Fluorocarbon Bibenzoxazole Polymers: Transitions and Thermal Stability

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Synopsis

The thermomechanical behavior (−180° to 500°C) in nitrogen is reported for two fluorocarbon bibenzoxazole homopolymers and a corresponding copolymer. The dynamic mechanical spectra were generated at low frequencies (~1 Hz) by an adaptation of the torsional pendulum, torsional braid analysis (TBA), which uses polymer/glass braid composites as specimens. The effects of the variations in molecular structure on physical transitions and thermal stability are discussed. Of particular interest are the specific submolecular assignments for the two glassy-state transitions ($T < T_g$) found for each polymer.

INTRODUCTION

The synthesis of an interesting series of fluorocarbon bibenzoxazole polymers has been reported recently.[1] Earlier polymers of this type were highly crystalline, with glass and melting transitions well above room temperature.[2] In the more recent polymers, additional flexibility was incorporated in the polymer backbone by varying the linkages between the substituted benzene rings.

This investigation is concerned with the transitions and thermal stability of three polymers from the recently synthesized series, two of which are homopolymers with the following structures for the repeat units[1]:

A

B
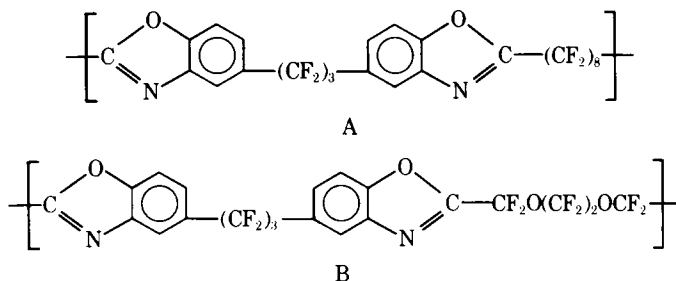
The third polymer is a random copolymer of 0.337 mole of A and 0.663 mole of B (based on the stoichiometry of the reaction mixture).[3] The physical transitions of the polymers were determined from thermomechanical spectra generated by torsional braid analysis (TBA),[4,5] and thermal stability was in-

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vestigated using TBA and thermogravimetric analysis (TGA). The effects of the variations in molecular structure on transitions and thermal stability were considered. In particular, the glassy-state secondary transitions $(T < T_g)$ were assigned to the onset of motion of specific fluorocarbon chain segments.
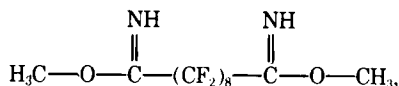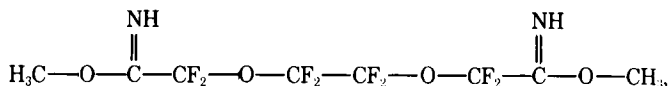
EXPERIMENTAL

Materials

The polymers were synthesized and characterized by Dr. R. C. Evers of the Air Force Materials Laboratory (AFML), Wright-Patterson Air Force Base, Dayton, Ohio.[1,3] After preparation of the monomer,[1]
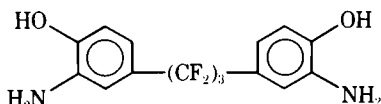
polycondensations were carried out with dimethyl perfluorosebacimidate,

to produce polymer A, with dimethyl perfluoro-3,6-dioxasuberimidate,

to give polymer B, and with both of these reagents to make the copolymer A/B. The reactions were carried out under nitrogen for long periods of time (192 hr for A, 240 hr for B, and 432 hr for A/B) at 50°C in hexafluoroisopropanol (HFIP) in the presence of glacial acetic acid. The polymers were isolated by precipitation in methanol, then redissolved in HFIP and reprecipitated in methanol. After extraction in a Soxhlet apparatus with methanol, the polymers were dried at 100°C under vacuum (0.1 mm Hg).

