of 1-3-mil thickness were solution cast from an appropriate solvent, typically methylene chloride, chloroform, or *n*-methylpyrrolidinone. Prior to testing, the films were dried under vacuum to a temperature approximately 15 °C above the glass transition temperature of the polymer to ensure the elimination of solvent contamination. To standardize thermal history, all films were rapidly quenched from above the T_g to room temperature prior to dynamic mechanical testing. Films with other thermal histories were used to distinguish β and γ relaxations for selected polymers.

An Imass Autovibron dynamic mechanical viscoelastomer or Rheovibron was used to measure the mechanical spectra of these films at 110 Hz from -150 to +200 °C at a heating rate of approximately 1 °C/min. A dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories operated at 1 Hz from -150 to +300 °C was used when a higher temperature range was needed. A Perkin-Elmer differential scanning calorimeter (DSC), at a heating rate of 20 °C/min, was used to measure the glass transition temperature of the polymers. The T_g was calculated from the second trace using the midpoint method. All these polymers were amorphous with no crystalline melting point seen by DSC. Densities of the films were measured using a density gradient column based on aqueous calcium nitrate solutions.

Effects of the Substitution of Methyl Groups on the Bisphenol Rings. The elastic, E' , and loss, E'' , moduli, plus $\tan \delta$ are shown as a function of temperature for bisphenol A polysulfone (PSF), dimethyl polysulfone (DMPSF), and tetramethyl polysulfone (TMPSF) in Figure 1. The peaks of the $\tan \delta$ curves are labeled in order of descending temperature as α , β , or γ . The glass transitions, or α relaxations, become apparent above about 150 °C and are much larger than the sub- T_g peaks. The structure of the bisphenol monomer for each material is shown in Table I.

The magnitude of the elastic modulus in the glassy region is highest for DMPSF, and the decrease at 170 °C reflects the onset of its glass transition. The T_g 's of PSF and of TMPSF are higher. Relative to PSF, T_g increases with tetramethyl substitution and decreases slightly with dimethyl substitution. It appears as though the symmetric, bulky substitution retards long-chain

Table I
Structures and Properties of Polysulfones with Symmetric and Unsymmetric Methyl Substitutions

bisphenol monomer	polymer	T_g , °C	T_β , °C	T_{γ_1} , °C	T_{γ_2} , °C	ρ g/cm ³	FFV (($V - V_0$)/ V)	
	PSF	186	85		-80	1.240	0.156	
	DMPSF	180		80	-60	1.213	0.149	
	TMPSF	242			-10	-92	1.151	0.171

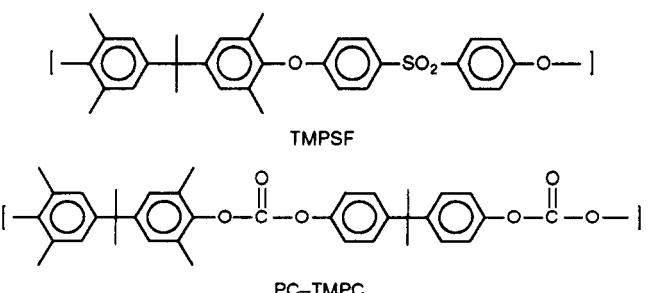
motion in TMPSF while the asymmetric substitution in DMPSF does not. The reasons for the relatively low T_g of DMPSF are not clear; however, these results are consistent with other mono- and disubstituted unsymmetrical aromatic polymers.^{11,18,27}

PSF exhibits a small β dispersion at 85 °C that is distinguished from γ peaks by its sensitivity to thermal annealing. The effect of annealing on this relaxation for PSF has been documented by Fried.¹⁶ A β peak is not observed for the substituted polysulfones; however, this relaxation may be hidden by the larger γ_1 peak in the same temperature region. To ensure that this large high-temperature peak, γ_1 , is not a β relaxation, an annealed sample of DMPSF was tested. The resulting $\tan \delta$ curves for the annealed and quenched samples are completely identical. This verifies that the peak identified as γ_1 is not a β relaxation since it is not diminished by annealing.

For aromatic polymers like these polysulfones, motions involving phenylene rings tend to be the most dominant contribution to the γ relaxation.^{11,18,45,57} Replacement of hydrogens on the phenylene rings with methyl groups hinders these motions considerably and results in the appearance of two separate γ peaks for polysulfones as observed earlier by Robeson.¹⁸ We believe that the γ_1 peaks are associated with motions of the substituted rings (from the bisphenol monomers) and surrounding groups, while the γ_2 peaks reflect motions of the unsubstituted rings (from the diphenyl sulfone monomer) and the sulfone unit. Since all of the rings in bisphenol A polysulfone or PSF are unsubstituted, the motions of the rings from both monomers occur at about the same temperature so only one γ relaxation temperature is observed for this polymer. However, for both TMPSF and DMPSF there is a γ_1 peak at a temperature higher than the γ_2 peak due to the greater steric hindrance and moment of inertia for the methyl-substituted rings than the unsubstituted ones.

Both the dimethyl- and tetramethyl-substituted polysulfones are less tough than bisphenol A polysulfone.¹⁸ This increase in brittleness is accompanied by an increase in T_{γ_1} and a corresponding decrease in the magnitude of the γ_2 peak.

To understand how intramolecular factors contribute to the sub- T_g relaxations, one can compare the parallel structures of TMPSF and the 1/1 molar alternating copolymer of PC and TMPC. While TMPSF exhibits two separate γ peaks that we



associate with different monomer units, the PC-TMPC copolymer has only one broad intermediate peak.¹⁴ PC-TMPC copolymers apparently require relatively long sequences of identical units before the individual homopolymer peaks of PC and TMPC are observed.¹⁴ The current results suggest that the polysulfone monomer units can move rather independently while

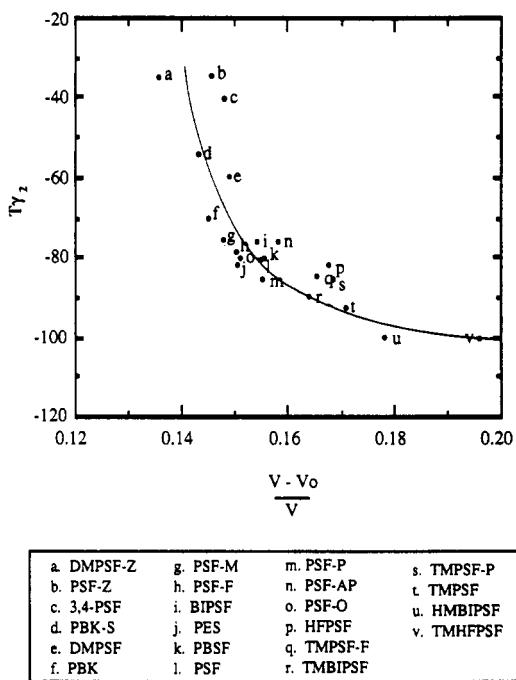


Figure 2. Relationship between the sub- T_g transition temperature T_{γ_2} and fractional free volume.

the polycarbonate units require a cooperative motion of several repeat units. The γ peak is calculated to occur at 111 °C⁵⁸ at 110 Hz for TMPC, whereas, for TMPSF the γ_1 peak, that we attribute to motions of the tetramethyl bisphenol units, occurs at -10 °C. Evidently the ether linkages in the polysulfones permit greater freedom of rotation of the connected rings and, thus, provide less coupling of their motions than do carbonate units. We examine this issue in some detail in Appendix B using molecular modeling.

