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MOLECULAR TAILORING OF FLUOROCARBON ETHER BIBENZOXAZOLE POLYMERS TO LOWER GLASS TRANSITION TEMPERATURES

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION ✓

AUGUST 1975

TECHNICAL REPORT AFML-TR-75-11

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AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

NOTICE

This technical report has been reviewed and is approved for publication.

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Project Scientist

FOR THE COMMANDER

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R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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The synthesis of fluorocarbon ether bis(o-aminophenol) monomers was accomplished by a multistep route from long-chain fluorocarbon ether diiodides and the reaction conditions optimized. Polycyclocondensation of these monomers with novel, long-chain fluorocarbon ether diimidate esters led to linear fluorocarbon ether bibenzoxazole (FEB) polymers soluble in hexafluoroisopropanol and Freon 113. Polymer structures were verified by elemental and infrared analysis. Some of the FEB polymers were obtained in moderate to high →

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molecular weights with inherent viscosities in the range of 0.4 to 0.5 dl/g. High fluorocarbon ether content gave the desired low glass transition temperatures without significant sacrifices in thermooxidative stabilities. Rubbery polymers with glass transition temperatures as low as -58°C (-72°F) were obtained. With respect to thermooxidative stability, onset of weight loss of the FEB polymers during thermogravimetric analysis in an air atmosphere occurred in the 350-400°C (660-750°F) range. Based on these encouraging results, FEB polymers appear to have great potential as a class of polymers for broad use temperature range elastomer applications which surpass current state-of-the-art materials.

FOREWORD

This effort was accomplished by the Polymer Branch, Nonmetallic Materials Division of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials." It was administered under the direction of Dr. R. C. Evers (AFML/MBP), Project Scientist.

This report covers work conducted from June 1973 to September 1974. This manuscript was submitted by the author in January 1975 for publication as a technical report.

The author wishes to thank the Analytical Branch, Air Force Materials Laboratory for performing the elemental analysis determinations and Mr. Lee Smithson for the mass spectral data. Dr. G. F. L. Ehlers and Mr. Kurt Fisch contributed the thermal stability and differential scanning calorimetry data. The assistance of Mr. J. L. Burkett in many of the laboratory operations is gratefully acknowledged.

The polymer names were provided through the courtesy of Dr. K. L. Loening, Nomenclature Director, American Chemical Society, Chemical Abstracts Service.

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SUMMARY

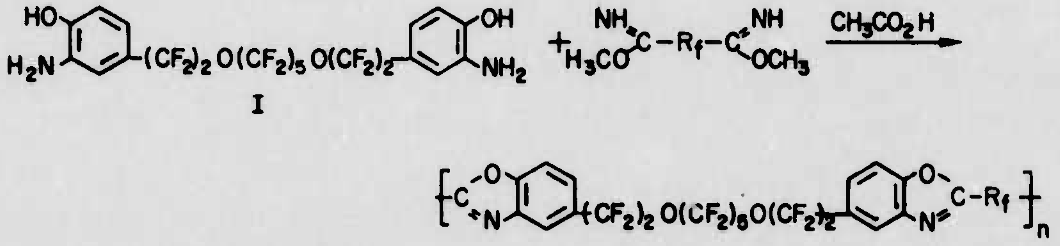
The synthesis of fluorocarbon ether bis(o-aminophenol) monomers was accomplished by a multistep route from long-chain fluorocarbon ether diiodides and the reaction conditions optimized. Polycyclocondensation of these monomers with novel, long-chain fluorocarbon ether diimidate esters led to linear fluorocarbon ether bibenzoxazole (FEB) polymers soluble in hexafluoroisopropanol and Freon 113. Polymer structures were verified by elemental and infrared analysis. Some of the FEB polymers were obtained in moderate to high molecular weights with inherent viscosities in the range of 0.4 to 0.5 dl/g. High fluorocarbon ether content gave the desired low glass transition temperatures without significant sacrifices in thermooxidative stabilities. Rubbery polymers with glass transition temperatures as low as -58°C (-72°F) were obtained. With respect to thermooxidative stability, onset of weight loss of the FEB polymers during thermogravimetric analysis in an air atmosphere occurred in the 350-400°C (660-750°F) range. Based on these encouraging results, FEB polymers appear to have great potential as a class of polymers for broad use temperature range elastomer applications which surpass current state-of-the-art materials.

