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CROSSLINKING CHEMISTRY FOR FLUOROCARBON ETHER BIBENZOXAZOLE POLYMERS

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NOVEMBER 1979

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Final Report for period May 1976 to June 1978

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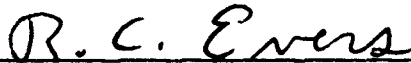
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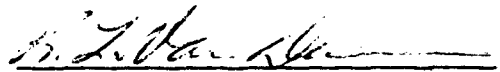
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sites into the FEB copolymer backbone. The novel cure site monomer was prepared by a multistep synthetic route based on the copper-promoted reactions of 1,2-diiodohexafluoropropane with 4-iodophenyl acetate and, subsequently, the resultant intermediate with trans-1,2-diiodoethylene. The FEB copolymers were obtained in moderate-to-high molecular weights; inherent viscosities as high as 0.51 dl/g were recorded. Copolymer structures were verified by elemental analysis and infrared spectral comparisons. Selection of monomer structures and proportion of cure site monomer governed the glass transition temperatures (T_g) of the resultant FEB copolymers. Low polymer T_g's were observed with high fluorocarbon ether content and minimum cure site monomer content, an optimum value of -47°C (-53°F) being achieved. Thermogravimetric analysis and isothermal aging studies indicated high thermooxidative stability almost comparable to analogous FEB polymers void of the hydrocarbon cure sites. Isothermal aging in air at 260°C (500°F) and 288°C (550°F) for 200 hours led to weight losses of 7 and 17 percent, respectively. Preliminary formulation and curing studies demonstrated the reactivity of the cure sites to radical-induced cure reactions. Based on the low temperature viscoelastic properties, the high thermooxidative and hydrolytic stability, as well as the ready curability of the FEB copolymers, a broader use temperature range capability than currently available in state-of-the-art elastomer materials is envisioned.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project/Task 2419/04, Work Unit 24190402, "Polymers for Broader Temperature Fluid Containment Materials." It was administered under the direction of the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. R. C. Evers as the AFML Project Scientist. Coauthors were Dr. R. C. Evers and Dr. Tonson Abraham, (AFML/MBP).

This report covers work conducted from May 1976 to June 1978. This manuscript was submitted by the authors in March 1979 for publication as a technical report.

The authors wish to thank Mr. J. L. Burkett for contributions in the synthesis operations and Dr. I. J. Goldfarb and Mr. E. J. Soloski for the thermal stability data. The Analytical Branch, Air Force Materials Laboratory contributed the elemental analysis and mass spectral data.

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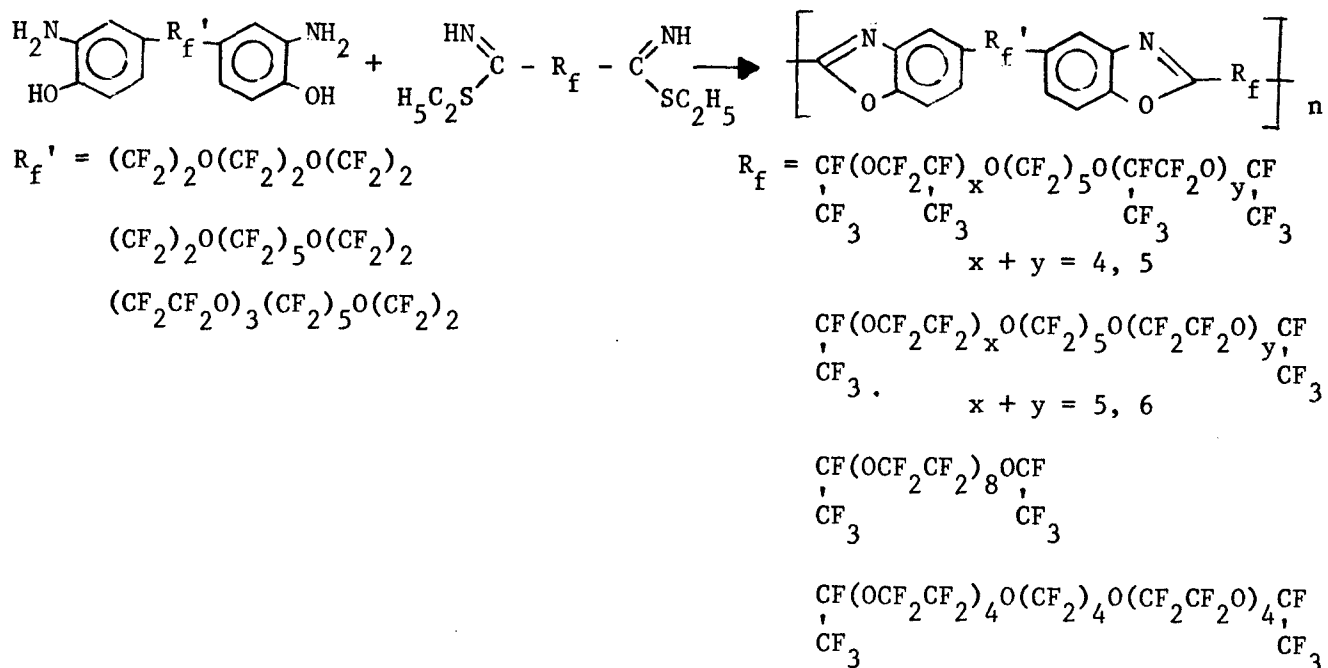
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SECTION I

INTRODUCTION

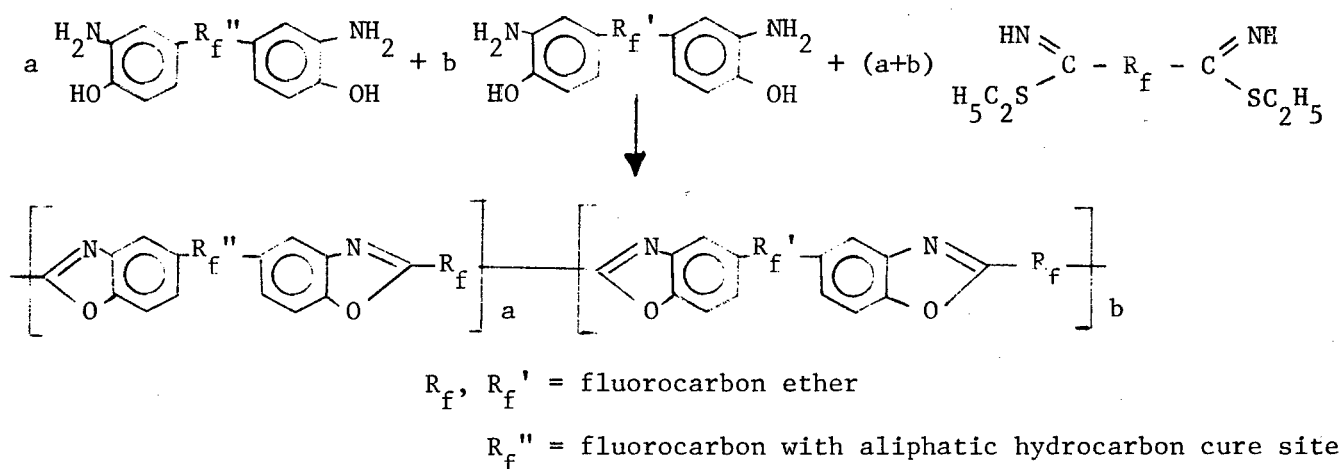
In order to meet the requirements for fluid containment in Air Force hydraulic systems, new polymeric materials are needed for seals which will retain elastomeric properties over a -65° to 600°F temperature range. In addition to high thermooxidative stability and superior low temperature viscoelastic properties, these materials should also exhibit other desirable properties such as fluid resistance, hydrolytic stability, and mechanical strength over this temperature range. Since present state-of-the-art materials do not fulfill needs for broad use-temperature range elastomers, continuing research efforts to synthesize new thermooxidatively stable polymers as base materials for seal applications have been carried on in this laboratory through both inhouse and contractual research programs.