The homopolymer structures were established[1] on the basis of elemental analyses and comparisons of infrared absorption characteristics of model compounds. Analyses are contained in Table I along with values for inherent viscosities at 25°C in HFIP (0.2 g/dl). Reported melting (T_m) and glass transitions (T_g), as determined by differential scanning calorimetry (DSC) at a heating rate of 20°C/min, are also listed in Table I. The copolymer sample

TABLE I
Homopolymers: Characterization Data[a]

Polymer	η_{inh},[b] dl/g	T_m,[c] °C	T_g,[c] °C	Analysis, calculated/(found)			
				C	H	N	F
A	0.27	187	106	38.29 (38.75)	0.77 (1.07)	3.57 (3.93)	53.29 (53.14)
B	0.94	—	29	40.93 (40.87)	0.97 (0.86)	4.54 (4.43)	—

[a] Data from reference 1.
[b] In HFIP (0.2 g/dl) at 25°C.
[c] DSC results, $\Delta T/\Delta t = 20°C/min$. Prehistory: 20° → 100° → 20°C (under vacuum).
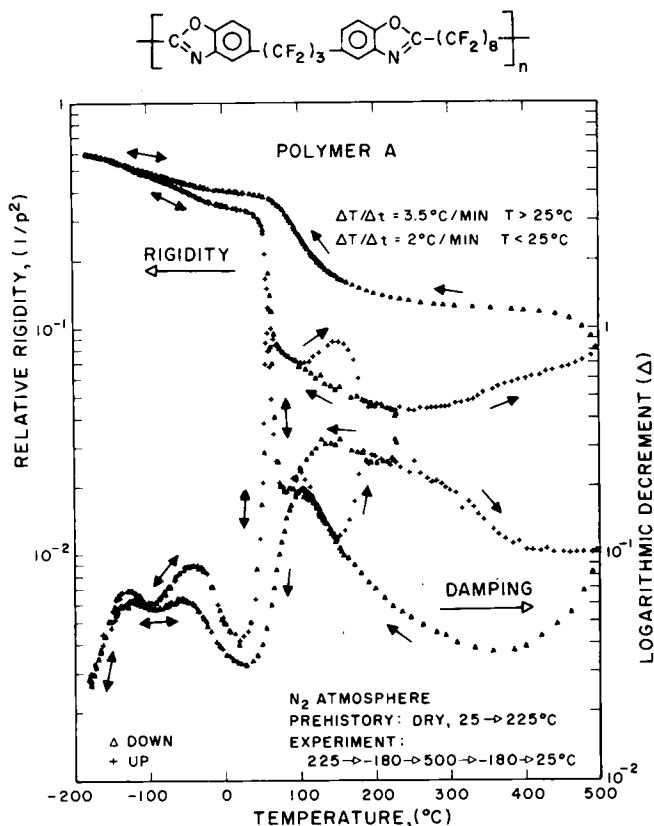
Fig. 1. Thermomechanical spectra of polymer A.

had an inherent viscosity[3] of 0.52; on the basis of the synthetic procedure, its structure was assumed to be a random combination of the homopolymer repeat units in proportion to the feed ratio.

Techniques

The thermomechanical data were generated at low frequencies ($\sim$1 Hz) under flowing nitrogen (with a water content of 8–10 ppm as determined by an on-line hygrometer) using a fully automated torsional braid apparatus (TBA) the operation of which has been described.[4,5]

Each specimen was prepared by soaking a glass braid in a 5% solution (g polymer/ml solvent) for 30 min. The solvent was HFIP (bp = 58°C). The polymer/HFIP/glass fiber composite was then mounted in the TBA apparatus and dried by heating at 3.5°C/min to 225°C in flowing nitrogen. The maximum temperature of the preheating was above the highest physical transition and yet below the onset of weight loss (by thermogravimetric analysis).

The period and decay of torsional oscillations induced in the specimen were measured regularly throughout the temperature sequence 225° → −180° → 500° → −180° → 25°C. The rate of change of temperature was ±3.5°C/min above room temperature and ±2°C/min below room temperature for all operations. A recently developed torsional pendulum data reduc-