Intermolecular considerations also influence the secondary relaxation behavior of these materials. As proposed above, the γ_2 relaxation stems from the diphenyl sulfone unit which is the same for all of the polysulfones; hence, this peak should be a good indicator of intermolecular effects. For our system of polymers, Figure 2 shows how the temperature at which this peak is maximum depends on intermolecular chain packing or free volume. The fractional free volume (FFV) used here was calculated from

$$FFV = (V - V_0)/V$$

where V is the specific volume computed from measured density and V_0 is the occupied chain volume obtained using the Bondi group contribution method described elsewhere.¹⁹ Bulky groups, like those on the tetramethylbisphenol unit, disrupt chain packing and lead to higher free volume. As FFV increases, intermolecular barriers to small-scale motions are reduced and the relaxation occurs at a lower temperature. Any intramolecular coupling of the γ motions between the substituted and unsubstituted portions of the repeat unit will restrict the mobility of the unsubstituted rings and lessen the intermolecular or free volume effect. Therefore, T_{γ_2} does not continue to decrease sharply with

Table II
Structures and Properties of Polysulfones with Different Phenylene Connector Groups in the Bisphenol Monomer

bisphenol monomer	polymer	T_g , °C	T_b , °C	T_{γ_1} , °C	T_{γ_2} , °C	ρ , g/cm ³	FFV (($V - V_0$)/ V)
<chem>Oc1ccc(C)c(Oc2ccc(O)cc2)cc1</chem>	PSF	186	85		-80	1.240	0.156
<chem>Oc1ccc(Oc2ccc(O)cc2)cc1</chem>	PSF-O	181	70		-80	1.330	0.150
<chem>Oc1ccc(S(=O)(=O)c2ccc(O)cc2)cc1</chem>	PES	225			-80	1.370	0.151
<chem>Oc1ccc(cc1)C2CCCC2</chem>	PSF-Z	211	140		-35	1.237	0.146
<chem>Oc1ccc(cc1)C2(C)CCCC2</chem>	PSF-F	179		-8	-78	1.282	0.151
<chem>Oc1ccc(cc1)C2CCC2</chem>	BIPSF	225		40	-75	1.291	0.154
<chem>Oc1ccc(cc1)C2(C)C6CCCC6C2</chem>	PSF-AP	214		10	-75	1.239	0.158
<chem>Oc1ccc(cc1)C2(C)C6CCCC6C2</chem>	HFPSF	192	70		-83	1.427	0.168

increasing FFV but tends toward an asymptotic value of about -100 °C for the more open polymers like TMPSF and TMH-FPSF. For DMPSF, intermolecular effects apparently hinder the small-scale mobility of the unsubstituted portion of the repeat unit, shifting T_{γ_2} up to -60 °C. The FFV of DMPSF is less than that of PSF. Whereas the tetramethyl groups disrupt chain packing and enhance FFV, the dimethyl pendent groups appear to fill the void space between chains, increasing packing efficiency rather than increasing free volume. Thus, T_{γ_2} is higher for the more densely packed DMPSF than for the more open PSF and TMPSF.

While the γ relaxation temperatures are higher for the unsymmetric polymer, DMPSF, than for PSF, the glass transition temperature is lower. Unsymmetric substitutions to PPO also have been found to affect oppositely the sub- T_g and T_g relaxations.¹³ It appears as though the unsymmetrically substituted polysulfones take on conformations which allow them to pack well and have more hindered γ relaxations and yet a lower T_g . On the other hand, tetramethyl placement on the phenyl rings leads to dramatic increases in FFV, T_{γ_1} , and T_g .

Effect of the Phenylene Connector Group. Several polysulfones with different phenylene connector groups than the isopropylidene unit of the familiar PSF were examined. The structure of each bisphenol monomer in this series is shown in Table II along with transition temperatures and free volume information. The $\tan \delta$ curves for each of these polysulfones are shown in Figures 3 and 4. The curves in Figure 3 are offset by a decade each for clarity. Unlike the methyl-substituted polymers, only one γ peak is observed for most of the polymers in this series. A small second peak at a higher temperature, tentatively labeled γ_1 in Figure 3, is seen for PSF-AP, BIPSF, and PSF-F. These are quite minor events as compared to the three peaks labeled γ_1 in Figure 1. There is the possibility that these peaks represent some small, slightly restricted motion caused by the structural modification; however, the exact reasons for this remain unclear. Another possible explanation is that they are β relaxations resulting from packing defects and could be eliminated by annealing; however, β relaxations typically occur at higher temperatures.

The nature of the connector group has a significant influence on T_g ; however, with the exception of PSF-Z, there is little influence on the T_{γ_2} peak. Evidently, the phenylene motions, which are believed to dominate the γ relaxation, are generally not affected significantly by these changes. In a previous paper,¹⁹

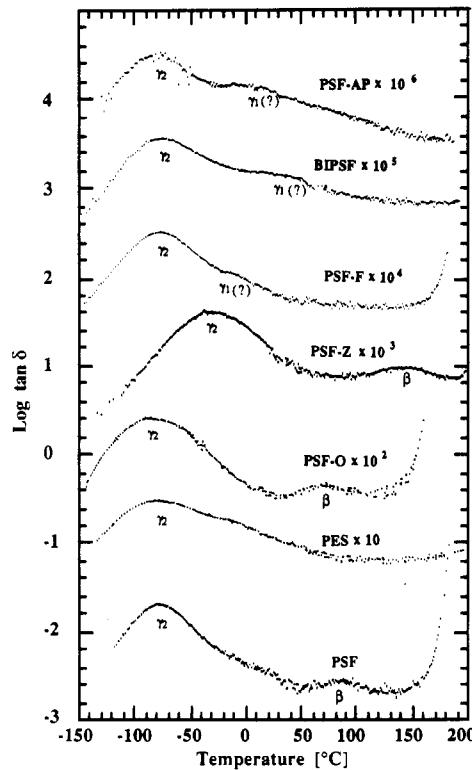


Figure 3. $\tan \delta$ curves at 110 Hz for polysulfones with various phenylene connector groups.

we reported a Rheovibron scan for HFPSF with two peaks that were labeled T_b and T_{γ_2} . Figure 4 confirms that the 80 °C peak is indeed a β relaxation since it disappeared upon annealing at 150 °C for 1 week.