As part of a continuing AFML inhouse research program, the synthesis of thermooxidatively and hydrolytically stable fluorocarbon ether bibenzoxazole (FEB) polymers was recently achieved by the acetic acid-promoted polycondensation of fluorocarbon ether bis(o-aminophenol) monomers with fluorocarbon ether dithioimide ester monomers (References 1-6). The dithioimide esters had been specifically structured to impart hydrolytic stability to the resultant polymers and were synthesized by synthetic routes in which hexafluoropropylene oxide (HFPO) or a combination of tetrafluoroethylene oxide and hexafluoropropylene oxide (TFEO:HFPO) was used.



The high thermooxidative stability, low glass transition temperatures (T_g), and superior hydrolytic stability generally exhibited by these FEB polymers indicated great potential for achieving a broader use temperature range than currently available in state-of-the-art elastomers. However, the FEB polymers had been shown to be impervious to radical-induced cures under normal curing conditions and to exhibit poor mechanical properties upon being cured under drastic curing conditions which may have partially degraded the polymer gums (Reference 7). In order for the FEB polymers to exhibit and maintain adequate mechanical properties over the expected broad use-temperature range, the problem of poor curability needed to be addressed and additional molecular tailoring of the polymer structure performed.

The introduction of chemically reactive cure sites into the polymer backbone was considered the most feasible approach to the effective curing of the FEB polymers. Extensive formulation and curing studies (Reference 8) of hexafluoropropylene-vinylidene fluoride copolymers (Viton or Fluorel) to give thermooxidatively stable elastomers have demonstrated the ready reactivity of aliphatic hydrocarbon moieties in the fluorocarbon copolymer backbone to a magnesium oxide/benzoyl peroxide-induced curing reaction. Based on these studies, the radical-induced coupling of appropriately-structured, aliphatic hydrocarbon cure sites within the FEB polymer backbone was considered a viable approach to the effective curing of the FEB polymers. In order to achieve a curable and hydrolytically stable FEB polymer, appropriate modification of the FEB polymer structure was carried out by the introduction of cure sites into the polymer backbone. This was achieved through the copolycondensation of HFPO- or, preferably, TFEO:HFPO-derived fluorocarbon ether dithioimide esters with fluorocarbon ether bis(o-aminophenol) monomers and a novel fluorocarbon bis(o-aminophenol) monomer containing an aliphatic hydrocarbon cure site.



Control of the stoichiometry (mole proportions a and b) of the copolycondensation reactions permitted the synthesis of FEB copolymers containing a predetermined number of cure sites adequate to permit attainment of good mechanical properties with retention of high thermo-oxidative stability and good low temperature viscoelastic properties. Through judicious choice of monomers and proper control of monomer stoichiometry, readily curable, hydrolytically stable FEB copolymers with potential for good mechanical properties over a broad use-temperature range were obtained.

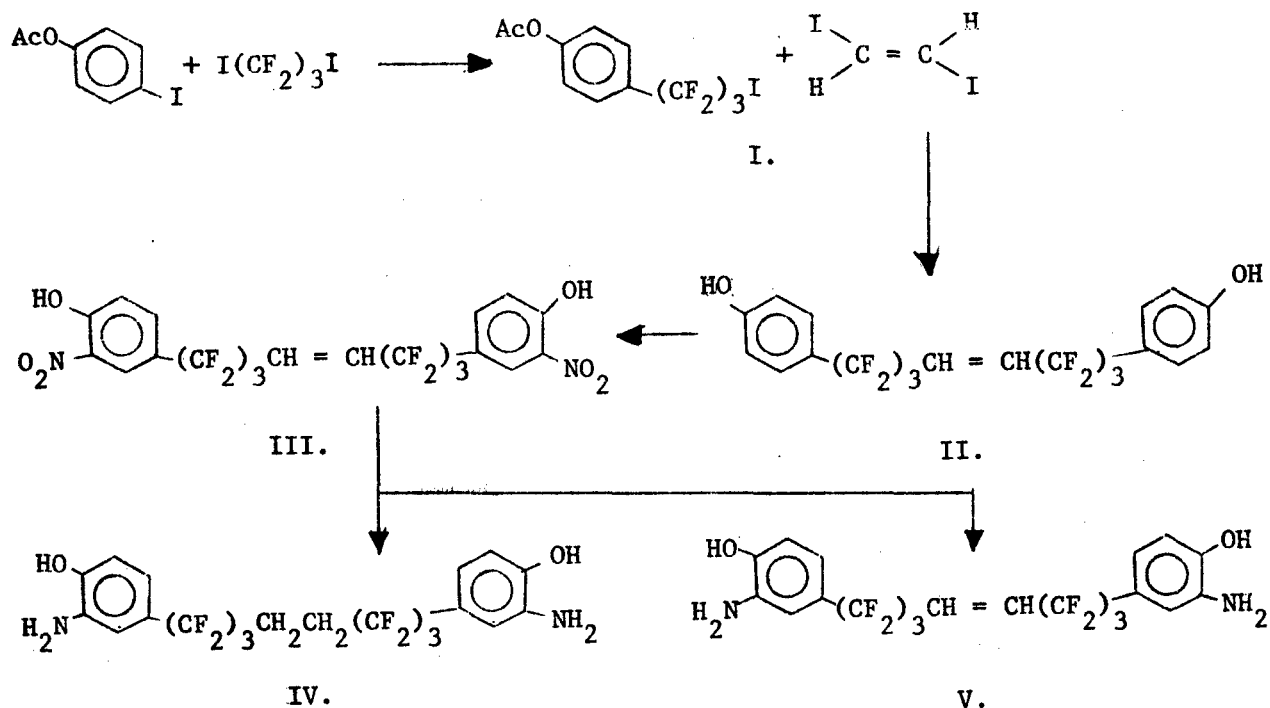
The synthesis of the requisite fluoro-carbon bis(o-aminophenol) monomer containing the aliphatic cure site is given below. The subsequent copolycondensation reactions are also described along with the characterization and evaluation of the resultant curable FEB copolymers.

SECTION II

DISCUSSION

1. MONOMER SYNTHESIS

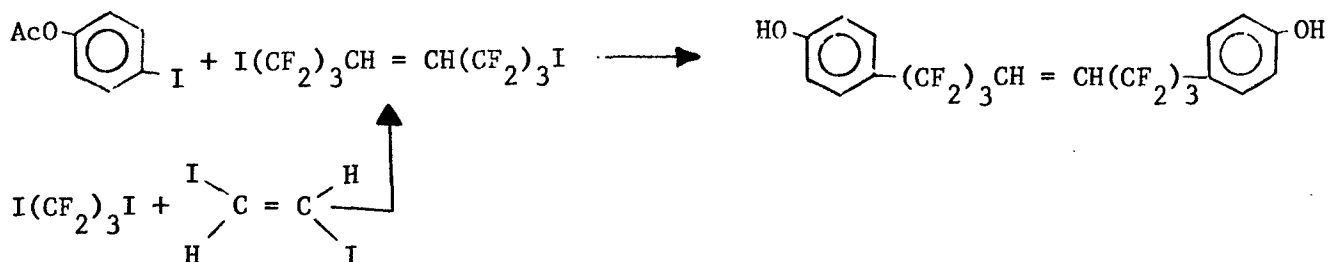
The selected cure site monomer (IV) contained an aliphatic moiety directly adjacent to fluorocarbon groups which were expected to exert an activating effect during the radical-induced cure reaction. In addition, this fluorocarbon character was expected to impart sufficient solubility and reactivity to the monomer during the copolycondensation reactions to permit incorporation of the cure sites into the FEB copolymers.



