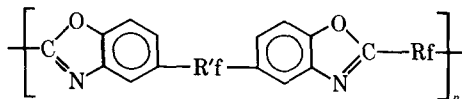


## Structure-Property Relationships in Bibenzoxazole Polymers Containing Fluorocarbon Linkages

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### Synopsis

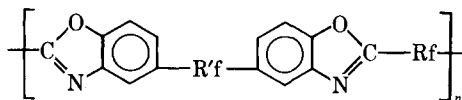
A series of bibenzoxazole polymers with general formula



where  $R'f$  and  $Rf$  are fluorocarbon-containing linkages has presented a unique opportunity to determine relationships between physical transitions and molecular structure. The results of oscillatory thermomechanical experiments ( $\sim 1$  Hz) show two glassy-state and a glass transition as amorphous transitions for each material above  $-180^\circ\text{C}$ . Each glassy-state transition is correlated with onset of motion of specific linkages, the flexibilities of which depend on the structure and molecular positions of the linkages. The glass transition temperatures depend on the two relaxations ( $T < T_g$ ) in a systematic manner.

### INTRODUCTION

Torsional braid analysis (TBA),<sup>1</sup> an adaptation of the torsional pendulum, has been used to determine certain structure-property relationships for members of a series of bibenzoxazole polymers with the general structure



where  $R'f$  and  $Rf$  are fluorocarbon-containing linkages. The polymers were synthesized by Dr. R. C. Evers of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Dayton, Ohio.<sup>2</sup>

The structure-property relationships that were established in the course of this work were those between the structure and position of the fluorocarbon-containing chain linkages,  $R'f$  and  $Rf$ , and the physical transitions of the amorphous states of the polymers, i.e., the glassy-state secondary transitions,  $T_{sec}$  ( $T_{sec}' > T_{sec}''$ ), and the glass transition,  $T_g$ .

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TABLE I  
Structure and Characterization of the Bibenzoxazole Polymers

Polymer	(R. C. Evers' trial no.) <sup>a</sup>	R'f	Rf	$\eta_{inh}^b$ , dl/g <sup>b</sup>
A	(2)	(CF <sub>2</sub> ) <sub>3</sub>	(CF <sub>2</sub> ) <sub>8</sub>	0.27
B	(6)	(CF <sub>2</sub> ) <sub>3</sub>	CF <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	0.94
A/B	(copolymer)	(CF <sub>2</sub> ) <sub>3</sub>	(CF <sub>2</sub> ) <sub>8</sub> and CF <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	0.52 <sup>c</sup>
C	(7)	(CF <sub>2</sub> ) <sub>3</sub>	(CF <sub>2</sub> ) <sub>4</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	0.51
D	(10)	(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub>	(CF <sub>2</sub> ) <sub>8</sub>	0.20
E	(14)	(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub>	CF <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	0.28
F	(17)	(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub>	(CF <sub>2</sub> ) <sub>4</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	0.44

<sup>a</sup> See reference 2.

<sup>b</sup> In HFIP (0.2 g/dl) at 25°C.

<sup>c</sup> See reference 4.

## EXPERIMENTAL

The synthesis of the polymers has been described.<sup>2</sup> Polymer structures were confirmed by elemental analyses and by using infrared absorption characteristics of model compounds.<sup>2</sup> Structures and inherent viscosities are listed in Table I.