The free volume variation among these polymers is generally small. However, HFPSF has a somewhat higher FFV relative to the other polymers in this series, as noted previously,¹⁹ and has a higher T_g . Due to the small differences in free volume for these polymers, the γ_2 peak positions change by only a few degrees which is difficult to discern due to the broadness of the peaks. An exception is the polysulfone for which the phenyl rings are

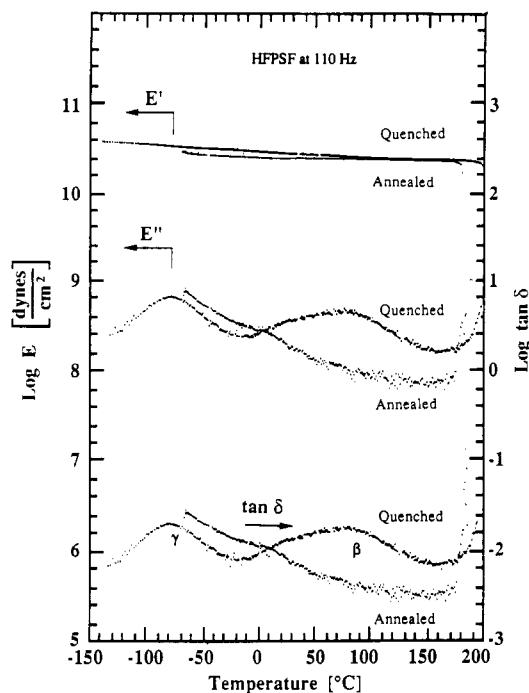


Figure 4. Dynamic mechanical spectra at 110 Hz for annealed and quenched samples of HFPSF.

connected by a single carbon of a cyclohexyl group, i.e., PSF-Z. For this polymer, T_{γ_2} is 45 °C higher than that of PSF. Similar results have been observed for polycarbonate Z.⁵⁹ The restriction in the mobility of the phenylene groups stems, at least in part, from the decrease in FFV caused by this substitution. Due to its inherent conformational flexibility, the bulky cyclohexyl group seems to be able to fill space between chains without increasing chain spacing. This results in a lower FFV and an increase in T_{γ_2} . Interpretation is complicated somewhat by the presence of conformational rearrangements between the two forms of the cyclohexyl ring estimated to occur at -55 °C when the frequency is 110 Hz.¹

It is important to note that the connector group is completely eliminated in the biphenyl polysulfone, BIPSF, and this does not result in a large shift in T_{γ_2} , although the chain is much more rigid since its T_g is approximately 40 °C higher than that of PSF. In addition, the free volume values for BIPSF and PSF are virtually the same. Although $\tan \delta$ curves of PSF and BIPSF in the sub- T_g range are similar, the biphenyl polysulfone curve is somewhat broader with a small peak tentatively labeled γ_1 . It is not yet clear whether this latter peak is really the result of the rigid nature of the biphenyl structure or not. Space-filling molecular models indicate that the rotational motions of the phenyl rings around the bond that connects them are somewhat limited, owing to interference from hydrogens on the adjacent rings; however, this peak might involve packing defects or residual stresses that could be annealed out.

Effect of the Location of the Phenylene Linkages. The differences in relaxation behavior resulting from meta versus para phenylene linkages are examined in this series. The structure of each bisphenol monomer is shown in Table III along with peak temperatures and free volume information. Compared to PSF, polysulfone P (PSF-P) has an additional para phenyl-isopropylidene group in the recurring bisphenol monomer. For polysulfone M (PSF-M) the additional group is connected in the unsymmetrical meta position. In addition, the meta isomer of PSF, 3,4-polysulfone (3,4-PSF), was examined. The $\tan \delta$ curves for these polymers are shown in Figure 5.

For the meta isomers the glass transition temperatures are significantly lower and the densities are higher than for the para isomers. These observations agree with reports on other polymeric isomers.³⁰⁻³⁷ Since the chemical compositions of the isomers are the same, the higher density of the unsymmetrical structures directly reflects the lower free volume available relative to the symmetric molecules. While there may be some cause and effect relation between the observed lower specific volume and lower

T_g for unsymmetrical materials compared to their symmetric forms, the fundamental reasons for this phenomenon are not clear and will be further examined in a subsequent paper.

It is apparent that the addition of the extra ring and isopropylidene unit to the bisphenol monomer does not dramatically affect the γ relaxation temperature when the connection is made in the para position. Indeed, the $\tan \delta$ curves of PSF and PSF-P are virtually identical. This is not surprising since the added phenylene linkages in PSF-P are similar in nature to those in PSF. However, there is a difference in the relaxation spectra when the phenylene group is added in the meta position (PSF-M); viz., the latter exhibits separate γ_1 and γ_2 peaks. The T_{γ_1} for PSF-M is 115 °C higher than T_{γ_2} , perhaps reflecting the hindered mobility about the asymmetric meta linkage compared to the para linkage. It is anticipated that 3,4-PSF has a similar high-temperature γ_1 peak resulting from the meta linkage; however, due to the brittleness of this polymer, it could not be tested at temperatures greater than 80 °C. 3,4-PSF has a higher γ_2 relaxation temperature than PSF perhaps as a result of its lower free volume. In addition, the peak is not large or well-defined.

Effect of Naphthalene Groups. In this series, three polysulfones based on dihydroxynaphthalene isomers were studied. These naphthalene polysulfones, 1,5-NPSF, 2,6-NPSF, and 2,7-NPSF, are more rigid than bisphenol A polysulfone as evidenced by their higher glass transition temperatures (Table IV). However, the T_g s of these polymers with fused phenylene rings are not higher than that for BIPSF. The 1,5-naphthalene linkage seems to hinder mobility most effectively since 1,5-NPSF has a T_g of 240 °C which is 10–15 °C greater than that for the other two isomers.

All three polymers based on naphthalene units have two sub- T_g peaks as shown in Figure 6. Again, the lower peak at approximately -80 °C is believed to be a result of the unsubstituted diphenyl sulfone groups while the higher γ peak is the result of the more hindered motions of the naphthalene unit. In their investigation of naphthalene-based polyesters, which also have two sub- T_g peaks, Blundell and Buckingham⁶⁰ attributed the upper one to the naphthyl moieties and the lower one to phenylene motions. Because the large, rigid naphthalene units must move as a single unit, unlike the unsubstituted para phenyls that comprise bisphenol A polysulfone, it is not surprising that they begin their sub- T_g motions at higher temperatures. However, there is the possibility that the unsymmetric nature of the naphthalene linkages also contributes to the sub- T_g spectra. Like the meta-linked polysulfones, it could be the difficulty of motions about the unsymmetric linkages, not the size and rigidity of the naphthalene group, that shifts the γ_1 peak to high temperatures.

There is a difference in the γ_1 relaxations among the three naphthalene-containing materials. The T_{γ_1} for 1,5-NPSF is approximately 100 °C higher than that of the other isomers. In addition, the amplitude of the 2,7-NPSF γ_1 peak is substantially lower than that for the other two naphthalene polysulfones. Although there is a suppression in the magnitude of the γ_1 peak for 2,7-NPSF, its T_{γ_1} is lower than those for 1,5-NPSF and 2,6-NPSF which indicates that the γ_1 relaxation is not as restricted as the other isomers. There is also a slight difference between the γ_2 relaxations. The amplitude of the 1,5-NPSF peak is lower than that of its isomers; however, the variation among T_{γ_2} values is small. While all of the naphthalene linkages are unsymmetric, it appears that the position of the chain linkages, as in the case of the meta and para isomers, significantly affects the freedom of the sub- T_g motions.