The requisite fluorocarbon bis(o-aminophenol) monomer (IV) was prepared by a multistep reaction sequence. The key reactions entailed the copper-promoted coupling of fluorocarbon iodides with aromatic and olefinic iodides

under reaction conditions initially reported by McLoughlin and coworkers (References 9-12). In the initial step, the carefully controlled reaction of equimolar quantities of 4-iodophenyl acetate and 1,3-diiodohexafluoropropane in the presence of copper bronze and dimethyl sulfoxide proceeded smoothly to give 4-(3-iodoperfluoropropyl)phenyl acetate (I). This intermediate, upon reaction with trans-1,2-diiodoethylene in the presence of copper bronze and N,N-dimethylacetamide, was converted through work-up with methanolic hydrochloric acid into trans-1,2-bis[3-(4-hydroxyphenyl)perfluoropropyl]ethylene (II). Nitration in acetic acid yielded trans-1,2-bis[3-(4-hydroxy-3-nitrophenyl)perfluoropropyl]ethylene (III) which in turn was readily reduced (the olefinic group as well as the nitro groups) by catalytic hydrogenation with Pd/C to the desired 1,2-bis[3-(4-hydroxy-3-aminophenyl)perfluoropropyl]ethane (IV). An overall yield of 15% was recorded. Alternatively, the nitro groups in III could be selectively reduced either chemically with sodium dithionite or via catalytic hydrogenation with Pd/BaSO₄ to give trans-1,2-bis[3-(4-hydroxy-3-aminophenyl)perfluoropropyl]ethylene (V) in 55% yield.

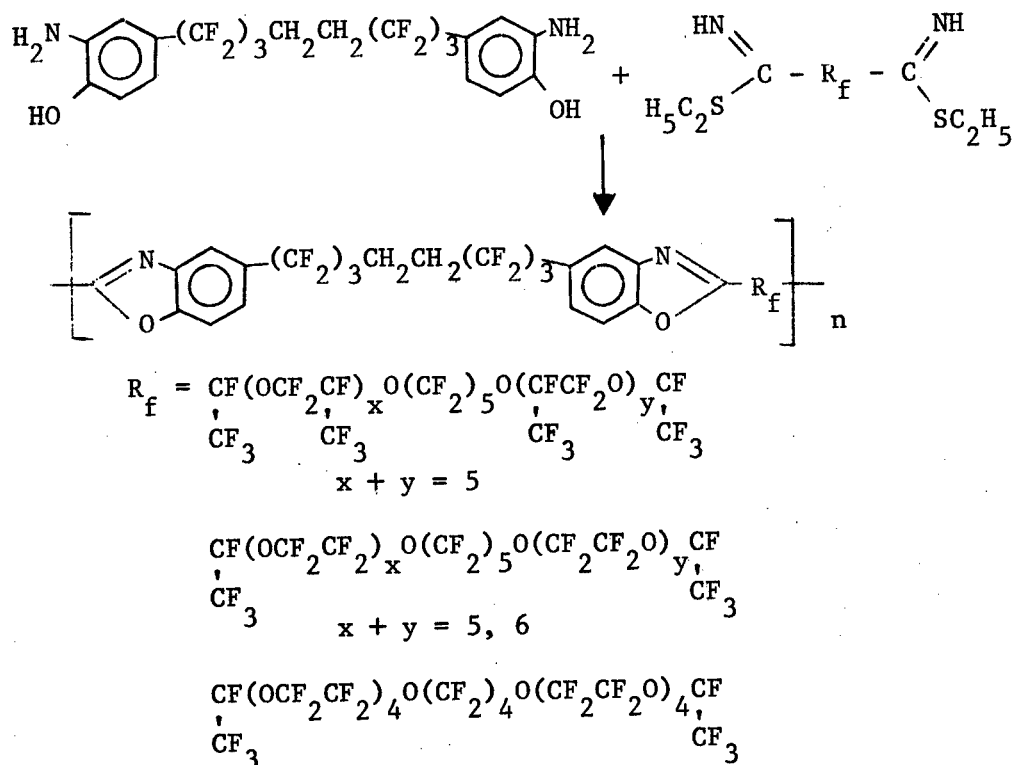
An alternate synthesis of the diphenol intermediate II was briefly explored. This approach entailed the copper-promoted coupling of 4-iodophenyl acetate with an olefinic fluorocarbon diiodide. The requisite



1,2-bis(3-iodoperfluoropropyl)ethylene was prepared by the copper-promoted coupling of 1,3-diiodohexafluoropropane with trans-1,2-diiodoethylene. Because of the very low yields of diiodide intermediate realized through the coupling reaction, this approach was not pursued further.

2. POLYMER SYNTHESIS

As in the previous FEB polymer syntheses (References 1-7), the polycondensation reactions were carried out in hexafluoroisopropanol (HFIP) at 50-55°C in the presence of approximately four molar equivalents of glacial acetic acid. The reaction conditions are summarized in Table I. In order to assess the reactivity of cure site monomer IV under the above reaction conditions, initial polymer synthesis efforts were directed toward the polycondensation of this fluorocarbon bis(o-aminophenol) monomer with both HFPO- and TFEO:HFPO-derived dithioimide ester monomers (Trial Nrs. 1-4). Unlike the fluorocarbon ether bis(o-aminophenol) monomers, monomer IV



exhibited limited solubility in the reaction medium and was incompletely soluble even at the relatively low reaction concentrations used. Only after the reactions had proceeded for 3-5 days did the polymerization mixtures become clear. The resultant polymers were isolated as moderate-to-high molecular weight, rubbery gums which exhibited inherent viscosities in the range of 0.22 to 0.62 dl/g.

The copolycondensation reactions of cure site monomer IV and fluorocarbon ether bis(o-aminophenol) monomers with HFPO- and TFEO:HFPO-derived dithioimide ester monomers (Trial Nrs. 5-10) were run under conditions similar to those described above. Although sizable mechanical losses were incurred in some cases, soluble amber-colored gums which exhibited inherent viscosities in the range of 0.26 to 0.51 dl/g were obtained in yields of up to 90 percent.