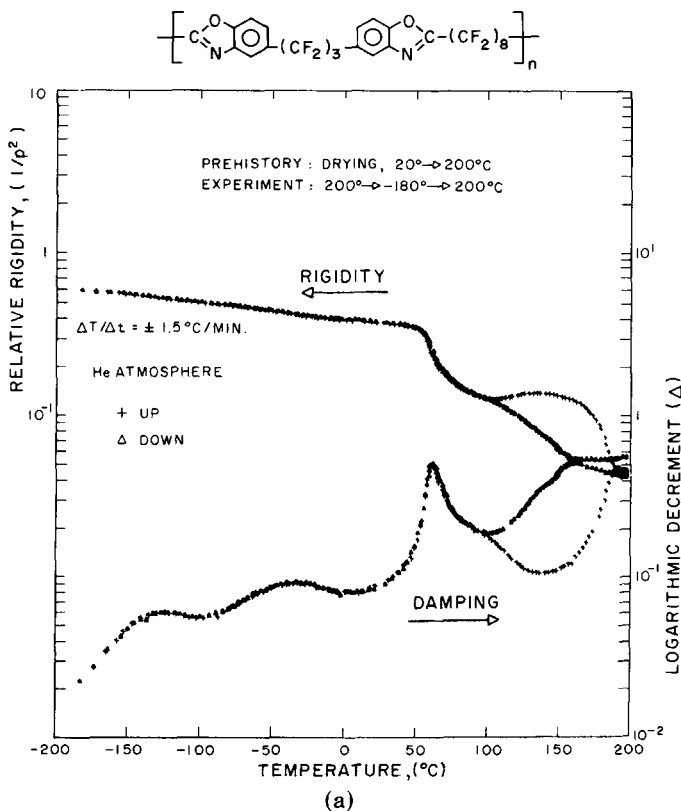


Fig. 1 (continued)

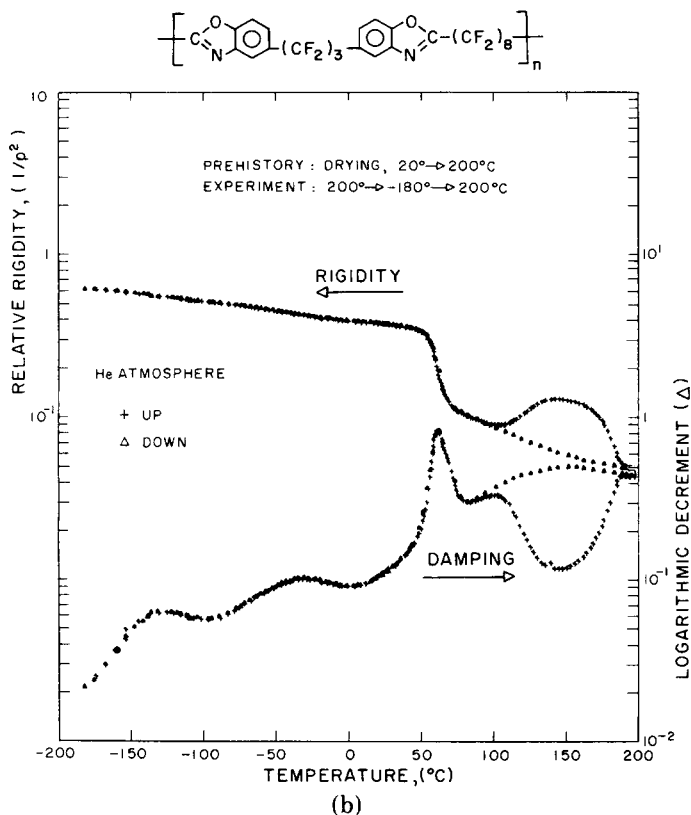


Fig. 1. (a) Thermomechanical behavior of polymer A. (b) Thermomechanical behavior of polymer A. Prehistory:  $20^{\circ} \rightarrow 200^{\circ}\text{C}$ ,  $\Delta T/\Delta t = 3^{\circ}\text{C}/\text{min}$ . Experiment:  $200^{\circ} \rightarrow 70^{\circ}\text{C}$ ,  $\Delta T/\Delta t = -5^{\circ}\text{C}/\text{min}$ .,  $70^{\circ} \rightarrow -180^{\circ} \rightarrow 200^{\circ}\text{C}$ ,  $\Delta T/\Delta t = \pm 1.5^{\circ}\text{C}/\text{min}$ .

The physical transitions of the polymers were determined from dynamic mechanical spectra generated at low frequencies ( $\sim 1$  Hz) under flowing nitrogen using a fully automated torsional braid apparatus which included a dedicated hard-wired data analyzer.<sup>1,3</sup> The TBA technique involves the use of a polymer/glass braid composite as the specimen. In these experiments, the specimen was prepared by soaking a heat-cleaned glass braid (length 2 in.) in a 5% (g polymer/ml solvent) solution in hexafluoroisopropanol (HFIP) for 30 min. The specimen was then mounted in the apparatus at  $20^{\circ}\text{C}$  and dried by heating to  $200^{\circ}\text{C}$  in flowing nitrogen at  $3^{\circ}\text{C}/\text{min}$ .