SECTION I

INTRODUCTION

In order to meet the requirements for fluid and fuel containment in Air Force systems, new polymeric materials are needed for seals which will retain elastomeric properties over a -65° to 600°F temperature range. 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 thermally stable polymers as base materials for these applications have been carried on in this laboratory through both inhouse and contractual research programs.

In the first phase of a continuing AFML inhouse research program, the synthesis of several thermally stable, novel fluorocarbon ether bibenzoxazole (FEB) polymers was achieved by the acetic acid-promoted polycondensation of a novel fluorocarbon ether bis(o-aminophenol) monomer (I) with available fluorocarbon ether diimidate esters (Reference 1).



$R_f = CF_2O(CF_2)_2O\,CF_2\,, (CF_2)_4O(CF_2)_2OCF_2\cdot$

This work was a follow-on to the research of Madison and Burton (Reference 2), but represented a significant advance over their work in light of the significantly improved low temperature viscoelastic properties which were achieved without significant loss of thermooxidative stability. However, due to lack of sufficient flexibility in the polymer backbone, the glass transition temperatures (Tg) were still well above those needed to satisfy -65°F use temperature requirements.

In order to introduce additional flexibility into the polymer backbones and thus expand the range of viscoelasticity, the synthesis of several new long-chain fluorocarbon ether bis(o-aminophenol) monomers was carried out in the current phase of the research effort. Polycondensation of these novel monomers as well as the previously prepared Monomer I with novel long-chain fluorocarbon ether diimidate esters (synthesized by Dr. C. Tamborski of this laboratory) (Reference 3) would be expected to lead to new FEB polymers with increased fluorocarbon ether content and lower Tg's.

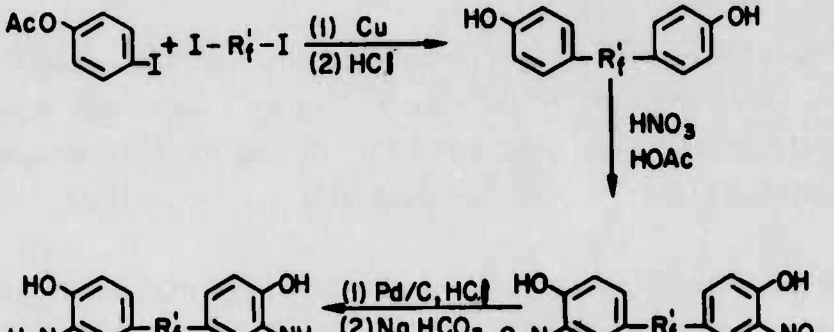
The synthesis of these novel fluorocarbon ether bis(o-aminophenol) monomers as well as the synthesis and characterization of the new FEB polymers is discussed in Section II.

SECTION II

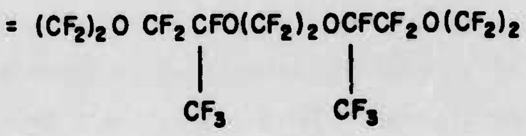
DISCUSSION

1. MONOMER SYNTHESIS

The key reaction in the synthesis of the new fluorocarbon ether bis(o-aminophenol) Monomers II and III was the coupling of 4-iodophenyl acetate with 1,14-diiodoperfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane and 1,17-diiodoperfluoro-3,6,9,15-tetraoxaheptadecane in the presence of copper bronze and N,N-dimethylformamide. As in the case of the previously reported synthesis of Monomer I (Reference 1), it was found that relatively low reaction temperatures ($\lesssim$115°C) and long reaction times (> 3 days) were necessary to effect successful coupling. Conversion of the resultant bisphenols to Monomers II and III was readily achieved via the following reaction sequence in overall yields of 12 and 15%, respectively. The infrared spectra of Monomers II and III are shown in Figures 1 and 2.