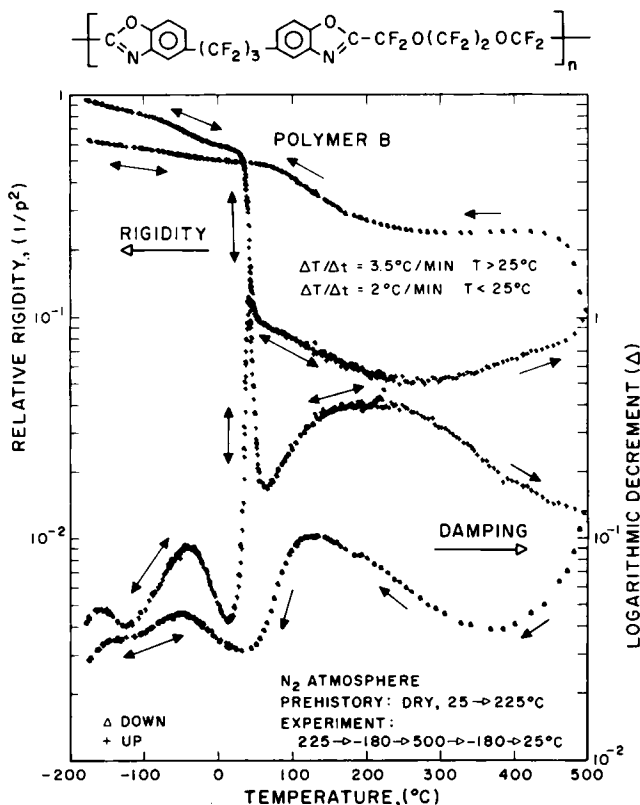Fig. 2. Thermomechanical spectra of polymer B.

TABLE II
Polymer Transitions From TBA Experiments[a]

Transition	A	B	A/B
T''_{sec}[b]	−127°C (0.7 Hz)	−155°C (0.95 Hz)	−132°C (0.9 Hz)
T'_{sec}[b]	−42 (0.6 Hz)	−38 (0.8 Hz)	−40 (0.8 Hz)
T_g[b]	61 (0.4 Hz)	44 (0.5 Hz)	50 (0.5 Hz)
T_{crys}	100,[c] 130[d]	—	—
	(on heating)		
T_m	180,[d] 192[e]	—	—
$T_{crosslink}$[c]	254	280	270
On Cooling from 500°C			
T_g[b]	105	135	130
T'_{sec}[b]	−58	−50	−57
T''_{sec}[b]	−125	−148	−126
Transition Ratios			
T''_{sec}/T_g (T in °K)	0.44	0.37	0.44
T'_{sec}/T_g (T in °K)	0.69	0.74	0.72
T_g/T_m (T in °K)	0.74,[d] 0.72[e]	—	—

[a] Thermal prehistory: 25° → 225°C, $\Delta T/\Delta t$ = 3.5°C/min.
[b] From damping peaks.
[c] From onset of rigidity increase on heating.
[d] From maximum rate of change of relative rigidity on heating.
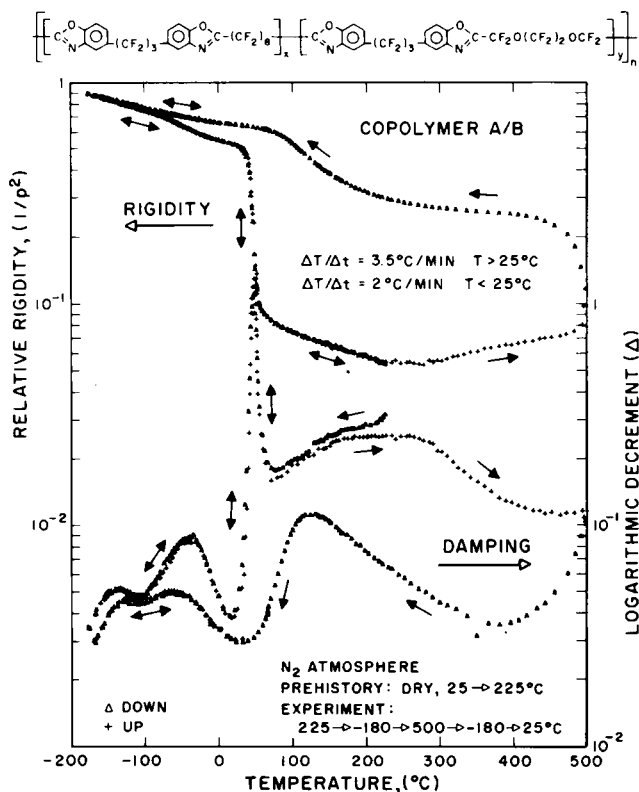[e] From end of melting as determined by relative rigidity.

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

er[5] printed out the numerical values of the period (P, seconds), damping parameter (logarithmic decrement, Δ), and temperature (mV). These digital results were processed by a computer which provided plots of logarithmic decrement and relative rigidity ($1/P^2$) versus temperature such as those shown in Figures 1–3. Glass and secondary (T_{sec}) transitions were determined from the temperatures of the damping peaks; melting and crystallization transitions were determined from changes in rigidity (see Table II).

