

A Dynamic Mechanical Study of the Effect of Chemical Variations on the Internal Mobility of Linear Epoxy Resins (Polyhydroxyethers)

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Synopsis

A series of polyhydroxyethers prepared from various bisphenols and their diglycidyl ethers has been investigated for dynamic mechanical behavior in a temperature range from -180°C . up to their glass-rubber transition region, employing a torsion pendulum method for frequencies of about 0.1 hz and a vibrating-reed method for frequencies of about 100 hz. Glass-rubber transition temperatures ranged from 85 to 170°C . and are interpreted in terms of polarity, segment bulkiness, and packing capability of the polymer molecules. In most cases the activation energy of this transition was found to be extremely high, of the order of 500 kcal./mole. Fair consistency is found regarding the role played by methyl or chlorine substitution of the bisphenol rings, increasing bulkiness and steric hindrance, but reducing polar interaction. At least one and, in some cases, two secondary transitions were found well below the glass-rubber transition region. One is ascribed to a change in mobility of the glyceryl ether segments common to all nonesterified polymers of the series. While this is in general agreement with the findings of other authors, we found a spread in transition temperature values (-70 to -102°C . at ≈ 1 hz) and activation energies which can be related to the detailed chemical structure of these polymers. With methyl substitution of the bisphenol rings of the highly polar polymers symmetry seems to be an important factor. In addition, another secondary transition appeared, which we ascribe to an onset of ring rotation.

INTRODUCTION

Epoxy resins based on 2,2-bis(4-hydroxyphenyl) propane of relatively low molecular weight (up to ≈ 5000) have become familiar as thermosetting resins. In the past few years high molecular weight materials of the same or similar overall structure have come to the fore. Reinking, Barnabeo, and Hale in a series of papers¹ have given an interesting review of some properties of that polymer, of a large number of related homopolymers, and of copolymers and ester derivatives of these. Besides, the gas permeabilities the glass transition temperatures were given as the most significant characteristic for these compounds.

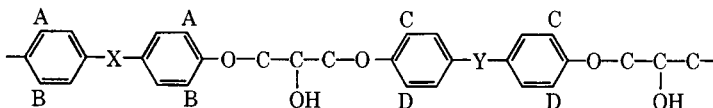
The present paper deals with similar types of polymer. However, a different choice of polymers has been made, and other methods of investigation have been applied.

EXPERIMENTAL

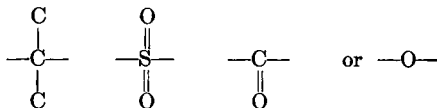
Polymers

A detailed description of polymer preparation is outside the scope of this paper, but we may mention that polymerization was effected through the condensation reaction of bisphenols with diglycidyl ethers of such compounds in a 1:1 molar ratio.

Accordingly, the resulting polymers may be represented by the general formula of the repeating segment:



where the ring substituents A, B, C, and D are hydrogen, methyl, or chlorine, and the bisphenol bridge groups X and Y are



The molecular weights M_w , as determined by light scattering, varied between 25,000 and 300,000, depending on the reaction conditions. For the present study use was made of polymers with a M_w of roughly 100,000. The copolymers studied were of the alternating type, obtained by using one bisphenol and the diglycidyl ether of another. Interchanging of these two bisphenols should and did yield the same polymer, apart from the end segments.

Table I lists the bisphenols used in this work together with their structures and the abbreviations used for naming the various polymers and copolymers we investigated. Thus, the polymer name DPP + DPS expresses briefly that the polymer has been prepared either from bisphenol DPP and the diglycidyl ether of bisphenol DPS or from bisphenol DPS and the diglycidyl ether of bisphenol DPP.

Measuring Methods

All polymers were subjected to two dynamic mechanical testing procedures from which a modulus (i.e., real part of the complex modulus) and a loss tangent were derived. Typical samples were 5 to 10 cm. long, 1 cm. wide, and 0.05 to 0.1 cm. thick, cut from hot-pressed sheets. Low-frequency determinations (0.01 to 1 hz) were done with a torsion pendulum, yielding the shear modulus G and the loss factor in shear, $\tan \delta_s$. For the higher frequencies (20 to 200 hz) use was made of a vibrating-reed type of apparatus employing only the fundamental bending vibration of the sample, which most accurately yields Young's modulus E and the loss factor in bending, $\tan \delta_b$. The former method involves free, damped, vibrations, whereas the latter is a forced-vibration resonance method. For a discussion

TABLE I
Names, Abbreviations, and Structures of Bisphenols

Bisphenol	Abbreviation	Structure
Bis(4-hydroxyphenyl) propane or <i>p,p'</i> -diphenylolpropane	DPP	
Bis(3,5-dimethyl-4-hydroxyphenyl) propane	TMDPP (tetramethyl-DPP)	
Bis(3,5-dichloro-4-hydroxyphenyl) propane	TCIDPP (tetrachloro-DPP)	
Bis(4-hydroxyphenyl) sulfone or <i>p,p'</i> -diphenylolsulfone	DPS	
Bis(3-methyl-4-hydroxyphenyl) sulfone	DMDPS (dimethyl-DPS)	
Bis(3,5-dimethyl-4-hydroxyphenyl) sulfone	TMDPS (tetramethyl-DPS)	
Bis(4-hydroxyphenyl) ketone or <i>p,p'</i> -dihydroxybenzophenone	DHBP	
Bis(4-hydroxyphenyl) ether	DHPE	

of these methods we refer to a number of textbooks on polymer physics.²⁻⁴ Measurements were done at intervals of about 10°C. At each temperature a sample was allowed to accommodate for about 20 min. When a maximum in $\tan \delta$ was approached, a smaller temperature interval was chosen. Accordingly, a maximum was located with an accuracy of +2 or -2°C.