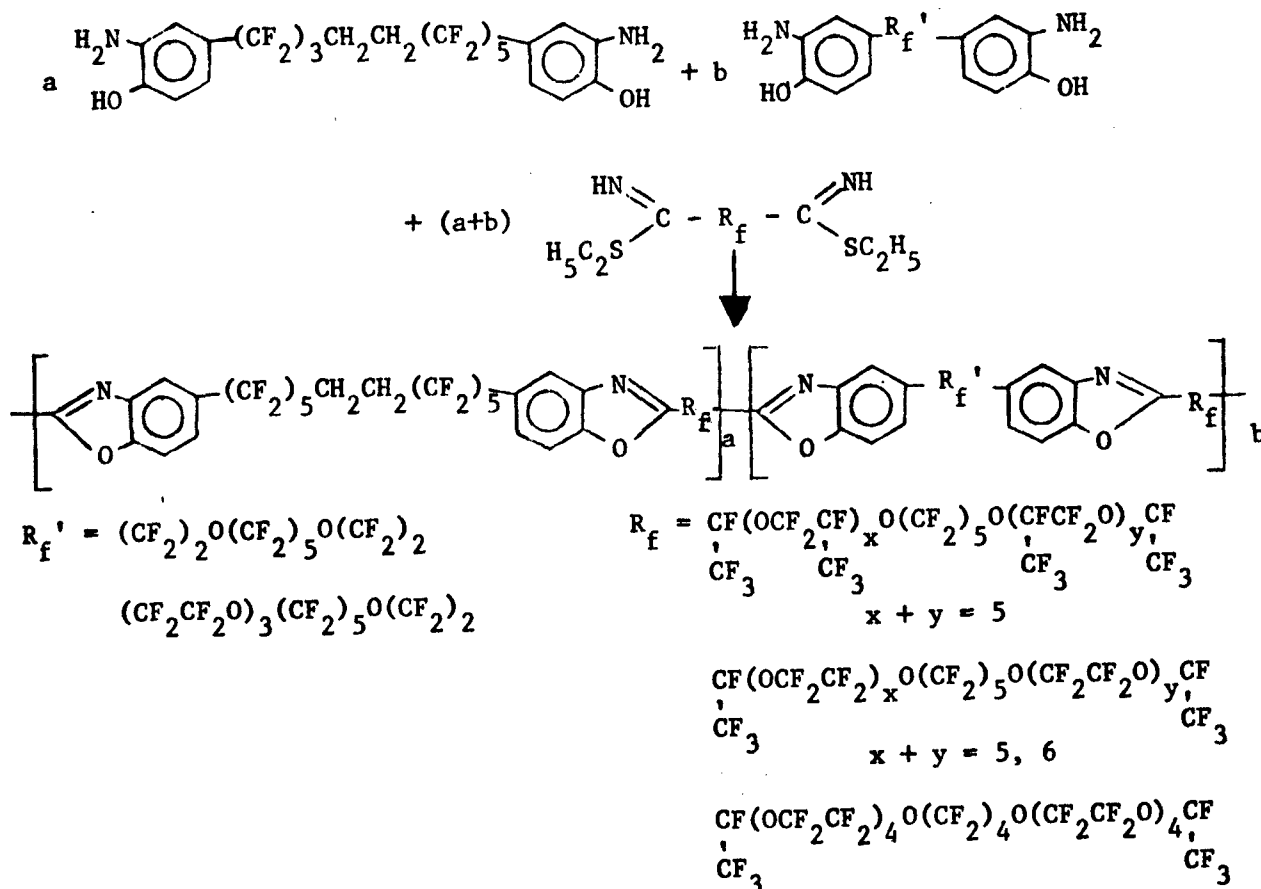


TABLE I
PREPARATION AND PROPERTIES OF CURABLE POLYMERS

Trial Nr.	Mole Proportion (a)	R _f ¹¹	Note Proportion (b)	R _f ¹	R _f	Time- Hours	Reaction Concentration- % monomer ($\frac{1}{V}$)	(1) η_{inh} - dl/g	T _g ⁽²⁾ °C	Analysis -	calc'd found	
										C	H	N
1	1.00	(CF ₂) ₃ CH ₂ CH ₂ (CF ₂) ₃			CF(OCF ₂ CF ₂) ₂ O(CF ₂) ₅ O(CF ₂ CF ₂ O) ₂ CF ₃ CF ₃ x + y = 5	240	13	0.22	-4	29.47 (29.39)	0.53 (0.28)	1.49 (1.61)
2	1.00	"			CF(OCF ₂ CF ₂) ₂ O(CF ₂) ₅ O(CF ₂ CF ₂ O) ₂ CF ₃ CF ₃ x + y = 5	240	15	0.62	-14	30.31 (30.81)	0.62 (0.31)	1.72 (1.90)
3	1.00	"			" x + y = 5	240	11	0.36	-26	29.67 (29.59)	0.58 (0.02)	1.60 (1.72)
4	1.00	"			CF(OCF ₂ CF ₂) ₂ O(CF ₂) ₄ O(CF ₂ CF ₂ O) ₂ CF ₃ CF ₃ x + y = 6	336	13	0.29	-40	28.74 (28.64)	0.52 (0.29)	1.46 (1.48)
5	0.10	"	0.90	(CF ₂) ₂ O(CF ₂) ₅ O(CF ₂) ₂	CF(OCF ₂ CF ₂) ₂ O(CF ₂) ₅ O(CF ₂ CF ₂ O) ₂ CF ₃ CF ₃ x + y = 5	480	72	0.26	-17	27.98 (27.91)	0.32 (0.11)	1.39 (1.86)
6	0.15	"	0.85	"	CF(OCF ₂ CF ₂) ₂ O(CF ₂) ₅ O(CF ₂ CF ₂ O) ₂ CF ₃ CF ₃ x + y = 5	240	16	0.45	-24	28.63 (28.64)	0.37 (0.02)	1.59 (1.73)
7	0.10	"	0.90	"	" x + y = 5	600	90	0.48	-35	28.06 (27.89)	0.34 (0.11)	1.49 (1.39)
8	0.10	"	0.90	"	" x + y = 6	576	90	0.46	-35	28.06 (28.10)	0.34 (0.08)	1.49 (1.57)
9	0.10	"	0.90	"	CF(OCF ₂ CF ₂) ₂ O(CF ₂) ₄ O(CF ₂ CF ₂ O) ₂ CF ₃ CF ₃ x + y = 6	672	85	0.40	-44	27.56 (27.40)	0.32 (0.01)	1.37 (1.39)
10	0.10	"	0.90	(CF ₂ CF ₂ O) ₃ (CF ₂) ₅ O(CF ₂) ₂	"	504	76	0.51	-47	26.89 (26.70)	0.29 (0.09)	1.24 (1.28)
11	0.10	(CF ₂) ₃ CH = CH(CF ₂) ₃	0.90	(CF ₂) ₂ O(CF ₂) ₅ O(CF ₂) ₂	CF(OCF ₂ CF ₂) ₂ O(CF ₂) ₅ O(CF ₂ CF ₂ O) ₂ CF ₃ CF ₃ x + y = 5	480	70	0.20	-19	27.98 (27.92)	0.31 (0.10)	1.39 (1.40)

(1) 0.2 g/dl, 25°C, HFIP.

(2) Differential Scanning Calorimetry ($\Delta T = 20^\circ\text{C}/\text{min}$).

The low molar proportion ($a = 0.10$ to 0.15) of cure site monomer IV present in the copolycondensation reactions permitted the use of high monomer to solvent concentrations to minimize intramolecular reaction of the FEB oligomers and suppress formation of macrocyclic compounds. Because of the limited solubility of cure site monomer IV in HFIP, the reaction mixtures did not become homogeneous until after 3-5 days of reaction time had elapsed. The limited solubility of monomer IV would be expected in the early stages of the copolycondensation reactions to lead to preferential formation of FEB oligomers almost void of cure sites; subsequent reaction of cure site monomer IV with the FEB oligomers would lead to a relatively uniform distribution of cure sites within the copolymer backbone.

The copolycondensation of potential cure site monomer V and a fluorocarbon ether bis(o-aminophenol) monomer with a TFEO:HFPO-derived dithioimide ester was also carried out (Trial Nr. 11). Monomer V also had limited solubility in the reaction medium but gradually dissolved to permit the formation of a viscous, amber-colored solution. The resultant gum exhibited an inherent viscosity of 0.20 dl/g.