Relative rigidity and logarithmic decrement (damping) parameters were measured continuously over the range  $200^{\circ} \rightarrow -180^{\circ} \rightarrow 200^{\circ}\text{C}$  ( $\Delta T/\Delta t = \pm 1.5^{\circ}\text{C}/\text{min}$ ) immediately after drying, and were plotted as a function of temperature to give the thermomechanical spectra contained in Figures 1–7. Physical transitions ( $^{\circ}\text{C}$ ) were determined from damping peaks and are listed in Table II along with values for the ratios  $T_g/T_{sec}'$  and  $T_g/T_{sec}''$  (temperatures in  $^{\circ}\text{K}$ ).

Polymer A was semicrystalline. This is evident from the thermomechanical hysteresis seen in Figure 1a. The semicrystalline nature of the polymer did not seem to affect the secondary and glass transition temperatures. A

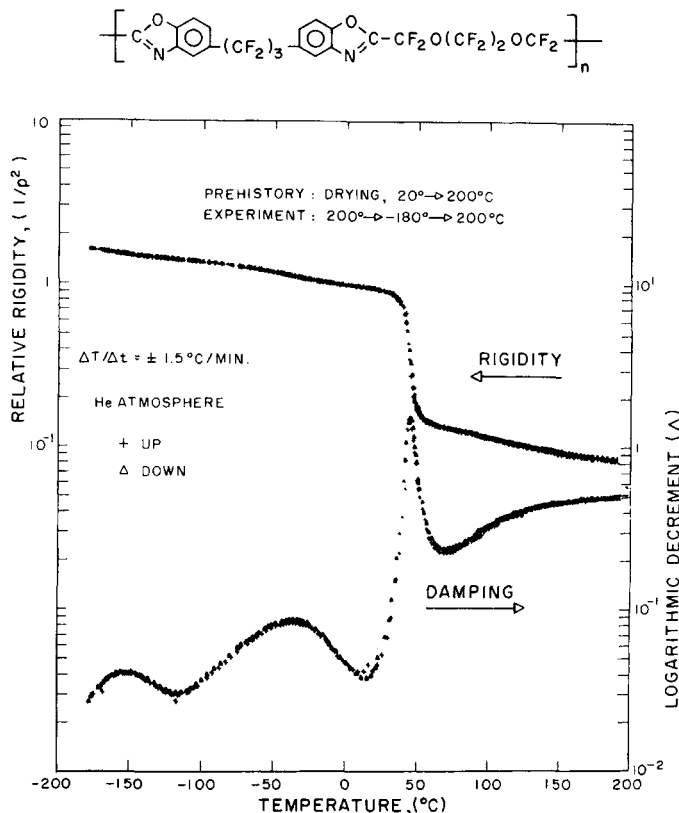


Fig. 2. Thermomechanical behavior of polymer B.

sample that was heated above the melting point and then cooled at  $5^{\circ}\text{C}/\text{min}$  to about  $70^{\circ}\text{C}$  to minimize crystallization gave the same values for these transitions (Fig. 1b). The other polymers appeared to be completely amorphous. This is evident from the essentially reversible data obtained on cooling and on subsequent heating.

## RESULTS AND DISCUSSION

An investigation involving three polymers in this bibenzoxazole series has been published.<sup>4</sup> The present study covers seven polymers and develops relationships between structure and properties. (A preliminary account of the current work has also been presented.<sup>5</sup>) The bibenzoxazole polymers studied may be divided into two groups, one in which R'f, the fluorocarbon-containing linkage between the substituted benzene rings, is  $-(\text{CF}_2)_3-$  (polymers A, B, A/B, and C) and the other in which R'f is  $-(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2-$  (polymers D, E, and F). The linkage between the oxazole groups, Rf, may be  $-(\text{CF}_2)_8-$ ,  $-\text{CF}_2\text{O}(\text{CF}_2)_2\text{OCF}_2-$ , or  $-(\text{CF}_2)_4\text{O}(\text{CF}_2)_2\text{OCF}_2-$ . In the first group, polymers A, B, and A/B each showed a glassy-state secondary transition ( $T_{sec}$ ) near  $-35^{\circ}\text{C}$  as indicated by a damping peak (see Table II, also Figs. 1-3). It appears that the same relaxation occurred in each polymer. The only entity in all three polymers that is capable of motion producing