Temperature-cycling experiments were carried out on polymer A in order to determine the effect on physical transitions of heating the material to increasingly higher temperatures. The cycling sequence was $200° \rightarrow -180° \rightarrow 300° \rightarrow 100° \rightarrow 400° \rightarrow -180° \rightarrow 430° \rightarrow -180° \rightarrow 470° \rightarrow -180° \rightarrow 500° \rightarrow -180° \rightarrow 525° \rightarrow -180° \rightarrow 25°C$. These results are shown as a line drawing in Figure 4.

Thermogravimetric analyses (TGA) were performed in flowing nitrogen with a du Pont 900 thermoanalyzer. In order to correspond with the thermomechanical experiments, each sample was cast from a 5% polymer solution, dried in the thermobalance to 225°C, and cooled to room temperature before the experiment was carried out. The heating rate used was the same as in the TBA experiments (3.5°C/min). The results for the three polymers are presented in Figure 5.

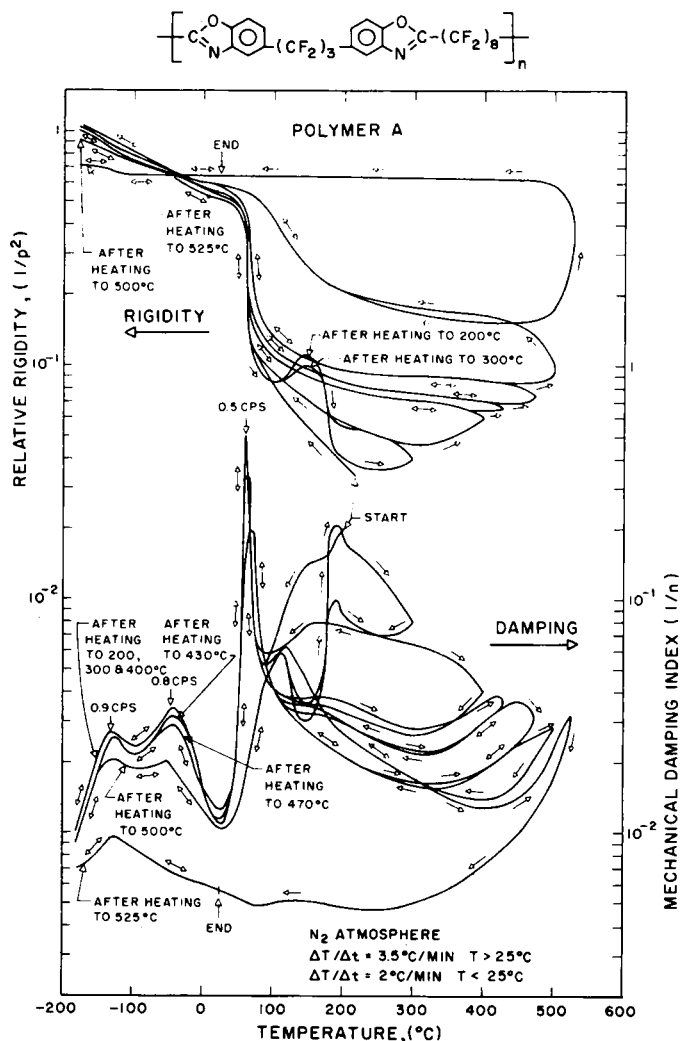Fig. 4. Thermomechanical cycling of polymer A. Drying: $25° \rightarrow 200°C$. Experiment: $200° \rightarrow -180° \rightarrow 300° \rightarrow -100° \rightarrow 400° \rightarrow -180° \rightarrow 430° \rightarrow -180° \rightarrow 470° \rightarrow -180° \rightarrow 500° \rightarrow -180° \rightarrow 525° \rightarrow -180° \rightarrow 25°C$.