3. POLYMER CHARACTERIZATION AND EVALUATION

Polymer and copolymer structures were verified by elemental analysis and infrared spectroscopy data. Elemental analysis values are given in Table I. The infrared spectra were very similar to those previously reported for FEB polymers (References 1,7). In some cases, however, additional
-1
absorptions in the 2800-2900 cm^{-1} region were observed. These were attributable to the C-H stretching vibrations (Reference 13) arising from the

aliphatic hydrocarbon cure sites and were more readily observed in the polymers (Trial Nrs. 1-4) which had a much larger aliphatic hydrocarbon content than the copolymers (Trial Nrs. 5-10). An infrared spectrum exhibiting these absorptions can be seen in Figure 1.

The Tg's of the polymers and copolymers were determined by differential scanning calorimetry and are given in Table I. No crystallinity was detected in any of the samples. As expected, incorporation of cure site monomer IV into the FEB polymers resulted in an increase in Tg attributable to the stiffening effect of the relatively inflexible - $(CF_2)_3CH_2CH_2(CF_2)_3$ - segment in the copolymer backbone. This observed increase in polymer Tg was a function of the mole proportion of monomer IV in the copolymer chain as evidenced by the data in Table II. Comparison of previously-synthesized FEB polymers void of cure site monomer IV, FEB copolymers containing 10 to 15 mole percent of monomer IV, and the polymers containing 100 mole percent of monomer IV demonstrated the increase in Tg with increased cure site content within the copolymer backbone. This undesirable effect was least pronounced with FEB polymer and copolymer structures synthesized from the non-isomeric TFEO:HFPO-derived dithioimide ester (Examples 3 and 4); copolymer Tg's of $-44^\circ C$ ($-47^\circ F$) and $-47^\circ C$ ($-53^\circ F$), respectively, were recorded.

Exposure of an FEB copolymer sample (Trial Nr. 9) to a 95% relative humidity, $93^\circ C$ ($200^\circ F$) environment for 30 days did not appear to adversely affect the sample as no changes were observed in the infrared spectrum. The thermooxidative stability of this FEB copolymer was evaluated by thermogravimetric analysis (TGA) and isothermal aging in air. Comparisons were made

between these data and the data obtained from the analogous FEB polymer void of cure sites. Comparative TGA and isothermal aging curves are shown in Figures 3 and 4, respectively. Initial weight loss for the FEB copolymer observed under TGA in air occurred at 250°C (482°F); approximately 5 and 10 percent weight losses were observed at 400°C (752°F) and 450°C (842°F), respectively. The analogous FEB polymer void of cure sites exhibited initial weight loss at 280°C (536°F) and 3 and 8 percent weight losses at 400°C (752°F) and 450°C (842°F), respectively. Under isothermal aging in air, the FEB polymer and copolymer exhibited almost identical behavior. At 288°C (550°F), unexplained early weight gains of 3 percent were followed by slow, steady weight losses which amounted to 17% after 200 hours. At 260°C (500°F), the 7% weight losses recorded after 200 hours occurred almost completely within 100 hours. Based solely on these data, the aliphatic cure sites within the FEB copolymers do not significantly decrease the thermooxidative stability of the copolymers.

Preliminary formulation and curing of the FEB copolymers confirmed the ready reactivity of the aliphatic hydrocarbon cure sites to a radical-induced curing reaction (Reference 14). Effective cures were achieved and the resultant vulcanizates exhibited superior resistance to severe environments. Optimum properties were observed in the case of the FEB copolymers (Trial Nrs. 9 and 10) synthesized from the non-isomeric TFEO:HFPO-derived dithioimidate ester monomer (Reference 1). Complete results of the formulation and curing studies will be disclosed in the future.

TABLE II
Tg COMPARISON OF FEB POLYMERS AND COPOLYMERS

Example	Mole Proportion (a)	R _f "	Mole Proportion (b)	R _f '	R _f	Tg- C ⁽¹⁾
1	0.00	(CF ₂) ₃ CH ₂ CH ₂ (CF ₂) ₃	1.00	(CF ₂) ₂ O(CF ₂) ₅ O(CF ₂) ₂	CF(OCF ₂ CF ₂) _x O(CF ₂) ₅ O(CF ₂ CF ₂ O) _y CF ₃ x + y = 5	-35
	0.15	"	0.85	"	"	-24
	1.00	"	0.00	"	"	-14
	0.00	(CF ₂) ₃ CH ₂ CH ₂ (CF ₂) ₃	1.00	(CF ₂) ₂ O(CF ₂) ₅ O(CF ₂) ₂	CF(OCF ₂ CF ₂) _x O(CF ₂) ₅ O(CF ₂ CF ₂ O) _y CF ₃ x + y = 6	-38
2	0.10	"	0.90	"	"	-35
	1.00	"	0.00	"	"	-26
3	0.00	(CF ₂) ₃ CH ₂ CH ₂ (CF ₂) ₃	1.00	(CF ₂) ₂ O(CF ₂) ₅ O(CF ₂) ₂	CF(OCF ₂ CF ₂) ₄ O(CF ₂) ₄ O(CF ₂ CF ₂ O) ₄ CF ₃	-45
	0.10	"	0.90	"	"	-44
	1.00	"	0.00	"	"	-40
4	0.00	(CF ₂) ₃ CH ₂ CH ₂ (CF ₂) ₃	1.00	(CF ₂ CF ₂ O) ₃ (CF ₂) ₅ O(CF ₂) ₂	CF(OCF ₂ CF ₂) ₄ O(CF ₂) ₄ O(CF ₂ CF ₂ O) ₄ CF ₃	-48
	0.10	"	0.90	"	"	-47
	1.00	"	0.00	"	"	-40
5	0.00	(CF ₂) ₃ CH ₂ CH ₂ (CF ₂) ₃	1.00	(CF ₂) ₂ O(CF ₂) ₅ O(CF ₂) ₂	CF(OCF ₂ CF ₂) _x O(CF ₂) ₅ O(CF ₂ CF ₂ O) _y CF ₃ x + y = 5	-23
	0.10	"	0.90	"	"	-17
	1.00	"	0.00	"	"	-4

(1) Differential Scanning Calorimetry (ΔT = 20°C/min).

4. CONCLUSIONS

The results presented in this report demonstrate that a novel fluorocarbon bis(o-aminophenol) monomer containing a hydrocarbon cure site can be synthesized by a multistep reaction sequence, the key steps being the copper-promoted reactions of 1,3-diiodohexafluoropropane with 4-iodophenyl acetate and, subsequently, the resultant intermediate with trans-1,2-diiodoethylene. Copolycondensation of this appropriately structured cure site monomer and fluorocarbon ether bis(o-aminophenol) monomers with TFEO:HFPO-derived dithioimide esters lead to curable and hydrolytically stable FEB copolymers exhibiting inherent viscosities as high as 0.51 dl/g.

The limited solubility and reactivity of the cure site monomer during the polycondensation reactions would be expected to result in a relatively uniform distribution of cure sites within the copolymer chain. Through control of monomer stoichiometry, it is possible to achieve the synthesis of FEB copolymers containing a predetermined number of uniformly distributed cure sites adequate to permit effective curing of the copolymer while minimizing accompanying deleterious effects on thermooxidative stability and low temperature viscoelastic properties. Although incorporation of the cure site into the FEB copolymers leads to an increase in T_g , values as low as -47°C (-53°F) can nevertheless be achieved. The accompanying decrease in thermooxidative stability is minimal and is not observable under isothermal aging in air. Even after 200 hours at 260°C (500°F), only a 7 percent weight loss is observed.