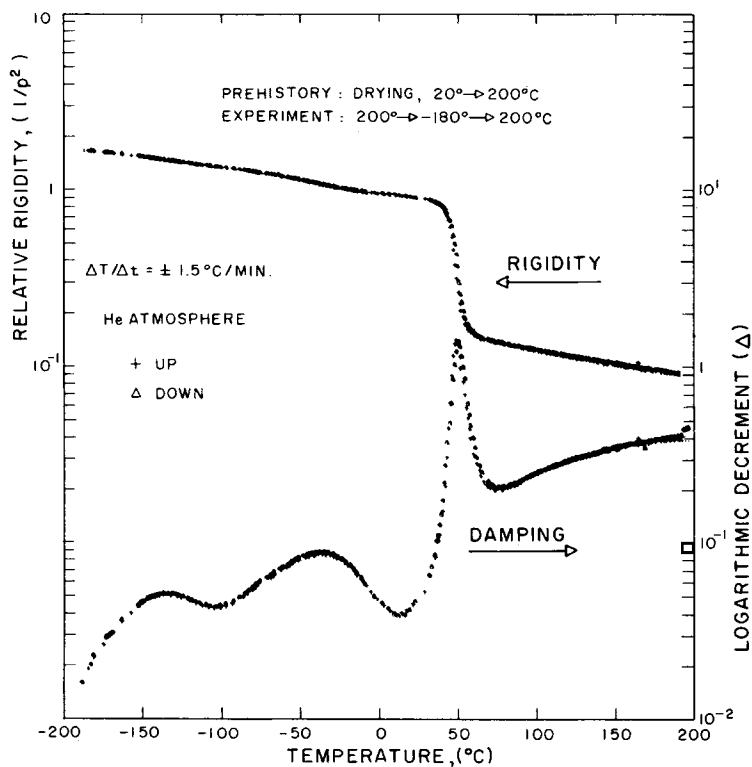
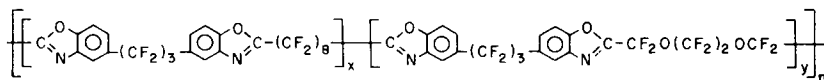


Fig. 3. Thermomechanical behavior of copolymer A/B.

TABLE II  
Physical Transitions of the Bibenzoxazole Polymers

Polymer	$T_g$ , °C [Hz]	Linkage	$T_{sec}$ , °C [Hz]	$T_g/T_{sec}$ , °K/°K
A	62 [0.5]	(CF <sub>2</sub> ) <sub>3</sub>	-34 [0.6]	1.40
		(CF <sub>2</sub> ) <sub>8</sub>	-126 [0.7]	2.28
B	45 [0.6]	(CF <sub>2</sub> ) <sub>3</sub>	-36 [1.0]	1.34
		CF <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	-152 [1.2]	2.63
A/B	50 [0.5]	(CF <sub>2</sub> ) <sub>3</sub>	-36 [1.0]	1.36
		(CF <sub>2</sub> ) <sub>8</sub> and CF <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	-135 [1.2]	2.34
C	26 [0.6]	(CF <sub>2</sub> ) <sub>3</sub>	-50 [1.0]	1.34
		(CF <sub>2</sub> ) <sub>4</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	-145 [1.2]	2.34
D	12 [0.5]	(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub>	-74 [0.9]	1.43
		(CF <sub>2</sub> ) <sub>8</sub>	-132 [1.0]	2.02
E	3 [0.7]	(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub>	-79 [1.2]	1.42
		CF <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	-150 [1.3]	2.24
F	-10 [0.7]	(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>5</sub> O(CF <sub>2</sub> ) <sub>2</sub>	-83 [1.1]	1.38
		(CF <sub>2</sub> ) <sub>4</sub> O(CF <sub>2</sub> ) <sub>2</sub> OCF <sub>2</sub>	-147 [1.2]	2.09