RESULTS AND DISCUSSION

Physical Transitions

The physical transitions are given in Table II along with values for the ratios (temperatures in $°K$) T''_{sec}/T_g, T'_{sec}/T_g, and, for polymer A only, T_g/T_m. Each of the three polymers showed a glass transition region above room temperature and two low temperature glassy-state secondary transitions. Onset of chain stiffening and/or crosslinking occurred in the $250-280°C$ region; in air, these changes were noticeable about $10°C$ lower. Glass transition temperatures measured in air (spectra not shown) were identical to those determined in nitrogen. Due to the similarities in structure, the various transition temperatures for the two homopolymers were not very different; and, as
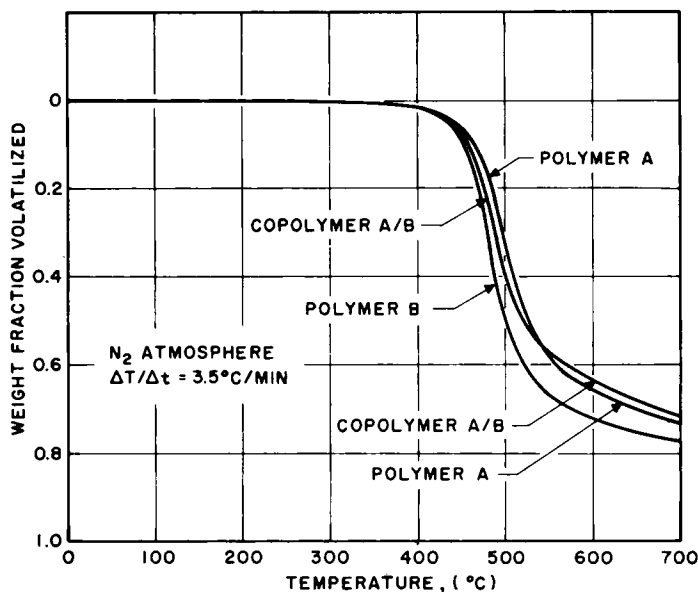
Fig. 5. Thermogravimetric analyses of the polymers. Thermal prehistory: 25° → 225° → 25°C.

would be expected, the copolymer transition temperatures were between those of the two homopolymers.

Polymer A was semicrystalline. It showed definite temperatures of crystallization (T_{crys}) and melting (T_m) which gave rise to thermomechanical hysteresis (see Fig. 1). The extent of crystallization was dependent on the thermal history of the material. For example, crystallization was observed on cooling only if the specimen was cooled slowly (~1°C/min) from above the melting point. At the standard cooling and heating rate used in the experiments (3.5°C/min), there was no noticeable T_{crys} on cooling, but definite crystallization on heating, which was revealed by the rigidity increase which began at ~100°C and peaked at ~150°C (Fig. 1). Neither polymer B nor the copolymer showed signs of crystallinity, the TBA curves being essentially reversible below the maximum drying temperature of 225°C (see Figs. 2 and 3).

All three polymers had glassy-state secondary transitions (T'_{sec}) at about −40°C. The similar locations, intensities, and shapes of the T'_{sec} damping peaks indicated that they were due to the same submolecular motions. The chain segment common to all three polymers which appears capable of motion producing such a secondary transition is the —$(CF_2)_3$— linkage connecting the substituted benzene rings. It is interesting to note that the T'_{sec}/T_g (T in °K) ratio values (Table II) of approximately 0.7 correspond to T_β/T_g (T in °K) ratios that have been determined for a number of polymers.[6,7]

The lower temperature glassy-state transitions (T''_{sec}) were assigned to the onset of motion in the other fluorocarbon chain segments in the polymers; i.e., —$(CF_2)_8$— in polymer A, —$CF_2O(CF_2)_2OCF_2$— in polymer B, and, presumably, both linkages in the copolymer. Polymer B would be expected to show a lower T''_{sec} transition than polymer A since the ether linkages in —$CF_2O(CF_2)_2OCF_2$— are more flexible than the carbon–carbon linkages in —$(CF_2)_8$—. For the same reason, polymer B should also have a lower glass

transition temperature. The copolymer would be expected to exhibit behavior intermediate to the homopolymers. The measured T''_{sec} and T_g values are consistent with this hypothesis; $T''_{sec} = -127°C$ for polymer A, $-155°C$ for polymer B, and $-132°C$ for copolymer A/B; $T_g = 61°C$ for polymer A, $44°C$ for polymer B, and $50°C$ for copolymer A/B.

Since the $-(CF_2)_3-$ and $-(CF_2)_8-$ bridges are each short lengths of the poly(tetrafluoroethylene) (PTFE) chain, it is interesting to compare their transition temperatures at $-40°$ and $-127°C$ (both at ~0.7 Hz) with the γ transition at $-97°C$ (0.6 Hz) that has been assigned to the onset of motion in the amorphous regions of PTFE.[8] The dissimilar transition temperatures are presumably due to the different molecular environments of each of the $-(CF_2)_x-$ groups and to their differences in length.