RESULTS AND DISCUSSION

General

Table II lists the polymers and copolymers studied in this context, together with data referring to the various transition points. For some of these polymers the full temperature-dependent dynamic-mechanical behavior is illustrated in Figures 1-8, representative of the various types of

TABLE II
Transition Temperatures T_i ($^{\circ}\text{C}$.), $\tan \delta$ and G or E Modulus (10^9 dyne/cm.²) at T_i

Polymer	In shear (G modulus)			In bending (E modulus)		
	$T_i, \tan \delta$	$T_i, \tan \delta$	$T_i, (\infty) = T_g$	$T_i, \tan \delta$	$T_i, \tan \delta$	$T_i, (\infty) = T_g$
DPP + DPP	-80 0.072		+100	-40 0.075	+60 0.018	+100
DPS + DPP	-85 0.056	+57 0.023	+130	-46 0.083		+140
DPS + DPS	-80 0.072		+165	-40 0.082		+170
DMDPS + DPP	-84 0.042	+31 0.040	+110	-80 & -54 0.036 & 0.040		+125
TMDPS + DPP	-90 0.059		+135	-46 0.08		+140
DMDPS + DPS	-99 0.049	+21 & +55 0.040 & 0.046	+140	-50 0.045	+70 0.052	+145
TMDPS + DPS	-91.5 0.065	+20 0.032	+135	-56 0.060	+70 0.035	+155
DMDPS + DMDPS	-102 0.039	+45 0.065	+130	-48 0.031	+75 0.067	+135
TMDPS + TMDPS	-90 0.067	+32 0.036	+145	-53 0.054		+160
DHBP + DPP	-70 0.075		+120	-40 0.069		+120
DHBP + DHBP	-80 0.061	+40 0.029	+130	-38 0.061		+130
DHPE + DPP	-80 0.065		+85	-46 0.078		+85
(DPS + DPS) acetate	-120 0.032	-20 0.033	+90	-120 & -65 0.033 & 0.030	+20 0.038	+90
Polycarbonate	-104 0.040		+155	-70 0.032		+155
DPP + TMDPP	-96 0.055		+100	-60 0.044		+100
DPP + TCIDPP	-90 0.052		+100	-60 0.054		+100
DPS + TMDPP	-80 0.078		+145	-50 0.072		+145
TMDPS + TMDPP	-94 0.053	+75 0.017	+145	-54 0.061	+80 ?	+145
TMDPP + TMDPP	-88 0.075		+130	-60 0.062		+130
TCIDPP + TCIDPP	-86 0.061		+135	-56 0.053		+135

behavior we came across. Besides the major (or glass-to-rubber) transition at the high-temperature end, one or more secondary transitions were found. In Reinking et al.^{1a} mention was made of only one minor transition, near -70°C . Our dynamic-mechanical methods, especially the damping measurements, seem to have been capable of revealing more detail and, moreover, allow energies of activation to be calculated for the minor transitions.

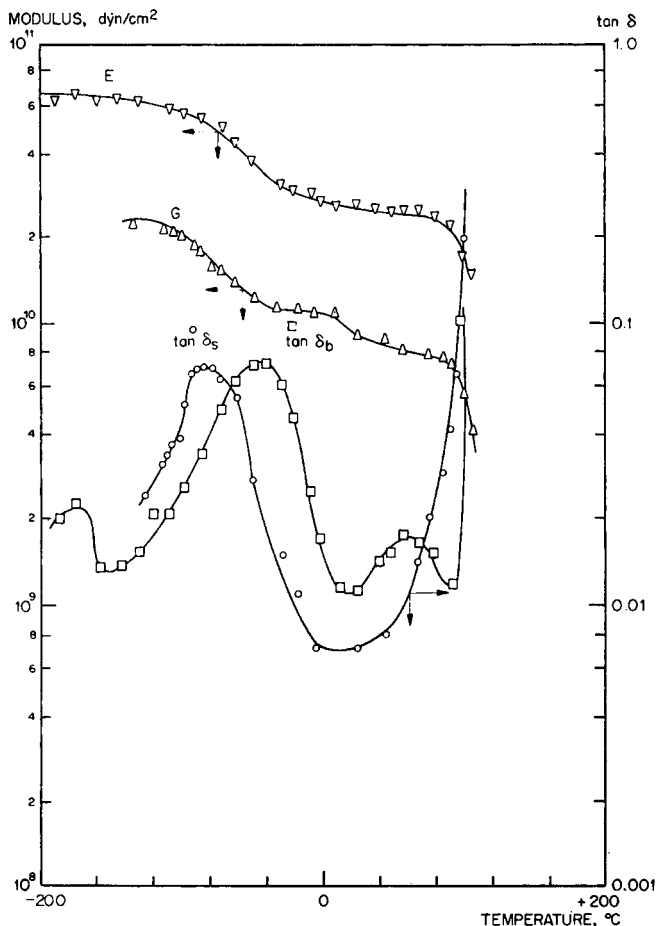


Fig. 1. DPP + DPP.