Combined Effects of the Phenylene Connector Group and Ring Methyl Substitutions. Table V shows the structures of bisphenol monomers where the connector group is varied and the rings are methyl substituted. The $\tan \delta$ curves for the corresponding polysulfones are shown in Figures 7–11. As observed for other methyl-substituted polysulfones, two or more peaks appear in the γ region for the tetramethyl-substituted polymers, TMPSF, TMPSF-F, and TMHFPSF (see Figure 7) whereas PSF has only one γ peak. In the region above the γ_2 peak, there is no well-defined γ_1 peak for TMPSF-F and TMHFPSF. However, the magnitudes of $\tan \delta$ in this region are considerably higher for these polysulfones than for PSF. This high background damping

Table III
Structures and Properties of Polysulfones with Para and Meta Phenylene Linkages

bisphenol monomer	polymer	T_g , °C	T_β , °C	T_{γ_1} , °C	T_{γ_2} , °C	ρ , g/cm ³	FFV ((V - V ₀)/V)
	PSF	186	85		-80	1.240	0.156
	3,4-PSF	156		?	-40	1.249	0.149
	PSF-P	191			-85	1.191	0.156
	PSF-M	150		40	-75	1.201	0.151

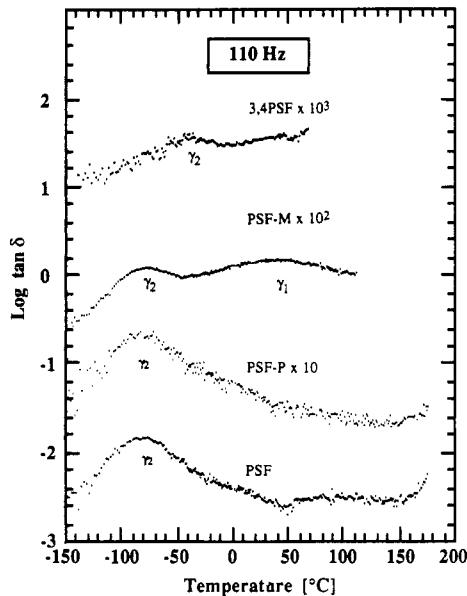


Figure 5. $\tan \delta$ curves at 110 Hz for meta- and para-linked polysulfones.

may indicate a very broad distribution of relaxation processes rather than a more narrowly distributed set of relaxation times necessary for a peak.

For these polymers, the position of the γ_2 peak, which we associate with the unsubstituted sulfone monomer, also follows the previously mentioned relationship with free volume. This peak occurs at the lowest temperature for TMPSF, the polymer with the highest free volume (see Table V). In contrast, T_g is increased by such substitutions because of a loss of large-scale chain mobility. The dimethyl substitution results in a depression of the glass transition temperature relative to PSF-Z which is consistent with the previous discussion of unsymmetrically substituted polymers.

Dimethylcyclohexyl polysulfone (DMPSF-Z) and DMPSF have similar sub- T_g spectra (Figure 8). The dimethyl substitution of PSF-Z results in the appearance of two γ peaks as in the case of dimethyl substitution of PSF to form DMPSF. Again, the methyl groups hinder the phenylene motions. Both of the DMPSF-Z sub- T_g peak maxima occur at higher temperatures than for DMPSF as a result of the lower FFV available due to the cyclohexyl connector group. However, once again, interpretation of the data may be influenced by the interference of motions of the cyclohexyl group itself which at 110 Hz can contribute a peak at -55 °C.¹

Figure 9 shows the effect on dynamic mechanical behavior of adding four methyl groups to the outer rings of PSF-P and PSF-M. As in other cases of methyl ring substitution, TMPSF-P shows two γ peaks. Tetramethyl substitution on the PSF-P chain causes an increase in the glass transition temperature; however, the increase is not as great as that between PSF and TMPSF. It can be inferred from this data that the additional phenylisopropylidene group in the bisphenol monomer allows for more long-chain flexibility by diluting out the rigidity imparted by the

tetramethyl substitutions. As in other cases of methyl ring substitution, TMPSF-P shows two γ peaks. Additionally, T_{γ_2} is higher for TMPSF-P than for TMPSF. This implies that the lengthened bisphenol unit increases the ability of the chains to pack efficiently because of the increased number of available conformations and by dilution of the disruptions caused by the pendent methyl groups. The meta isomer, TMPSF-M, also has two sub- T_g relaxations, with a much broader γ_1 peak, reminiscent of the PSF-M γ_1 peak. Sub- T_g data were not obtained for TMPSF-M above 150 °C due to film brittleness; hence, the temperature of the peak maximum, T_{γ_1} , is not listed in Table V.

The effect of methyl substitutions on the thermal transitions of biphenyl ether polysulfones has also been studied. Tetramethyl and hexamethyl substitutions onto the biphenyl rings result in glass transition temperatures that are 100 °C higher than that of PSF (see Table V). Combining the rigid, linear biphenyl bond with the highly substituted phenyl rings, leads to very rigid chains. Figure 10 shows how the methyl substitutions affect the sub- T_g behavior. There is a clear splitting of the $\tan \delta$ curve into two peaks for the tetramethylbiphenyl polysulfone (TMBIPSF). These two γ peaks are more distinct than the two γ peaks in TMPSF. While the elimination of the isopropylidene group in the tetramethyl polysulfone does not dramatically affect the γ_2 relaxation temperature, the motions associated with the γ_1 peak are more hindered.

The γ_1 peak for hexamethylbiphenyl polysulfone (HMBIPSF) is apparent in Figure 10, but evidently its maximum is slightly above the temperature range of the Rheovibron. The Polymer Laboratories DMTA was used to verify the presence of a γ_1 peak at approximately 200 °C and the α transition at 300 °C. This γ_1 relaxation is almost 300 °C higher than the γ_2 temperature. In addition, T_{γ_1} for HMBIPSF is 150 °C higher than that for TMBIPSF. It is apparent from space-filling molecular models that the ortho CH_3 group in HMBIPSF eliminates rotation of the phenyls about the biphenyl bond. The difference between the γ_1 relaxation temperatures suggests that while there is rotation around the biphenyl bond for BIPSF and TMBIPSF, it does not occur for HMBIPSF. Studies of other ortho substituents on biphenyls, such as for 6,6-dinitrobiphenyl-2,2-dicarboxylic acid, show that steric interactions can completely prevent rotation of the biphenyl rings with respect to each other.⁶¹

For both the tetramethyl- and hexamethyl-substituted biphenyl polysulfones, the γ_2 peak is shifted to a lower temperature, -90 °C compared to -75 °C for BIPSF, because of the increase in the FFV. However, it should be noted that the T_{γ_2} for TMBIPSF is as low as that of TMPSF. It is also significant to note that there is a decrease in the intensity of the γ_2 peak as more methyl groups are added to the biphenyl rings. The substituted biphenyl groups may limit in some way the motions of the unsubstituted groups participating in the lower temperature relaxation. While this could be a result of intrachain cooperation, it would stand in significant contrast to the broad single peak that is observed for the PC-TMPC alternating copolymer. There is also the possibility that the T_{γ_2} peak reflects to some extent motions of the SO_2 group. The contribution of the SO_2 group to the peak at about -100 °C has been observed and could be superimposed on the transitions associated with the phenylenes and other groups. However, it is unlikely that the sulfone group alone could be responsible for this peak.