As may be seen from Tables I and II, the glass transition values determined by TBA differ considerably from those reported on the basis of DSC data[1]; the T_g for polymer A was found to be 61°C by TBA and 106°C by DSC; the T_g for polymer B was 44°C by TBA and 29°C by DSC. Since the TBA and DSC samples had quite different thermal prehistories and heating rates, it is possible, in the case of semicrystalline polymer A, that the levels of crystallinity were different. In consideration of this, TBA experiments were carried out in which one sample of polymer A was cooled (~5°C/min) so as to minimize crystallization, and another was held at 130°C for 16 hr in an attempt to maximize crystallization. The "quenched" specimen had a T_g of 61°C (identical to that noted in previous TBA experiments) and crystallized upon being heated above 100°C, while the other specimen gave a T_g of 72°C and showed no noticeable crystallization on heating. It appears that variations in crystallinity are not sufficient to explain the large difference between the glass transition of polymer A as determined by TBA and that reported on the basis of DSC measurements. These results also indicate that 61°C is the glass transition temperature of a sample of polymer A with minimum crystallinity.

The glass transition temperatures (°K) of the copolymer and homopolymers were substituted in a copolymer composition–glass transition temperature equation[9]
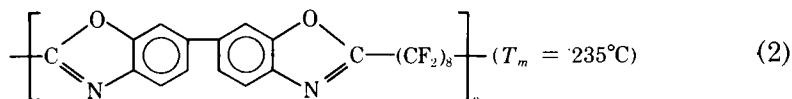
$$T_g = X_A T_{gA} + X_B T_{gB}$$

where T_g is the glass transition temperature of a copolymer containing mole fractions X_A and X_B of repeat units corresponding to homopolymers with glass transition temperatures of T_{gA} and T_{gB}, respectively. The equation gave $X_A = 0.353$ and $X_B = 0.647$. This indicated that the repeat unit mole fractions in the copolymers were close to those in the original reaction mixture (0.337 and 0.663) and supported the assumptions made as to the structure of the copolymer.

Thermal Stability in Nitrogen

Thermogravimetric analysis results are shown in Figure 5. In each case, weight loss commenced above about 260°C (which corresponded to an increase in rigidity noted in the TBA results), but was minimal (<2%) to 400°C, and did not become severe until about 450°C. By 500°C, polymer A had lost 32% of its weight; polymer B, 50%; and the copolymer, 39%. The lower stability of polymer B presumably was due to the presence of ether linkages.

An analogue of polymer A (with the benzene-to-benzene linkage in a different position),

$$\left[C \underset{N}{\overset{O}{\diagdown}} \underset{}{\bigcirc} \underset{}{\bigcirc} \overset{O}{\underset{N}{\diagdown}} C-(CF_2)_8 \right]_n \quad (T_m = 235°C) \qquad (2)$$

heated at 4°C/min in nitrogen, appeared to be more stable, losing only 10% of its weight by 500°C even though it began to lose weight in the same temperature region as polymer A.[10] Insertion of a —$(CF_2)_3$— linkage between the substituted benzene rings increases the flexibility of the molecule, but appears to lower its thermal stability.

After being heated to 500°C during the TBA experiments, each of the three polymers under study showed a small increase (2° to 7°C) in T''_{sec}, a decrease (12° to 17°C) in T'_{sec}, and a significant increase (44° to 91°C) in T_g. The latter was accompanied by a broadening and drop in intensity of the damping peak which indicated that molecular motions were being hindered by crosslinks (see Table II for transitions before and after heating to 500°C). Polymer B appeared to be the most crosslinked of the polymers by 500°C, since it showed the largest increase in T_g and underwent the greatest rise in relative rigidity above the glass transition (see Fig. 2) in spite of losing more weight.

A series of temperature cycling experiments was carried out in nitrogen on a sample of polymer A in order to study the effect of heat on the thermomechanical behavior of the polymer. The spectra are shown in Figure 4. The specimen was dried to 200°C, then cooled to −180°C to determine the initial values for the T_g and the secondary transitions. Changes in the transition temperatures, damping peak intensities, and rigidity levels were then monitored as the sample was cycled between −180°C and progressively higher temperatures (300°, 400°, 430°, 470°, 500°, and 525°C). The effects of cycling on transitions may be seen in Table III.