We did not continue the measurements beyond the major transition region, so that only estimates of activation energy can be given.

Qualitatively, the curves obtained from torsion and bending measurements were not always completely the same, as would be expected. In Figure 1, for instance, a small peak in $\tan \delta_b$ was found at about 60°C ., which did not show up in $\tan \delta_s$. We cannot offer a definite explanation, but we think that in this case a different heat treatment prior to measurement

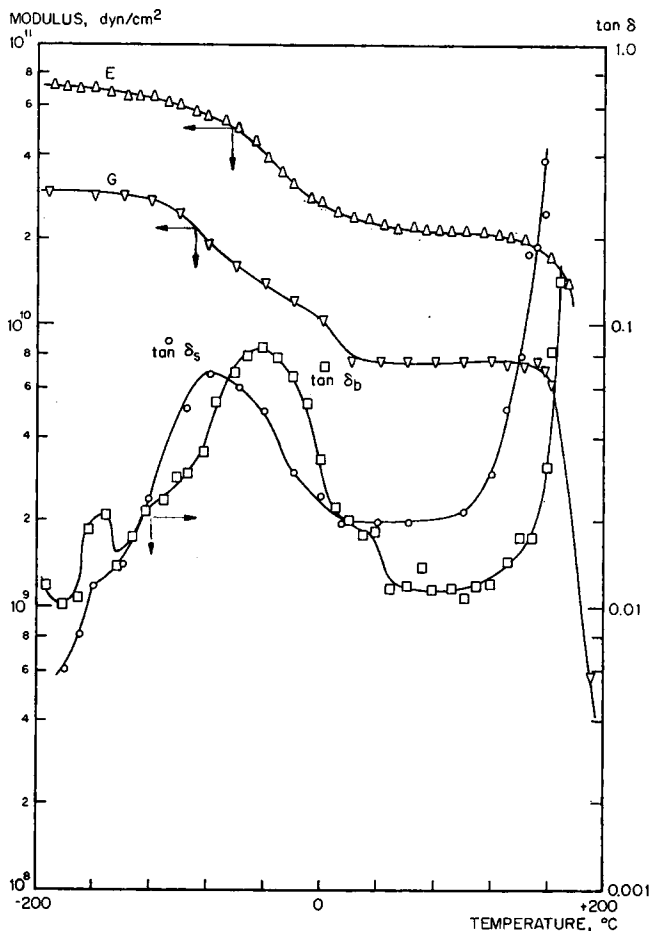


Fig. 2. DPS + DPS.

had to do with the small extra peak not far below the glass transition temperature.

Glass-Rubber Transition

The temperature T_g at which the glass-to-rubber transition takes place will depend on the internal chain stiffness of a single molecule, for which only a few monomer segments in succession need be considered, and on interactions between part of one molecule and either parts of other molecules or more distant parts of the same molecule.

We shall try to interpret our results in such terms, paying particular attention to interactions of steric and polar natures. We have to take these into consideration, because chain stiffness considerations alone, as put forward by Edgar and Hill,⁵ do not suffice to explain our results. Their view and calculations on the influence of the *p*-phenylene linkage

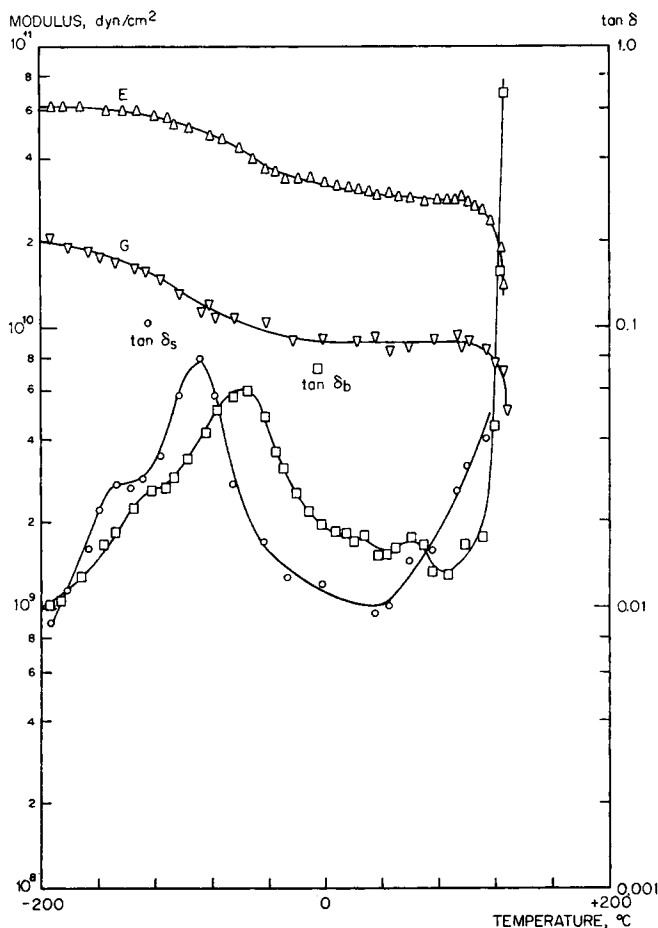


Fig. 3. TMDPP + TMDPP.

lead to the formula $T_g = T_{g0}(1 + N/100 \times M/m)$ in degrees Kelvin, N being the number of p -phenylene linkages per 100 aliphatic chain atoms, M the molecular weight of the phenylene unit, m the average molecular weight per chain atom of the aliphatic chain part, and T_{g0} the glass transition temperature of the chain without p -phenylene groups. Reasoning along the same lines, the TMDPP + TMDPP polymer should have a T_g 74°C. higher than that of DPP + DPP, whereas only a difference of 30° C. has been found. Similarly, TMDPS + TMDPS should have a T_g 80°C. higher than that of DPS + DPS, whereas in reality a lower T_g has been found.