Table IV
Structures and Properties of Naphthalene Polysulfones

bisphenol monomer	polymer	T_g , °C	T_β , °C	T_{γ_1} , °C	T_{γ_2} , °C	ρ , g/cm ³	FFV (($V - V_0$)/ V)
	PSF	186	85		-80	1.240	0.156
	1,5-NPSF	240		200	-80	1.328	0.148
	2,6-NPSF	227		110	-70	1.328	0.148
	2,7-NPSF	225		80	-70	1.339	0.142

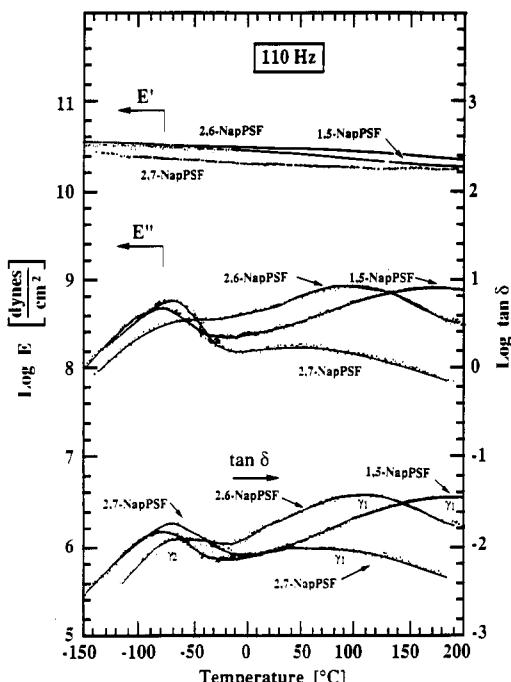


Figure 6. Dynamic mechanical properties at 110 Hz for naphthalene-based polysulfones.

Conclusions

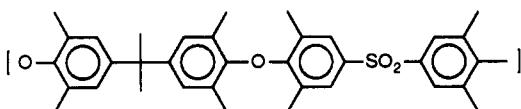
Analysis of the dynamic mechanical spectra of a broad range of polysulfones has produced important insight about the relative roles of intramolecular and intermolecular barriers to motions in these materials by observing how polymer structure affects the T_g and sub- T_g spectra. Especially noteworthy is the observed influence of chain packing or free volume on the temperature at which the γ relaxation occurs.

The glass transitions of these polysulfones are strongly affected by the nature of the structural modifications. Changes in the group connecting the phenylene rings in the bisphenol that allow more flexibility (e.g., PSF-O) decrease T_g . Conversely, more rigid connectors (e.g., the polysulfone based on 4,4'-biphenol) increase T_g . Symmetric tetramethyl substitutions on the bisphenol rings cause an increase in both T_g and the spacing between polymer chains. In contrast, unsymmetrical dimethyl substitution onto the bisphenol rings results in decreases in both T_g and free volume. Additionally, polysulfones with unsymmetric meta linkages between rings have much lower glass transition temperatures than their para isomers. There is an emerging trend that polymers with an unsymmetric nature, from either phenyl substituents or phenyl linkages, have more densely packed chains and sup-

pressed glass transition temperatures. This is in contrast with carbon chain polymers, e.g., vinyl versus vinylidene types, for which the unsymmetrical polymers have a higher T_g .⁶²⁻⁶⁴

The addition of methyl groups to the phenyl rings of the bisphenol unit of polysulfone or replacement with naphthalene diols consistently results in the splitting of the γ relaxation of the $\tan \delta$ curve into two peaks of comparable size. We proposed that the region of the γ_1 peak corresponds to the motions of the bisphenol unit, while the γ_2 peak corresponds to motions of the diphenyl sulfone unit. The two peaks are most distinctly separated for the polymers which have very rigid structures such as TMBIPSF and HMBIPSF and the naphthalene polysulfones. The limited mobility of the modified groups in these polymers shifts T_{γ_1} to higher temperatures yet leaves T_{γ_2} relatively unaffected. For these polysulfones, it appears there is relatively little intramolecular coupling between the relaxation process of the two monomer groups which is in contrast to the extended cooperation between monomer units that has been proposed for polycarbonates.^{12,14} This most likely reflects the inherent flexibility of the ether linkage in polysulfone. According to this view, the sub- T_g relaxation processes in polysulfones involve a smaller length of the chain than in the case of polycarbonates. This may explain the higher toughness of the polycarbonate based on bisphenol A than the corresponding polysulfone.

We suggest that determination of the dynamic mechanical behavior of polysulfones like



would help confirm whether the origin of the γ_2 peak resides in the diphenyl sulfone unit as proposed or not. If the assignment made above is correct, we would expect the γ_2 peaks observed here to be eliminated and that only a single high-temperature γ_1 peak (consistent with the 3,5-dimethyl-substituted phenyl rings) would be present. An alternative interpretation of the low-temperature γ_2 relaxation is that it arises from independent motions of the sulfone unit. If the dynamic mechanical spectra of the polymer suggested above resulted in only one high-temperature γ relaxation, this would provide evidence against this argument.

We observed that when the isopropylidene unit of bisphenol A polysulfone was replaced with other groups, the sub- T_g part of the $\tan \delta$ curve was usually not affected in a significant way, e.g., two separate peaks of equivalent size were not observed consistently. Even when the iso-

Table V
Structures and Properties of Polysulfones with Different Phenylene Connector Groups and Methyl Substitutions on the Phenyl Rings

bisphenol monomer	polymer	T_g , °C	T_β , °C	T_{γ_1} , °C	T_{γ_2} , °C	ρ , g/cm ³	FFV $((V - V_0)/V)$
	TMPSF	242		-10	-92	1.151	0.171
	TMPSF-F	232		?	-85	1.184	0.163
	TMHFFPSF	243		?	-100	1.286	0.196
	TMPSF-P	214		-10	-85	1.127	0.168
	TMPSF-M	175		?	-90	1.141	0.158
	DMPSF-Z	197		100	-35	1.227	0.136
	TMBIPSF	288		50	-90	1.195	0.164
	HMBIPSF	295		200	-100	1.144	0.178

Table VI
Structures and Properties of Poly(bisketones) and Poly(bissulfones)

polymer	T_g , °C	T_β , °C	T_{γ_1} , °C	T_{γ_2} , °C	density, g/cm ³	FFV $((V - V_0)/V)$
	150	90	-80	1.20	0.164	
PC						
	180		40	-70	1.119	0.146
PBK						
	219		55	-55	1.29	0.143
PBK-S						
	185	100	-85	1.240	0.156	
PSF						
	240	25	-80	1.267	0.155	
PBSF						

propylidene group is replaced by a flexible ether unit (PSF-O) or completely eliminated (BIPSF), the sub- T_g spectrum is relatively unchanged. However, when a para phenylene ring is replaced with a meta phenylene ring, the sub- T_g part of the tan δ curve is again split into two peaks. Since only modifications that directly affect the phenylene rings have a significant effect on the spectra in the γ region, it appears that the phenylene motions are the primary origin of the sub- T_g relaxations.