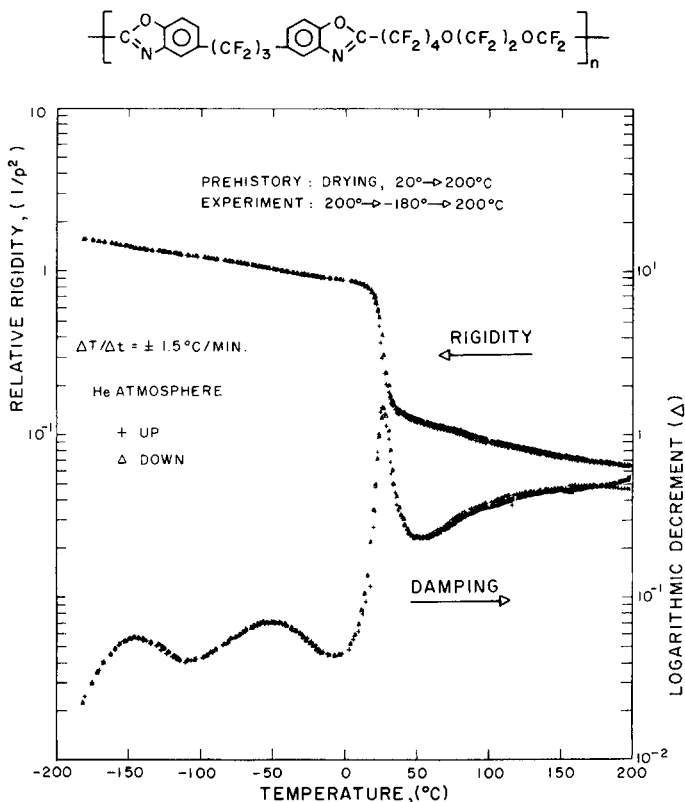


Fig. 4. Thermomechanical behavior of polymer C.

such a relaxation is the  $\text{---}(\text{CF}_2)_3\text{---}$  linkage in the R'f position. In consequence, the secondary transition at  $\sim -35^{\circ}\text{C}$  is assigned to this fluorocarbon chain linkage. Polymer C also contains the  $\text{---}(\text{CF}_2)_3\text{---}$  linkage, but it gave a secondary transition at  $\sim -50^{\circ}\text{C}$  rather than  $-35^{\circ}\text{C}$ . This difference may be due to the influence of the other, very flexible, linkage in the polymer  $\text{---}(\text{CF}_2)_4\text{O}(\text{CF}_2)_2\text{OCF}_2\text{---}$ .

The second group of polymers (D, E, and F) differs from the first (A, B, and C) in that R'f has been changed from  $\text{---}(\text{CF}_2)_3\text{---}$  to  $\text{---}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{---}$ . Each of these polymers exhibited a secondary transition ( $T_{sec}'$ ) in the region of  $-80^{\circ}\text{C}$  (see Table II, also Figs. 5-7). In the same manner as for the first group, this transition is assigned to the onset of motion in the fluorocarbon-containing linkage which is common to all three polymers, i.e.,  $\text{---}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{---}$ , which is in the R'f position.

This leaves the molecular assignments for the other, lower temperature, secondary transitions ( $T_{sec}''$ ) for both groups to be decided. Values for these secondary transitions proved to be nearly identical for each pair of polymers (A-D, B-E, and C-F) with the same linkages between the oxazole groups (Rf). Since the Rf linkage was assumed to be the only polymer segment in addition to R'f to show low temperature motion,  $T_{sec}''$  is assigned to the onset of motion in the Rf linkage in each polymer. Table II contains the transition temperatures and assignments.