Nevertheless, it is fairly certain that chain stiffening occurs when the mass of the aromatic rings is increased by substitution with chlorine or methyl groups, as is illustrated by the data grouped in pairs in Table III. The alternating copolymers DPP + TMDPP and DPP + TCIDPP do

not follow this trend, as they had virtually the same T_g as DPP + DPP. The reason for this deviation may be that stiffening by "loading" is counteracted by a reduction of the close-packing capability. The conclusion would then be that the close-packing capability is already destroyed by a small number of methyl or chlorine groups without a further effect

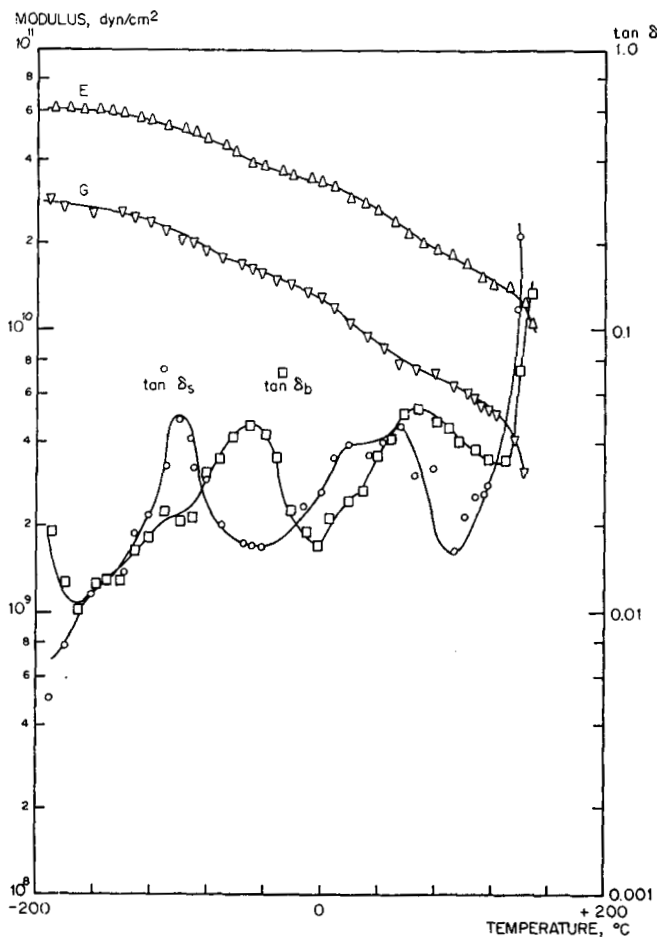


Fig. 4. DMDPS + DPS.

upon that number being doubled, whereas the loading effect would keep pace with the number of methyl or chlorine groups. A similar situation arises when a strongly polar group such as

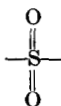


TABLE III
Glass Transition Temperature T_g as a Function of Aromatic Ring Bulkiness

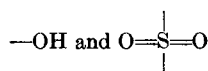
Polymer	T_g , °C.
DPP + DPP	100
TMDPP + TMDPP	130
DPP + DPP	100
TCIDPP + TCIDPP	135
DMDPS + DPP	110-125
TMDPS + DPP	135-140
DMDPS + DPS	140-145
TMDPS + DPS	135-155
DMDPS + DMDPS	130-135
TMDPS + TMDPS	145-160
DPS + DPP	130-140
TMDPS + TMDPP	145
DPP + TMDPP	100
TMDPP + TMDPP	130
DPP + TCIDPP	100
TCIDPP + TCIDPP	135

is involved. For example, DPS + DPP has a T_g of 130-140; DMDPS + DPP, 110-125; and TMDPS + DPP, 135-140. This point is further discussed below.

On the other hand, the influence of polarity may be read from Table IV in two groupings.

Similarly, the number of polar central groups is important, as shown in Table V.

Esterification of the —OH groups of the DPS + DPS polymer with acetic anhydride brought T_g down from 170 to 90°C. This indicates that it is to a large extent the



interaction by hydrogen bonding (besides other —OH interactions) that causes the high T_g for the sulfone-based polymers of this series. The acetylation virtually eliminates such interactions.

NOTE: Infrared absorption spectroscopy revealed that the OH stretching vibration, which gives a broad band with a peak maximum at 2.88 μ and a shoulder at 2.80 μ for the DPP + DPP polymer, has a much narrower band with a maximum at 2.85 μ for the DPS + DPS polymer. This shows that the hydrogen bond in the latter polymer is different from that in the former and must therefore be ascribed to —OH and —SO₂— interaction. In accordance herewith we observed a slight increase in S=O stretching vibration frequency upon acetylation of the DPS + DPS polymer.