The close proximity of the phenyl rings in the rigid biphenyl polymers leads to some special interactions of their sub- T_g motions. Biphenyl polysulfone has a much higher T_g than bisphenol A polysulfone, yet its T_{γ_2} is virtually the same. Moreover, there is a large difference between T_{γ_1} of HMBIPSF versus TMBIPSF. This suggests that while motions readily occur around the biphenyl bond in BIPSF and TMBIPSF, they are very suppressed for HMBIPSF if not eliminated altogether.

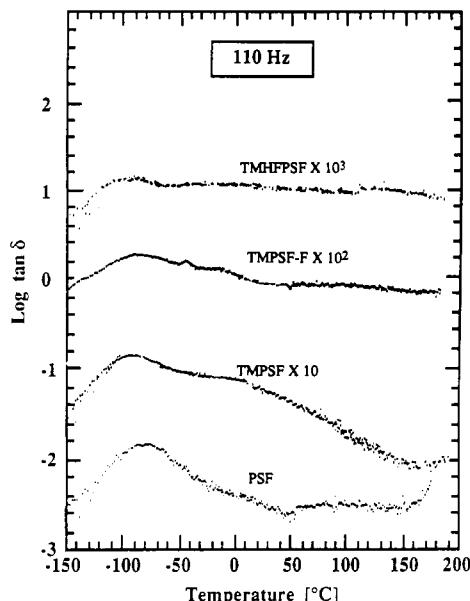


Figure 7. $\tan \delta$ curves at 110 Hz for polysulfones with the different phenylene connector groups and methyl substitutions.

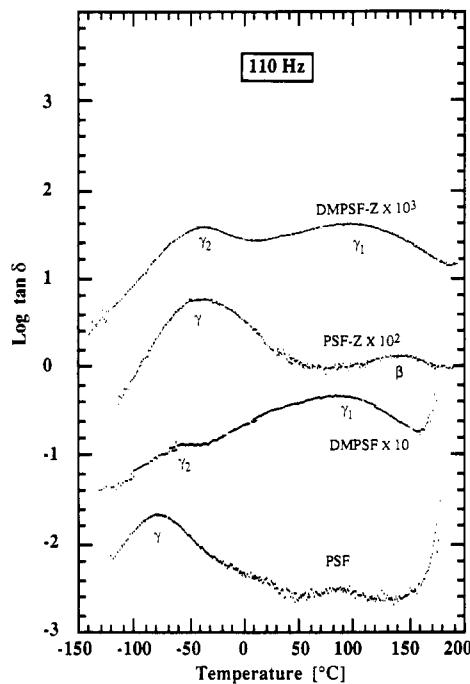


Figure 8. Effect of dimethyl substitution on sub- T_g spectra for polysulfones with a cyclohexyl connector group.

The mechanical relaxation temperatures of the polysulfones are also affected by intermolecular factors. There is a tendency for T_{γ_2} , attributed to the diphenyl sulfone units, to decrease as the fractional free volume of the polymer increases. Evidently an increase in intermolecular spacing between chains allows the motion contributing to the γ_2 relaxation to occur more freely.

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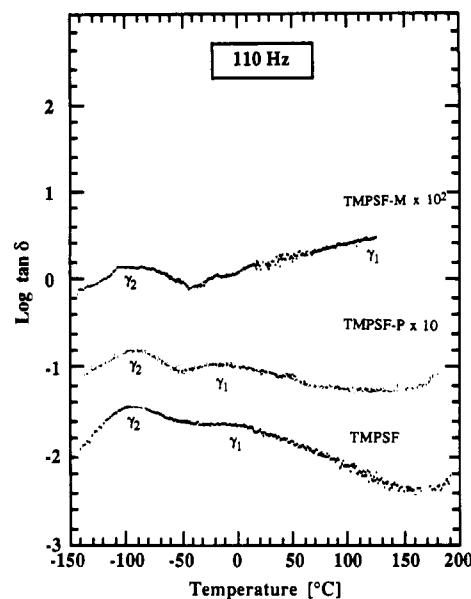


Figure 9. $\tan \delta$ curves at 110 Hz for TMPSF, TMPSF-P, and TMPSF-M.

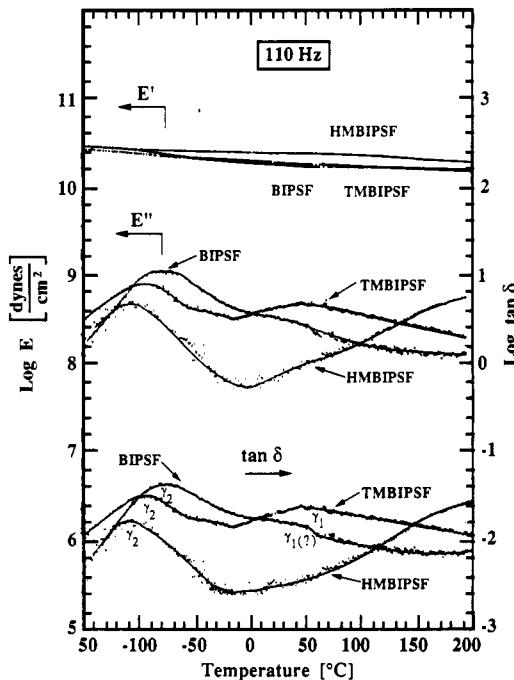


Figure 10. Dynamic mechanical properties at 110 Hz for BIPSF, TMBIPSF, and HMBIPSF.

Appendix A. Comparison of Bisketone and Bissulfone Polymers

The synthesis of poly(aryl ethers) requires the presence of an electron-withdrawing group to activate the aryl halogens for reaction with bisphenols. The sulfone unit serves this purpose for the synthesis of polysulfones. As mentioned in the text, there are some questions regarding possible roles of the sulfone unit in the dynamic mechanical relaxations below T_g . Thus, it would be instructive to consider polymers of comparable structures with and without the sulfone unit. Carbonyl units can serve a similar electron-withdrawing role as sulfone units and permit the synthesis of poly(ether ketones).

The polymers whose structures and physical properties are shown in Table VI were used to compare the effects of replacing the sulfone with a ketone group. Bisphenol A poly(bissulfone) (PBSF) differs from PSF by an additional diphenyl sulfone unit. PBSF is equivalent in

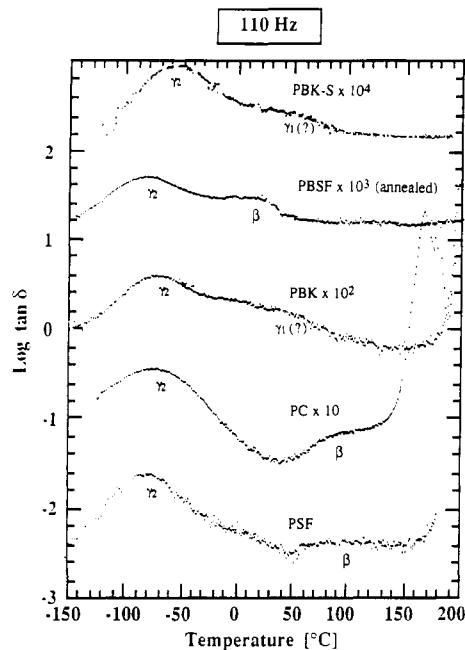


Figure 11. $\tan \delta$ curves at 110 Hz for poly(aryl bisketones) and poly(aryl bissulfones).