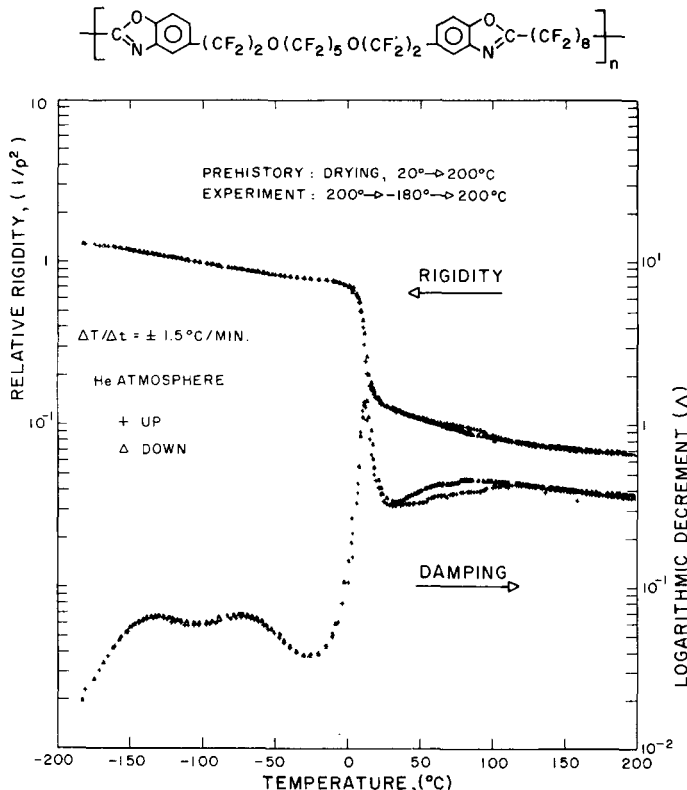


Fig. 5. Thermomechanical behavior of polymer D.

In these polymers the temperature of a secondary transition is an indication of the flexibility of the linkage involved; the most flexible segments have the lowest transition temperatures. Table III lists the chain linkages in decreasing order of flexibility as determined in this manner for these polymers. It will be noted that the more flexible linkages are those between the oxazole groups (Rf), while the less flexible are those between the substituted benzene rings (R'f). This might be considered merely coincidental, except for the fact that  $-(CF_2)_8-$  is found to be more flexible than  $-(CF_2)_2O(CF_2)_5O(CF_2)_2-$ —even though the structure of the latter would appear to give it greater flexibility due to the presence of ether linkages. Therefore, it appears that the secondary transition temperature and flexibility are dependent not only on the structure of the linkage but on its position as well.

TABLE III  
Flexibility of Linkages in Terms of Secondary Transition Temperatures  
(In Order of Decreasing Flexibility)

	$T_{sec}, ^\circ C$	Position
$-(CF_2)_nO(CF_2)_2OCF_2-$ where $n = 1$ or $4$	$\sim -150$	Rf
$-(CF_2)_8-$	$\sim -130$	R'f
$-(CF_2)_2O(CF_2)_5O(CF_2)_2-$	$\sim -80$	R'f
$-(CF_2)_3-$	$\sim -35$	R'f

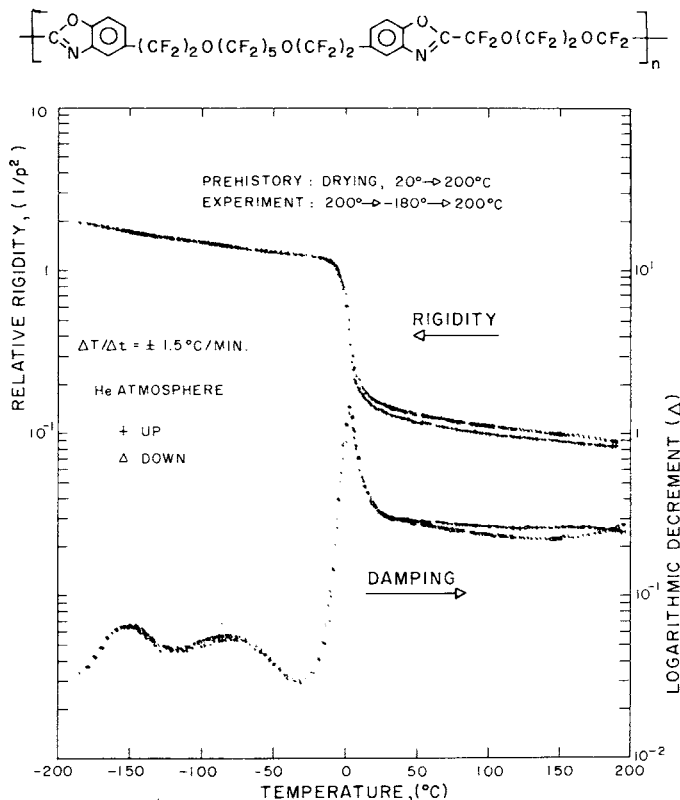


Fig. 6. Thermomechanical behavior of polymer E.