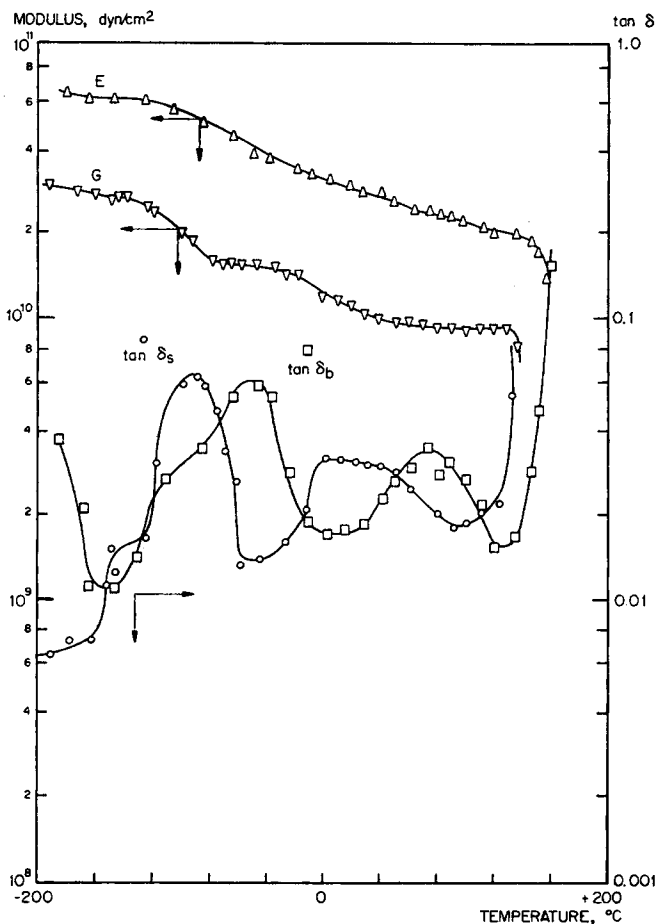
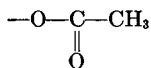
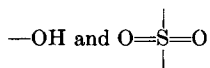


Fig. 5. TMDPS + DPS.

The replacement of —OH by



also implies a larger side-chain bulk. However, we expect that a typical bulk effect on T_g will be only small for such a relatively small group, since two opposing tendencies exist: a bulky group tends to increase the intermolecular distance between polymer chains and thus to lower T_g but, on the other hand, it “loads” and stiffens the flexible —O—C—C—C—O— segment, and thus tends to enhance T_g . Another fact pointing to the importance of



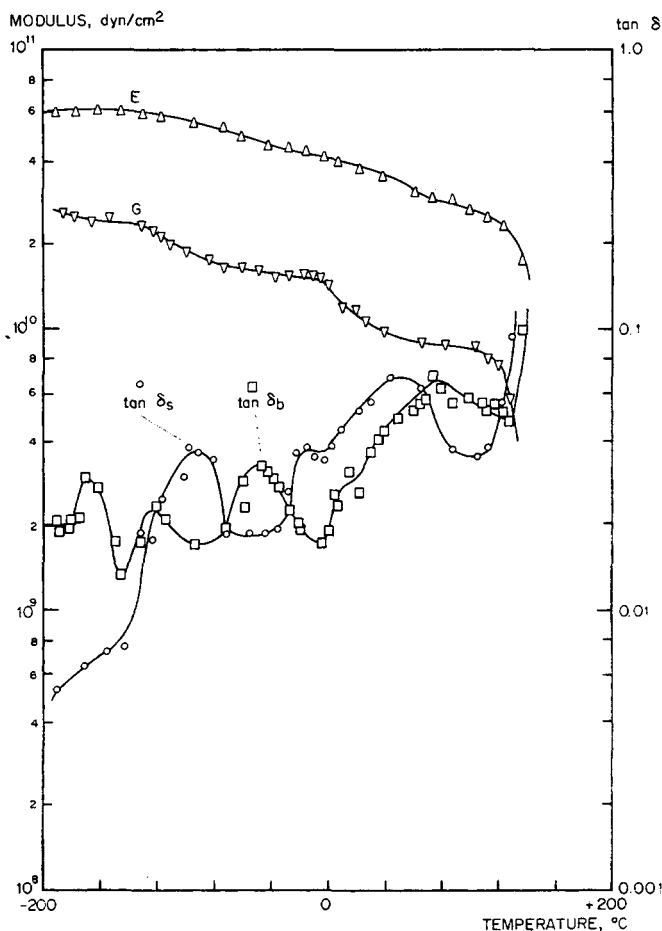


Fig. 6. DMDPS + DMDPS.

interaction is the relatively low T_g of those sulfone-based polymers of the present series which have methylated aromatic rings, the methyl groups tending to increase intermolecular distances.