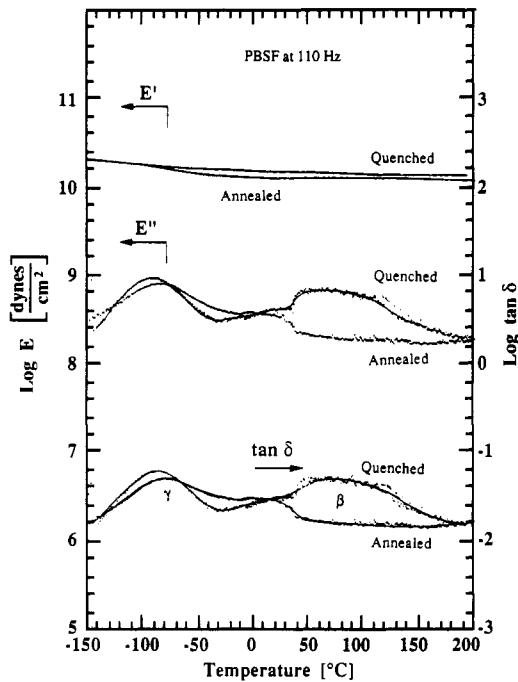
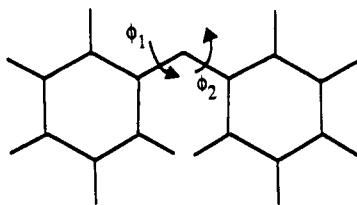


Figure 12. Dynamic mechanical spectra of quenched and annealed samples of PBSF.



$0^\circ, 0^\circ$

Figure 13. Conformation of diphenyl ether with $\phi_1 = 0^\circ$ and $\phi_2 = 0^\circ$.

structure to bisphenol A poly(bisketone) (PBK). Bisphenol S poly(bisketone) (PBK-S) has a sulfone group in place of the isopropylidene in PBK. The elastic moduli in the glassy state are virtually the same for all of these polymers,

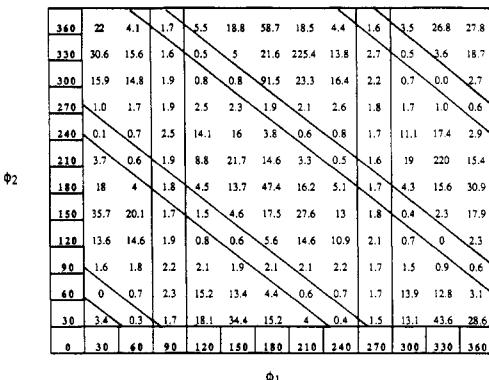
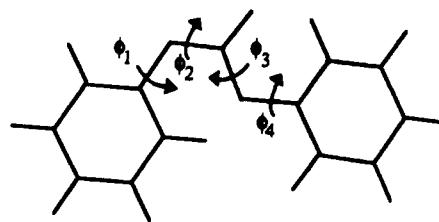
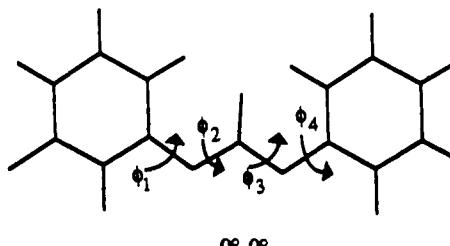


Figure 14. Conformational energy map of diphenyl ether (ΔE , in kcal/mol) as a function of the rotational bond angles ϕ_1 and ϕ_2 .



$0^\circ, 0^\circ$

Figure 15. Cis-trans conformation of diphenyl carbonate with $\phi_1 = 0^\circ$ and $\phi_4 = 0^\circ$.



$0^\circ, 0^\circ$

Figure 16. Trans-trans conformation of diphenyl carbonate with $\phi_1 = 0^\circ$ and $\phi_4 = 0^\circ$.

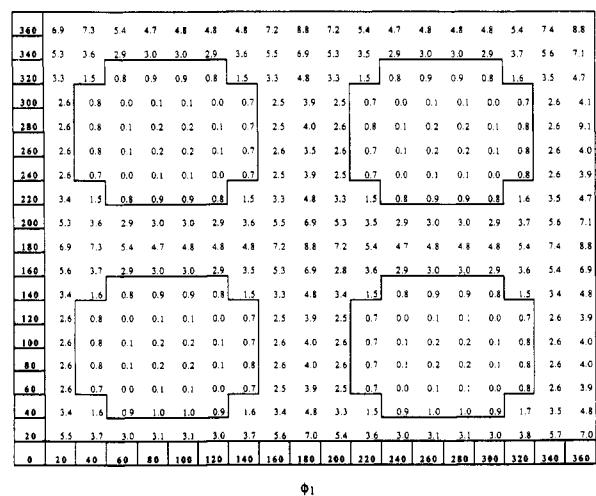


Figure 17. Cis-trans conformational energy map of diphenyl carbonate (ΔE , in kcal/mol) as a function of the rotational bond angles ϕ_1 and ϕ_4 .

viz., 2×10^{10} dyn/cm². $\tan \delta$ curves for each polymer are shown in Figure 11, offset by a decade each for clarity. The PBSF sample used was annealed while all other samples were quenched. Curves for PSF and PC are included for reference. All of the spectra are similar, with

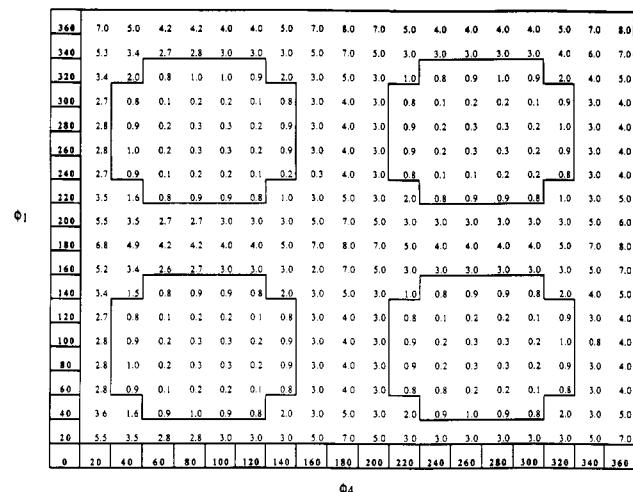


Figure 18. Trans-trans conformational energy map of diphenyl carbonate (ΔE , in kcal/mol) as a function of the rotational bond angles ϕ_1 and ϕ_4 .

a consistent peak at approximately -80°C ; however, there are subtle differences. All of the new polymers presented in Figure 11 show higher levels of damping above the γ peak than do PC or PSF. PBSF shows a small peak at about 20°C that is especially sensitive to thermal history; e.g., compare the large changes shown in Figure 12 between quenched and annealed PBSF samples; hence, we label this a β peak. It is unclear whether the peaks labeled γ_1 for PBK and PBK-S are also the result of packing defects (i.e., β relaxations) or of limited mobility of these structures. To clarify this, a more complete annealing study would be necessary.