Based on the TGA and isothermal aging results in air, long term use at temperatures approaching 260°C (500°F) is envisioned. The high thermooxidative and hydrolytic stability along with the low temperature viscoelastic properties of the TFEO:HFPO-based FEB copolymers are strongly indicative of a broader use temperature range than is currently available in state-of-the-art elastomer materials. Preliminary curing studies demonstrate the ready reactivity of the aliphatic hydrocarbon cure sites to radical-induced cure reactions and further substantiate the potential of appropriately structured TFEO:HFPO-based FEB copolymers for use in severe environment seal applications in advanced aircraft and cruise missiles.

SECTION III

EXPERIMENTAL

1. PREPARATION OF SOLVENTS AND INTERMEDIATES

Hexafluoroisopropanol (HFIP) and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) obtained from Pierce Chemical Company and Dupont, respectively, were dried over magnesium sulfate and redistilled.

Copper bronze obtained from Gallard-Schlesinger was used as received.

1,3-Diiodohexafluoropropane and 4-iodophenyl acetate had been synthesized in an earlier phase of the current effort (Reference 15).

Trans-1,2-diiodoethylene

Acetylene was slowly bubbled at room temperature through a stirred solution of iodine (87.3 g, 344 mmol) and potassium iodide (200.0 g, 1198 mmol) in 3400 ml of water. After 23 hours, a white precipitate of the desired product was noted. The reaction was periodically stopped and the precipitate isolated by filtration. After two weeks, 60.5 g of the combined crops of white needles (63% yield based on iodine) was recrystallized from absolute ethanol to yield 39.0 g of pure product, mp 73.5-75.0°C (lit 73°C) (Reference 16).

2. PREPARATION OF MONOMERS

Trans-1,2-bis[3-(4-hydroxy-3-aminophenyl)perfluoropropyl]ethane

A solution of p-iodophenyl acetate (27.5 g, 105 mmol) and 1,3-diiodohexafluoropropane (52.0 g, 128.7 mmol) in 100 ml of anhydrous dimethyl sulphoxide was heated to 120°C under nitrogen. Copper powder

(13.5 g, 211 mmol) was added to the vigorously stirred solution in five approximately equal amounts at 20 minute intervals. After the addition of copper was complete, the reaction mixture was stirred at 120°C for an additional 1.5 hours. On cooling, saturated aqueous ammonium chloride together with methylene chloride was added to the reaction vessel. The excess copper and cuprous salts were filtered off, the organic layer separated, and the aqueous layer extracted with more methylene chloride. The organic extracts were combined, washed well with water, dried over anhydrous magnesium sulfate, and reduced in volume to a light yellow oil. The oil was refluxed in 25 ml of acetic anhydride for 45 minutes and the excess acetic anhydride and acetic acid were distilled under reduced pressure. Distillation of the residual oil yielded 24.9 g of crude 4-(3-iodoperfluoropropyl)phenyl acetate, bp 126-127°C/3.4 mm Hg, mp 75-81°C. Recrystallization of this material from hexane gave 20.8 g (43% yield) of purer material, mp 84.5-88°C. Repeated recrystallization from hexane raised the melting point to 88.5-89.5°C, which could not be improved upon by further recrystallization. The infrared, nuclear magnetic resonance, and mass spectroscopy data were consistent with the proposed structure.

Analysis: Calc'd: C, 31.37; H, 1.71; I, 30.79.

 Found: C, 32.33; H, 1.28; I, 30.09.

Molecular weight (mass spectroscopy) Calc'd: 412; Found 412.

Copper powder (10.0 g) was added to a solution of 4-(3-iodoperfluoropropyl)phenyl acetate (15.0 g, 36.14 mmol) and trans-1,2-diiodoethylene (5.25 g, 18.7 mmol) in 90 ml of anhydrous N,N-dimethyl

acetamide. The reaction mixture was maintained under nitrogen at 120°C for 12 hours with vigorous stirring. Saturated aqueous ammonium chloride and methylene chloride were then added to the cooled reaction mixture. The excess copper and cuprous salts were filtered off, the organic layer separated, and the aqueous layer extracted with more methylene chloride. The organic extracts were combined and washed with 15% hydrochloric acid followed by a thorough washing with water. Drying of the organic phase over anhydrous magnesium sulfate followed by evaporation of the extract yielded a crude, light brown solid. This solid was taken up in 95 ml of methanol and refluxed for one hour after the addition of 5 ml of conc. hydrochloric acid. Water was then added. Extraction of the cold methanolic solution with methylene chloride followed by evaporation of the solvent after washing with water and drying over anhydrous magnesium sulfate yielded a solid which could be recrystallized from methylene chloride-hexane. Trans-1,2-bis[3-(4-hydroxyphenyl)perfluoropropyl]ethylene (6.02 g) was obtained in 65% yield as white crystals, mp 134-137.5°C. Crystals with mp 137.5-138°C could not be further purified by recrystallization. The infrared, nuclear magnetic resonance and mass spectroscopy data were consistent with the proposed structure.

Analysis: Calc'd: C, 48.66; H, 2.36.

 Found: C, 47.29; H, 1.62.

Molecular weight (mass Spectroscopy) Calc'd: 512; Found 512.

Trans-1,2-bis[3-(4-hydroxylphenyl)perfluoropropyl]ethylene (5.66 g) was warmed in 20 ml of acetic acid until a clear solution formed. After the addition of conc. nitric acid (4.0 ml), the reaction solution was

stirred at 45-55°C until an exotherm occurred after 5-10 minutes of heating. During the exotherm the temperature was maintained at 60°C by means of an ice bath. The red color that developed during this period gradually faded to a light yellow color on continued stirring at 55-60°C for 4.5 hours. The precipitate that appeared gradually increased as stirring continued. The acetic acid was then chilled, the light yellow precipitate filtered off, washed with pentane and dried to give 5.06 g (75% yield) of trans-1,2-bis[3-(4-hydroxy-3-nitrophenyl)perfluoropropyl]ethylene, mp 122-123°C. This melting point could not be improved by recrystallization from methylene chloride-hexane solution. The infrared, nuclear magnetic resonance, and mass spectroscopy data were consistent with the proposed structure.

Analysis: Calc'd: C, 39.88; H, 1.67; N, 4.65.

 Found: C, 40.29; H, 0.92; N, 5.05.

Molecular weight (mass spectroscopy) Calc'd: 602; Found 602.

A solution of trans-1,2-bis[3-(4-hydroxy-3-nitrophenyl)perfluoropropyl]ethylene (5.0 g) in 60 ml of ethyl acetate containing 10% palladium on charcoal (1.0 g) was deoxygenated with nitrogen. It was then agitated under 50 psi of hydrogen for five hours at room temperature. After filtering off the catalyst, the ethyl acetate solution was reduced in volume and recrystallization induced by adding hexane to the hot ethyl acetate solution. 1,2-Bis[3-(4-hydroxy-3-aminophenyl)perfluoropropyl]ethane was obtained as white crystals in two fractions: 1.97 g, mp 202-202.5°C (dec., sealed cap) and 0.98 g, mp 202°C (dec., sealed cap.) for a total yield of 59%. The higher melting material could not be further purified

by recrystallization. The infrared, nuclear magnetic resonance, and mass spectral data were consistent with the proposed structure.

Analysis: Calc'd: C, 44.29; H, 2.60; N, 5.16.

 Found: C, 44.28; H, 2.61; N, 4.75.