Inspection of a molecular model (assembled from "Stuart models") was highly instructive, since it showed that especially the sulfone-based polymer molecules can quite easily be folded up to a dense configuration in such a way that the SO₂ groups lie in one line and in one plane, the sulfur atoms with the ether oxygen atoms forming another plane at right angles to the first, with the aromatic rings in planes at right angles to the latter plane and inclined to the former. Thus, we obtain a rather rigid herringbone-like configuration. A projection of the molecule on the sulfur-ether oxygen plane then looks as sketched in Figure 9. In Figure 10 a projection on the plane through the SO₂ groups is drawn, indicating how far the aromatic rings protrude without and with methyl groups present. Clearly, the SO₂

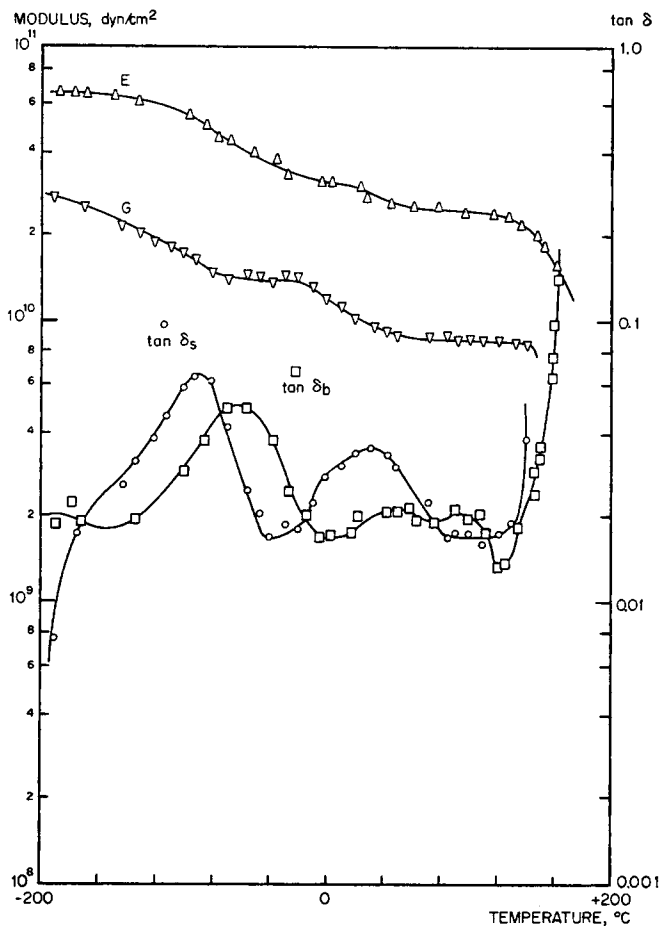
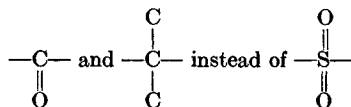


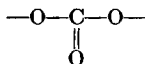
Fig. 7. TMDPS + TMDPS.

groups are less accessible with methyl groups present, and the overall packing density is lower, as can also be seen in Table VI.

In the case of



the closest packing is much less dense, but of a similar type, which must be ascribed to the flexibility of the $\text{---O---C---C---C---O---}$ segments in the polymer. In this respect the situation with polycarbonate is completely different, since the comparatively rigid



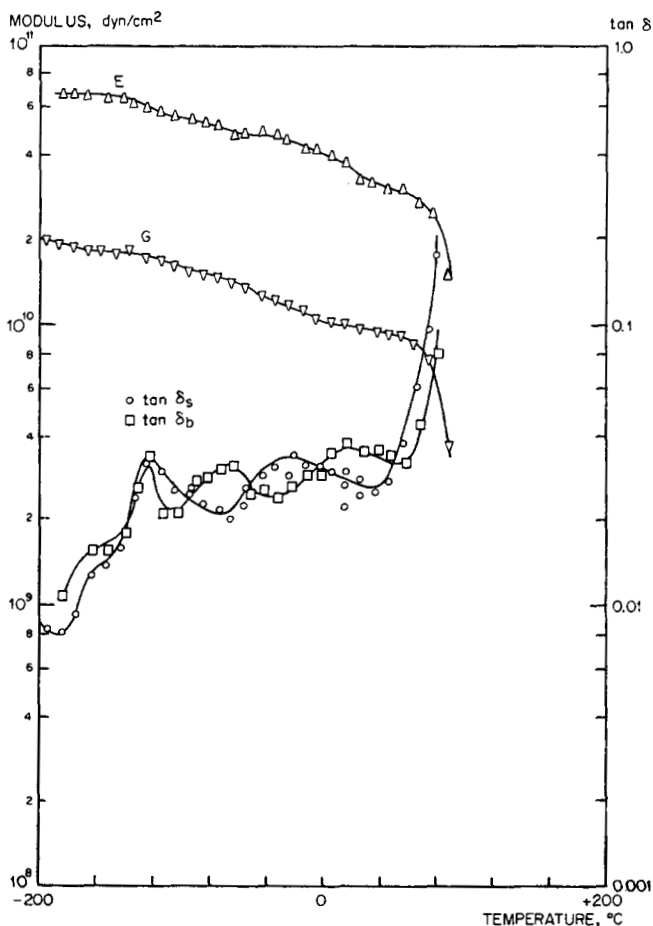
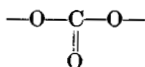


Fig. 8. DPS + DPS acetate.