The results summarized in Table II show that the glass transition temperature is dependent on the secondary relaxations (and, therefore, on the flexibilities) of the linkages. The lower the secondary transition temperatures (i.e., the more flexible the chain linkages), the lower the  $T_g$ . The numerical relationships are given by the  $T_g/T_{sec}$  ( $^\circ K/^\circ K$ ) ratios which had the following average values:  $T_g/T_{sec'} = 1.38 (\pm 0.05)$ ,  $T_g/T_{sec''} = 2.3 (\pm 0.3)$ . The precision of the  $T_g/T_{sec'}$  values is good and that of the  $T_g/T_{sec''}$  values acceptable, considering that the damping peaks for the secondary transitions were quite broad (which renders determination of exact transition temperatures difficult).

In apparent contradiction to the relationships discussed above, polymers E and F have almost identical secondary transition temperatures yet their  $T_g$  values differ (Table II). Their R'f ( $T_{sec'}$ ) linkages are the same and the Rf ( $T_{sec''}$ ) linkages are similar with polymer E containing  $-(CF_2O(CF_2)_2OCF_2)-$  and polymer F containing  $-(CF_2)_4O(CF_2)_2OCF_2-$ . Although both linkages commence their motion at about the same temperature ( $\sim -150^\circ C$ ), the longer linkage in polymer F forms a larger part of the entire polymer chain. Consequently, more of the polymer is in motion below the  $T_g$ . This leads to greater overall flexibility which produces a lower  $T_g$ . A similar analysis can



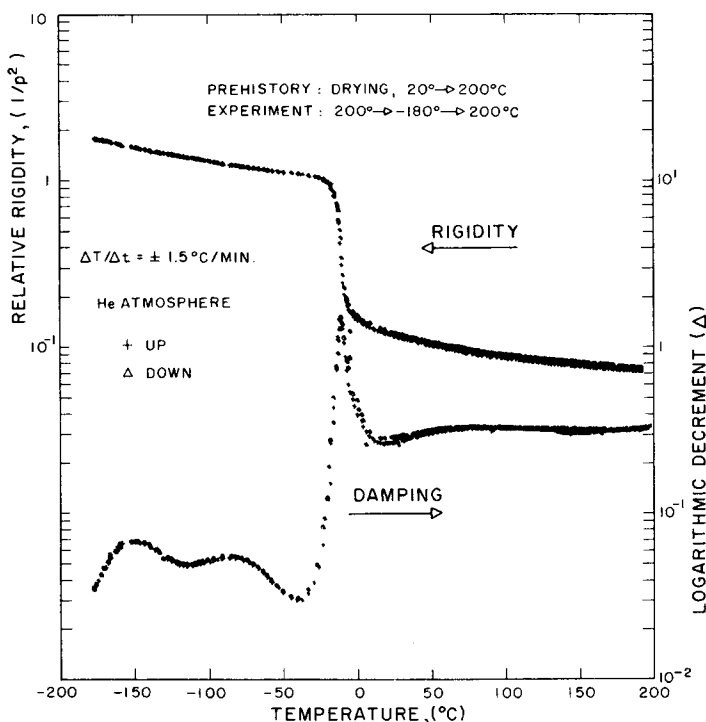
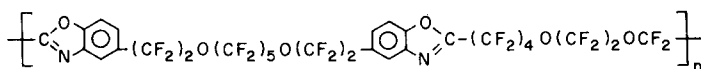


Fig. 7. Thermomechanical behavior of polymer F.

be carried out for polymers B and C. Therefore, in the case of two bibenzoxazole polymers having fluorocarbon linkages with the same flexibilities, the polymer with the longer  $T_{sec}$  chain linkage will have the lower  $T_g$ .

## CONCLUSIONS

This series of bibenzoxazole polymers has presented a unique opportunity to determine relationships between physical transitions and molecular structure. The results of the torsional braid analysis experiments show that the secondary relaxations and flexibilities of the fluorocarbon linkages are functions of the structure and molecular position of these linkages. Beyond this, it is possible to make definite correlations between the secondary transition temperatures and the onset of motion of specific fluorocarbon linkages. It is evident that the glass transition temperature depends on the secondary relaxations (and flexibilities) of the fluorocarbon linkages and also on their lengths.

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