The cycling experiments brought out a number of interesting points. For example, crystallization on heating (noted previously and shown in Fig. 1) occurred after the specimen had been cycled to 200° and 300°C, but was not observed after cycling to 400°C and cooling. T_m also disappeared after heating to 400°C, which indicated that the sample was no longer crystallizable. The rigidity began to increase from ~250°C and continued to rise at the high-

TABLE III
Effect of Thermal Cycling on the Transitions of Polymer A

After heating to, °C	T''_{sec}[a], °C	T'_{sec}[a], °C	T_g[a], °C	T_m, °C
200	−130	−44	61	177,[b] 190[c]
300	[d]	−44	61	177,[b] 190[c]
400	−130	−40	63	—
430	−120	−40	63	—
470	−120	−40	70	—
500	−128	−50	119	—
525	−130	—	>525	—

[a] From damping peaks.
[b] From maximum rate of change of relative rigidity.
[c] From end of melting as determined by relative rigidity.
[d] Not measured.

temperature end of each cycle; however, the T_g (originally 61°C) did not change until the polymer had been heated to 400°C and then increased only very slightly. Therefore, by 400°C (and 430°C) the crosslinking or chain-stiffening reactions that had commenced near 250°C had not yet begun to interfere with the motions associated with the glass transition, although slight increases had been noted in the temperatures of the two glassy-state secondary transitions. Heating to 470°C raised the T_g to 70°C. Cycling to 500°C raised the high-temperature rigidity further and increased the T_g to 119°C (as compared to an initial value of 61°C). In contrast, each of the glassy-state secondary transitions was about 10°C lower than in the previous (470°C maximum) cycle. The level of rigidity at temperatures below the original glass transition had tended to increase slightly with each cycle; but after being heated to 500°C, the rigidity level dropped, probably because of dimensional changes in the specimen due to loss of weight on pyrolysis.

Heating to 525°C had catastrophic effects on the specimen. The original T_g was eliminated and a new glass transition was expected above 525°C (as determined from extrapolation of the damping curve). The T'_{sec} damping peak observed in the previous cycles disappeared, but a less intense T''_{sec} peak remained at $\sim -130°C$, showing that some localized motions in the —$(CF_2)_8$— bridge were operative. The material obviously had undergone severe crosslinking and would remain vitrified below 525°C.

CONCLUSIONS

There are definite correlations between the glassy-state secondary transitions of the three fluorocarbon bibenzoxazole polymers and the onset of motion in particular fluorocarbon linkages. The secondary transition in the region of $-40°C$ (T'_{sec}) noted for each polymer was assigned to motion in the —$(CF_2)_3$— chain segment. The lower-temperature secondary transitions (T''_{sec}) were assigned to motions in the other fluorocarbon linkages — $(CF_2)_8$— in polymer A, —$CF_2O(CF_2)_2O\ CF_2$— in polymer B, and both linkages in the copolymer. The glass transition temperatures of the polymers were dependent on the flexibilities of their fluorocarbon linkages. For example, polymer A had the highest T''_{sec} (and, therefore, the least flexible linkage) and the highest T_g. This polymer crystallized, but the extent of crystallization could be controlled to some extent by varying the rate of cooling. The glass and secondary transitions specified for polymer A (Table II) are for a sample with minimum crystallinity. The glass transition temperatures of the three polymers were used in a copolymer composition–glass transition relationship to determine the repeat unit mole fractions in the copolymer. The results indicated that the repeat units were incorporated into the copolymer in approximately the same proportion as in the original reaction mixture.

The polymers showed considerable thermomechanical stability. The increases in T_g (44° to 91°C) on heating to 500°C were slight, considering that each of the materials began to crosslink in the region of 250–280°C, lost weight from about 250°C (rapid weight loss from $\sim 450°C$), and showed approximately 30–50% weight loss by 500°C.

Cycling experiments with polymer A in nitrogen indicated very little change in T_g until above 470°C and that severe breakdown in mechanical properties did not occur until the vicinity of 525°C.

The variations of thermomechanical behavior and thermal stability of the polymers were due to differences in the fluorocarbon chain segments, the ether linkages in polymer B being responsible for both its relatively low stability and lower T_g. Comparison of the thermal behavior of polymer A with that of an analogue which did not contain a —$(CF_2)_3$— chain between the aromatic rings indicated that this fluorocarbon link provided greater flexibility, but lowered the thermal stability of the material.

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