segment does not allow a zigzag configuration as described. Its density (1.200) is slightly higher than that of DPP + DPP, but its chain stiffness is much higher, as is reflected in its T_g of 155°C. It would be lower if between



and phenylene some methylene units were interposed as was suggested by Illers and Breuer.⁶

The T_g data of Table II show that the roughly 1000-fold frequency change from the 0.1 hz range, as in torsion, to the 100 hz range, as in bending, gives rise to small, or virtually no, changes in T_g . Making the simplifying assumption that the glass transition involves an activated rate process with one rate constant, we can estimate the activation energy as

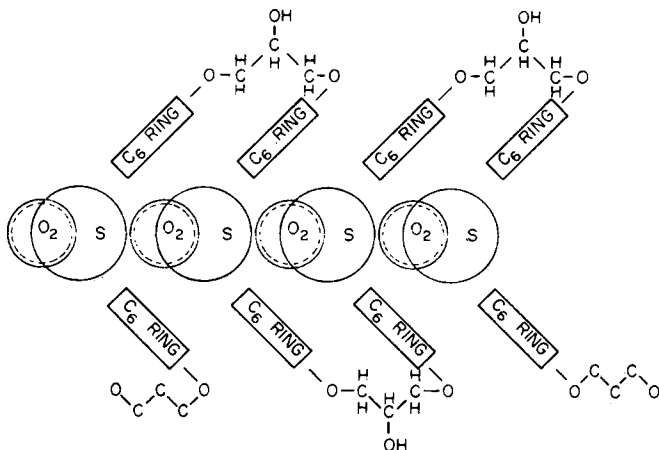


Fig. 9. Projection of herringbone configuration of DPS + DPS on a plane through the S backbone and the ether oxygen.

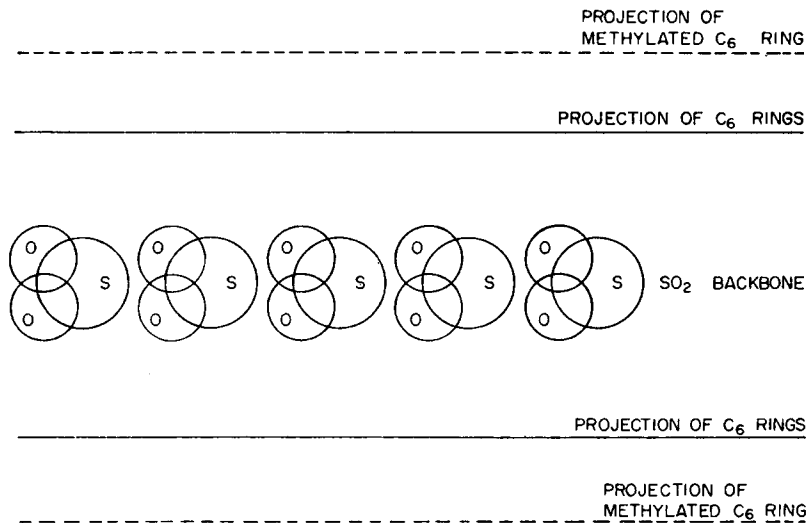


Fig. 10. Projection of herringbone configuration of DPS + DPS on a plane through the SO₂ groups (perpendicular to that of Fig. 9).

amounting to excessively high values (≈ 500 kcal./mole) for most of our polymers. For some of the present polymers more usual values, between 100 and 200 kcal./mole, are found.

Low-Temperature Transitions

As has been mentioned already, all polymers included in this study showed low-temperature damping maxima. In Reinking et al.^{1a,c} the neighborhood of -70°C . is mentioned as the region of a glass II transition, connected with the glyceryl ether moiety, a transition which we think we

TABLE IV
Influence of Polarity of Central Group in Bisphenol on Glass Transition Temperature T_g

Polymer	Central groups		$T_g, ^\circ\text{C.}$
	X	Y	
DPP + DPP	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \end{array}$	100
DPS + DPS	$\begin{array}{c} \text{O} \\ \\ -\text{S}- \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \\ -\text{S}- \\ \\ \text{O} \end{array}$	170
DHPE + DPP	$-\text{O}-$	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \\ \\ \text{C} \end{array}$	85
DHBP + DPP	$\begin{array}{c} -\text{C}- \\ \\ \text{O} \\ \\ \text{O} \end{array}$	$\begin{array}{c} -\text{C}- \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	120
DPS + DPP	$\begin{array}{c} \text{O} \\ \\ -\text{S}- \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \end{array}$	130-140

can identify with the damping peaks found by us between -80 and -100°C. with the low-frequency torsion method and between -40 and -60°C. with the higher-frequency bending method. Assuming that torsion and bending are equivalent with respect to these relaxation phenomena, we calculated energies of activation, which are listed in Table VII.

The gross average of the activation energies of the polymers possessing the glyceryl ether segment is 14.3 kcal./mole. Allowing for an accuracy of determination of roughly 1.5 kcal./mole, the spread of activation energy values may be considered fairly small. This finding and the narrow temperature range found for the transition lead to the conclusion that the transition is of the same pattern for the different polymers and is due to a change in molecular mobility of their common structural feature, the glyceryl ether segment.