There are small differences in the dynamic mechanical spectrum as a result of the ketone and sulfone contributions. PBK-S has the highest T_{γ_2} and lowest free volume of these polymers which, as shown in Figure 2, follow the relationship between FFV and T_{γ_2} . However, when the isopropylidene group of polysulfone is replaced with a sulfone unit in PES, there is no observable shift in the sub- T_g transition. Yet, from the similarity of the sub- T_g spectra between PBK and PBSF we must conclude that whatever the contribution of the SO_2 unit to the sub- T_g dynamic mechanical spectra, the carbonyl unit makes a similar one. In addition, the shape of the $\tan \delta$ curve for BIPSF is also very similar to PBK and PBSF, which suggests that the biphenyl unit contributes to a broadening of the γ peak.

Appendix B. Conformational Energy Analysis

To understand, on a molecular level, the differences between polysulfones and polycarbonates, a brief molecular modeling exercise appeared useful. It was proposed above that differences observed in the sub- T_g spectra of tetramethylbisphenol A polysulfone (TMPSF) and copolymers of bisphenol A polycarbonate (PC) and tetramethylbisphenol A polycarbonate (TMPC) may stem from differences in motions about the ether and the carbonate units. To investigate the relative flexibility of these molecules, conformational energy maps of isolated diphenyl ether and diphenyl carbonate molecules were generated using the Tripos software package SYBYL, operated on an Evans and Southerland 3000 system. The energy components of a molecule in the Tripos force field include bond stretching, angle bending, out-of-plane bending, torsional, van der Waals, and electrostatic energy terms. The electrostatic interaction energy is from the Coulombic potential where the point charges on the atoms are calculated by the Gast-Huck method, a combination of

the Gasteiger-Marsili and the Huckel methods. To calculate the minimum energy, two iterative methods were used in which the atomic coordinates were modified to decrease the energy. Initially a simplex method was applied. This nonderivative method was more compatible with discontinuities in the potential energy surface and its derivatives that were sometimes present in the highly stressed structures at the start of the minimization. At lower energies, the quasi-Newton procedure or Broyden, Fletcher, Goldfarb, and Shanno (BFGS)⁶⁵ was used to find the minimum energy. This procedure had better convergence properties than the other methods tried (Powell or steepest descent).

Following the procedure used by Sun,⁶⁶ the diphenyl ether bonds labeled ϕ_1 and ϕ_2 (see Figure 13) were independently rotated in 30° increments, after which all other internal coordinates were optimized to obtain the minimum energy. The minimum energies found are shown in Figure 14 as a function of the rotatable bond angles. The energy values are relative to the lowest conformational energy.

As Figure 15 illustrates, there are four rotatable bonds for diphenyl carbonate. The bonds labeled ϕ_1 and ϕ_4 were independently rotated in 20° increments, after which all other degrees of freedom were optimized to find the minimum conformational energy. This procedure was repeated for several starting angles of ϕ_2 and ϕ_3 to ensure that each point was a global rather than a local minimum. Minima occurred at ϕ_2 and ϕ_3 corresponding to the cis-trans and the trans-trans conformations. The cis-trans form is shown in Figure 15 while the trans-trans form is seen in Figure 16. The energy map with ϕ_2 and ϕ_3 in the cis-trans conformation is shown in Figure 17, while the trans-trans energy map is shown in Figure 18. A comparison shows that the trans-trans combinations of ϕ_1 and ϕ_4 are generally lower than the cis-trans version and that both energy maps have the same overall shape. The fact that the trans-trans form has slightly lower energies than the cis-trans form is in agreement with the MNDO and Gaussian 80/82 calculations of others.^{46,67}

There are obvious differences between the energy maps of diphenyl ether and diphenyl carbonate. For the former there are rotational paths that require relatively little energy to execute a complete rotation of at least one phenyl ring. These paths are highlighted in Figure 13. When one phenyl ring is fixed at either 90° or 270° , the other can undergo a complete rotation without encountering energy barriers significantly greater than RT . It is also important to note that the highlighted diagonals are "geared" paths; i.e., as one phenyl ring turns, the other turns to maintain the 180° offset. This motion encounters an even lower energy barrier than the two paths where one phenyl is fixed at 90° or 270° . In contrast, the energy map for diphenyl carbonate has four symmetric regions of low energy that are separated by higher energy barriers. In addition, there are no low-energy diagonal paths between these regions.

These energy maps indicate that rotational motions are severely more restricted in diphenyl carbonate than in diphenyl ether. Because of this rigidity, diphenyl carbonate segments in polycarbonate may tend to move as a single unit rather than gearing or independently rotating about the carbonate units. This would be consistent with Yee's hypothesis of a concerted motion of several (6-8) monomer units participating in the sub- T_g motions of polycarbonate. Therefore, the phenylene motions in PC may be more coupled than those in PSF as a result of differences in mobility about the carbonate and ether units; however,

such simple energy calculations for isolated molecules cannot provide a fully realistic model for motions in the glassy polymer matrix.

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Registry No. PSF (copolymer), 25154-01-2; PSF (SRU), 25135-51-7; DMPSF (copolymer), 134245-99-1; DMPSF (SRU), 58978-16-8; TMPSF (copolymer), 29658-28-4; TMPSF (SRU), 32034-67-6; PSF-O (copolymer), 30325-48-5; PSF-O (SRU), 32031-01-9; PES (copolymer), 25608-63-3; PES (SRU), 38885-52-8; PSF-Z (copolymer), 140659-75-2; PSF-Z (SRU), 31694-10-7; PSF-F (copolymer), 55267-41-9; PSF-F (SRU), 31694-05-0; BIPSF (copolymer), 25608-64-4; BIPSF (SRU), 25839-81-0; PSF-AP (copolymer), 25897-81-8; PSF-AP (SRU), 26635-20-1; HFPSF (copolymer), 90884-65-4; HFPSF (SRU), 31694-07-2; 3,4-PSF (copolymer), 74753-54-1; PSF-P (copolymer), 30794-90-2; PSF-P (SRU), 31514-67-7; PSF-M (copolymer), 126037-96-5; PSF-M (SRU), 125999-06-6; 1,5-NPSF (copolymer), 110098-80-1; 1,5-NPSF (SRU), 87091-79-0; 2,6-NPSF (copolymer), 123850-41-9; 2,6-NPSF (SRU), 123851-71-8; 2,7-NPSF (copolymer), 110098-79-8; 2,7-NPSF (SRU), 110084-72-5; TMPSF-F (copolymer), 87431-05-8; TMPSF-F (SRU), 87430-84-0; TMHFPSF (copolymer), 140659-76-3; TMHFPSF (SRU), 140659-80-9; TMPSF-P (copolymer), 140659-77-4; TMPSF-P (SRU), 140659-81-0; TMPSF-M (copolymer), 140659-78-5; TMPSF-M (SRU), 140659-82-1; DMPSF-Z (copolymer), 140659-79-6; DMPSF-Z (SRU), 134140-27-5; TMBIPSF (copolymer), 62318-40-5; TMBIPSF (SRU), 25839-82-1; HMBIPSF (copolymer), 133370-76-0; HM-BIPSF (SRU), 133370-59-9.