Molecular weight (mass spectroscopy) Calc'd: 542; Found 542.

Trans-1,2-bis[3-(4-hydroxy-3-aminophenyl)perfluoropropyl]ethylene

Sodium dithionite (10 g) in 30 ml of water was added slowly with stirring at room temperature to a solution of 1.0 g (1.7 mmol) of trans-1,2-bis[3-(4-hydroxy-3-nitrophenyl)perfluoropropyl]ethylene in 250 ml of methanol. The methanolic solution turned bright yellow and then slowly faded to water-white as reduction occurred. After addition of the sodium dithionite was completed, stirring was continued for an additional 30 minutes at which time water was added to give a total solution volume of 750 ml. The resultant white slurry was extracted three times with 200 ml portions of ether and the combined ether extracts were washed repeatedly with water. The ether solution was then dried over anhydrous magnesium sulfate and stripped to dryness under reduced pressure to give a white residue. Most of this solid was soluble in 900 ml of hot toluene which was treated with charcoal and reduced in volume to 100 ml. Cooling in dry ice gave 0.5 g (55% yield) of the olefinic product as white platelets, mp 187-188°C.

Analysis: Calc'd: C, 44.29; H, 2.60; N, 5.16.

 Found: C, 44.85; H, 2.79; N, 4.99.

Molecular Weight (mass spectroscopy) Calc'd: 542; Found 542.

The requisite fluorocarbon ether bis(o-aminophenol) monomers had been prepared under an earlier phase of the current effort (Reference 7) as had the HFPO- and TFEO:HFPO-derived fluorocarbon ether dithioimide esters (References 1-3,5).

3. PREPARATION OF POLYMERS

A typical preparative procedure for the FEB polymers is as follows.

Curable FEB Copolymer (Trial Nr. 9)

Redistilled hexafluoroisopropanol (1.3 ml) was added to a mixture of fluorocarbon ether bis(o-aminophenol) monomer (3.144 g, 4.5 mmol), cure site monomer IV (0.272 g, 0.5 mmol), and fluorocarbon ether dithioimide ester monomer (7.687 g, 5.0 mmol). Glacial acetic acid (1.25g, 20 mmol) was added to the resultant white slurry which was then stirred under nitrogen at 55°C. The suspended monomer gradually dissolved to give a clear amber solution after five days reaction time. The polycondensation reaction was allowed to continue for a total reaction time of 28 days at which time the polymer was precipitated from methanol. The supernatant liquid was decanted and the polymer dried at room temperature and 0.30 mm Hg for 24 hours. It was redissolved in 60 ml of Freon 113 and the solution filtered. The solution was reduced in volume to 20 ml and the polymer was then reprecipitated from methanol. The swollen, tacky polymer was dried at 100°C and 0.01 mm Hg for 24 hours to yield 9.2 g (89% yield) of light amber gum ($\eta_{inh} = 0.40$ dl/g in hexafluoroisopropanol at 25°C).

Analysis: Calc'd: C, 27.56; H, 0.32; N, 1.37.

 Found: C, 27.40; H, 0.11; N, 1.39.

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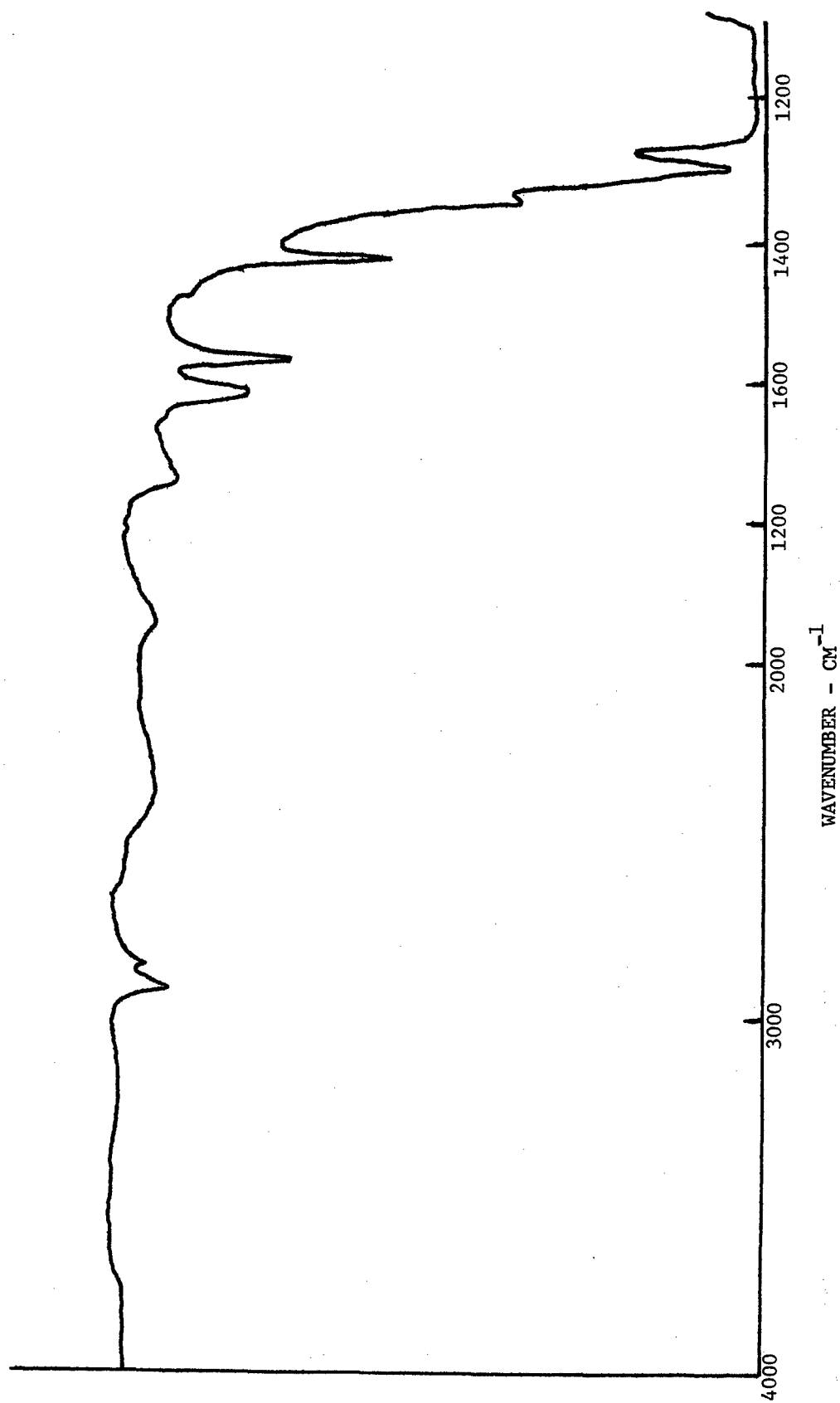


Figure 1. Infrared Spectrum of Curable FEB Polymer (Trial Nr. 2) (Film)