For some of them, however, the deviations from the range 13-16 kcal./mole are too large to go uncommented on. Especially, the role of the DMDPS segment is interesting, as is shown in Table VIII. In combination with DPP the activation energy is higher than if either DPS or TMDPS were used, but in combination with DPS the reverse holds true,

TABLE V
Influence of the Number of Polar Central Groups in Bisphenol on T_g

Polymer	Central group		T_g , °C.
	X	Y	
DPP + DPP	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \\ \\ \text{C} \end{array}$	100
DHBP + DPP	$\begin{array}{c} -\text{C}- \\ \\ \text{O} \end{array}$	$\begin{array}{c} -\text{C}- \\ \\ \text{C} \\ \\ \text{C} \end{array}$	120
DHBP + DHBP	$\begin{array}{c} -\text{C}- \\ \\ \text{O} \end{array}$	$\begin{array}{c} -\text{C}- \\ \\ \text{O} \end{array}$	130
DPP + DPP	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \\ \\ \text{O} \\ \\ \text{S} \end{array}$	$\begin{array}{c} \text{C} \\ \\ -\text{C}- \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	100
DPS + DPP	$\begin{array}{c} -\text{S}- \\ \\ \text{O} \\ \\ \text{O} \\ \\ \text{S} \end{array}$	$\begin{array}{c} -\text{C}- \\ \\ \text{C} \\ \\ \text{C} \end{array}$	140
DPS + DPS	$\begin{array}{c} -\text{S}- \\ \\ \text{O} \end{array}$	$\begin{array}{c} -\text{S}- \\ \\ \text{O} \end{array}$	170

TABLE VI
Effect of Aromatic Ring Methylation on Density and T_g

Polymer	Density (20°C.), g./cm. ³	T_g , °C.
DPS + DPS	1.38	170
DMDPS + DPS	1.35	145
DMDPS + DMDPS	1.30	135
TMDPS + DPS	1.27 ⁷	155
TMDPS + TMDPS	1.27 ⁴	160
DPP + DPP	1.18 ⁸	100
TMDPP + DPP	1.15 ⁴	100
TMDPP + TMDPP	1.13 ⁰	130

whereas among the sulfone homopolymers DMDPS + DMDPS shows the lowest activation energy. Obviously, with methylation the degree of symmetry is an important factor.

The behavior at a temperature intermediate between the transition region just discussed and the glass transition is also interesting as regards symmetry aspects. The loss peak found there was consistently higher

TABLE VII
Activation Energies for Relaxation Mechanisms at
Low and Intermediate Temperatures

Polymer	Activation energy, kcal./mole	
	Low temperature	Intermediate temperature
DPP + DPP	13.4	
DPS + DPP	13.1	
DPS + DPS	13.4	
DMDPS + DPP	16.9	≈33
TMDPS + DPP	11.9	
DMDPS + DPS	9.1	41
TMDPS + DPS	14.1	24.5
DMDPS + DMDPS	8.7	38.5
TMDPS + TMDPS	12.1	23.2
DHBP + DPP	18.2	
DHBP + DHBP	13.5	
DHPE + DPP	15.4	
TMDPP + DPP	14.1	
TCIDP + DPP	16.5	
TMDPP + DPS	17.1	
TMDPP + TMDPS	11.3	
TMDPP + TMDPP	17.8	
TCIDPP + TCIDPP	16.8	
Polycarbonate	14.0	

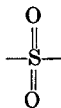
TABLE VIII
Influence of Symmetry in Methyl Substitution on Low-Temperature Transition

Polymer	Transition temp., °C.	Activation energy, kcal./mole
DPS + DPP	-85/-46	13.1
DMDPS + DPP	-84/-54	16.9
TMDPS + DPP	-90/-46	11.9
DPS + DPS	-80/-40	13.4
DMDPS + DPS	-99/-50	9.1
TMDPS + DPS	-91.5/-56	14.1
DPS + DPS	-80/-40	13.4
DMDPS + DMDPS	-102/-48	8.7
TMDPS + TMDPS	-90/-53	14.1

when DMDPS rather than TMDPS segments were present. The activation energies were of the order of 40 kcal./mole with DMDPS and 24 kcal./mole with TMDPS present.

These facts lead us to the conclusion that the relative orientation of consecutive monomethyl-substituted aromatic rings is of importance and that in a certain temperature range the rings gain freedom of rotation. This will then lead to a switch-over from a parallel to an antiparallel configuration of rings enclosing a glyceryl ether segment, with a fairly large difference in energy between these configurations. Dimethyl-substituted and nonsubstituted rings will, of course, tend to rotate as well, but a 180°

rotation does not bring about a change in configuration. Since the intermediate temperature loss peaks occurred only when a strongly polar central group was present, it must be the interaction between —OH and



that is influenced. In the DPS + DPS homopolymer the hydrogen bonding may be so strong that rotations either do not occur or do not give rise to a significant change in interaction energy.

The acetylation of DPS + DPS results in two small damping peaks. One lies at a much higher temperature than the glyceryl ether peak of the nonesterified polymers. It seems plausible that it is the loading of the glyceryl segment by a bulky group that causes the higher transition temperature. The low peak value reflects a small change in interaction energy, due mainly to reduction of polarity. The peak at -120°C . may be due to rotation of the acetyl group, as has been hinted in the literature.⁷

The author is indebted to C. F. H. van Rijn and D. Rond of the Koninklijke/Shell-Laboratorium, Amsterdam, for performing the measurements.

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Received June 15, 1967

Revised August 29, 1967