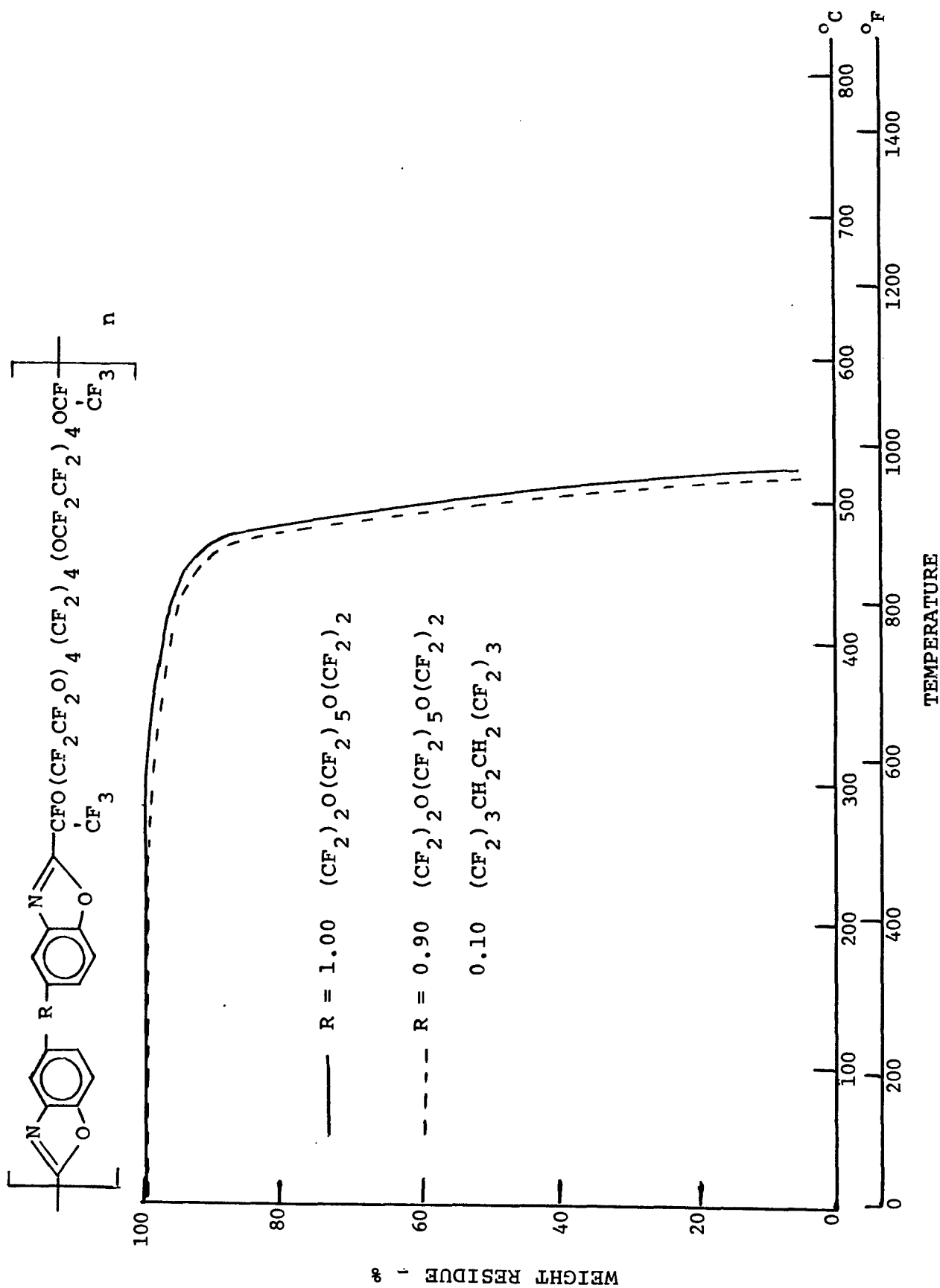


Figure 2. Comparative TGA Curves of FEB Polymer and Curable Copolymer (Trial Nr. 9) in Air ($\Delta T = 20^\circ\text{C/min}$)

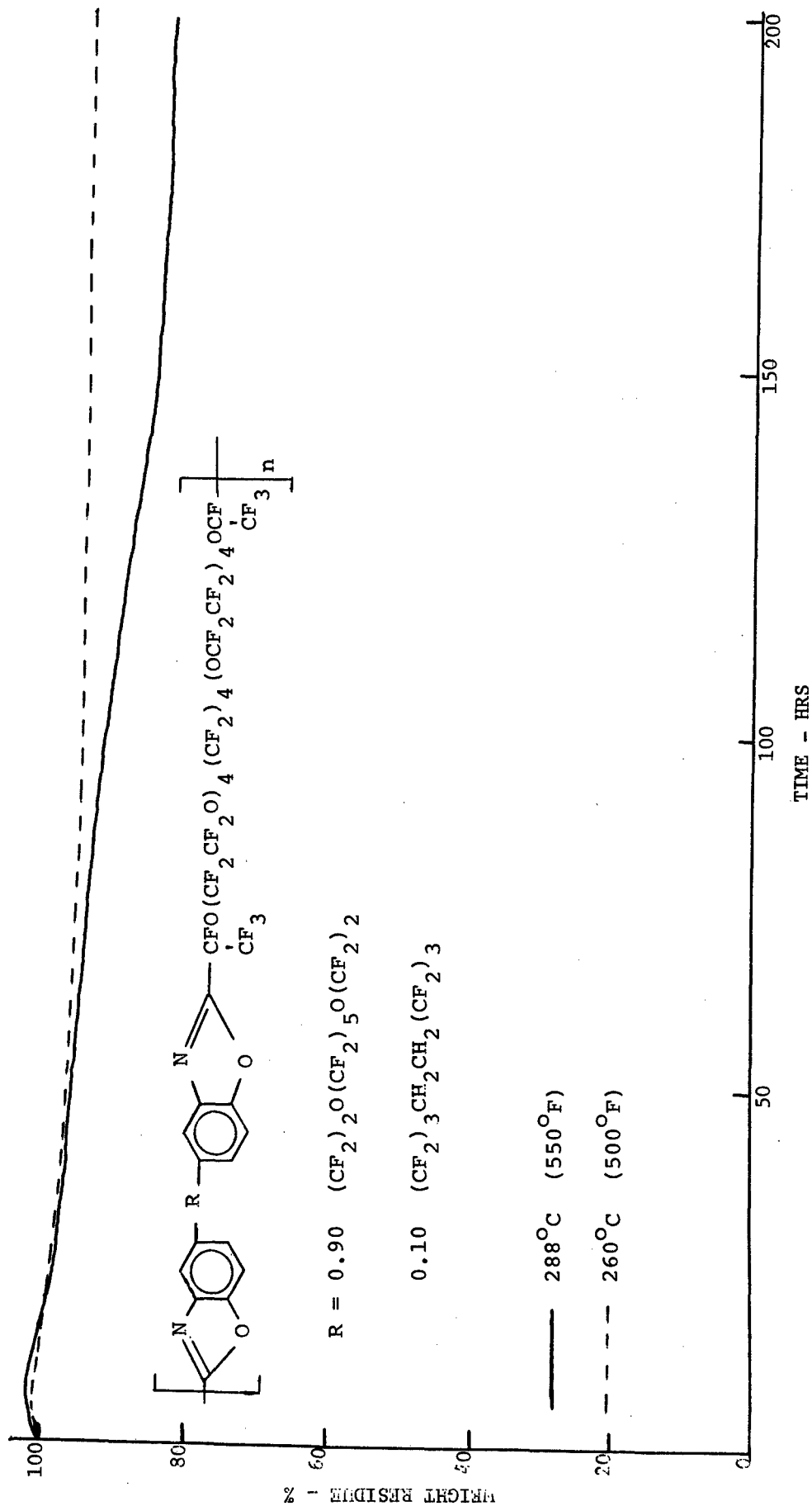


Figure 3. Isothermal Aging Curves of Curable FEB Copolymer (Trial Nr. 9) in Air