I $R_f' = (CF_2)_2O(CF_2)_5O(CF_2)_2$

II 
$$= (CF_2)_2O\,CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FO(CF_2)_2OC\!\!\!\underset{\displaystyle CF_3}{\underset{|}{}}\!\!\!FCF_2O(CF_2)_2$$

III $= (CF_2)_2O(CF_2)_2O(CF_2)_2O(CF_2)_5O(CF_2)_2$

2. POLYMER SYNTHESIS

The polycondensation reactions were carried out in hexafluoroisopropanol (HFIP) at 50-55°C in the presence of four molar equivalents of glacial acetic acid. The reaction conditions are summarized in Table I. The reaction solutions remained homogeneous throughout the course of the polycondensation due to the solubility of both the monomers and the polymers in HFIP. High reaction concentrations (~0.2g polymer/ml HFIP) were used to suppress undesirable intramolecular condensation of the growing polymer chains and formation of sublimable cyclic compounds (Reference 1). Rubbery, amber-colored polymers with inherent viscosities in the range of 0.11 to 0.47 dl/g were obtained. Yields of the crude polymers from the polymerization reactions varied considerably depending to a large extent upon the molecular weight of the polymer samples. Nearly quantitative recovery of crude polvmers was achieved in the case of the higher molecular weight samples. Even after purification, yields in the range of 75 to 80% were recorded.

3. POLYMER CHARACTERIZATION

The FEB polymers synthesized under this phase of the research program were clear, amber-colored, rubbery gums of varying toughness depending upon the polymer molecular weight and Tg. All of the polymer samples were completely soluble in HFIP or Freon 113.

The polymer structures were established by elemental analysis and comparisons of infrared absorption characteristics with previously reported model compounds and FEB polymers (Reference 1). Elemental analysis values of the polymer samples are given in Table I and representative infrared spectra are shown in Figures 3 and 4. Present in all cases, are bands at 6.1-6.2μ, 6.3-6.4μ, 6.9-7.0μ, and 7.2-7.3μ as well as the expected strong absorptions in the 8-9μ region, attributable to the C-F stretching vibrations (Reference 4). The latter absorptions are particularly pronounced in the spectra of the FEB polymers reported here due to the increased fluorocarbon ether content of the polymers.

TABLE I

PREPARATION AND PROPERTIES OF POLYMERS

No.	Rf'	Rf	Time-Hrs	ηinh-(a) dl/g	Tg-°C (b)	Analysis - Calc'd (Found) C	H	N
1.	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_4O(CF_2)_4O(CF_2)_4$	312	0.40	-20	31.18 (31.59)	0.44 (0.68)	2.08 (2.04)
2.	"	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	312	0.26	-32	32.08 (32.57)	0.50 (0.60)	2.34 (2.31)
3.	"	$(CF_2CF_2OCF_2CF_2)_4$	288	0.20	-39	29.64 (29.48)	0.38 (0.37)	1.77 (2.00)
4.	"	$CF_2O(CF_2CF_2O)m(CF_2)_5O(CF_2CFO)nCF_2$ m + n = 4	288	0.28	-41	29.21 (29.78)	0.38 (0.74)	1.79 (1.75)
5.	"	$CF_2O(CF_2CF_2O)m(CF_2)_5O(CF_2CF_2O)nCF_2$ m + n = 7	312	0.30	-55	27.66 (27.58)	0.31 (0.29)	1.47 (1.22)
6.	"	$(CF_2)_4O(\underset{CF_3}{CF}CF_2O)_3(CF_2)_4(OCF_2\underset{CF_3}{CF})_3O(CF_2)_4$	288	0.17	-43	27.15 (27.32)	0.26 (0.31)	1.19 (1.24)
7.	"	$(CF_2)_4O(\underset{CF_3}{CF}CF_2O)_2(CF_2)_4(OCF_2\underset{CF_3}{CF})_2O(CF_2)_4$	240	0.11	-40	28.05 (28.75)	0.30 (0.69)	1.39 (1.33)
8.	$(CF_2)_2OCF_2\underset{CF_3}{CF}O(CF_2)_2O\underset{CF_3}{CF}CF_2O(CF_2)_2$	$(CF_2)_4O(CF_2)_2OCF_2$	264	0.21	-25	30.96 (30.72)	0.47 (0.34)	2.19 (2.62)
9.	"	$(CF_2)_4O(CF_2)_4O(CF_2)_4$	432	0.41	-24	29.82 (30.17)	0.39 (0.35)	1.83 (1.66)
10.	0.5 " 0.5 $(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_4O(CF_2)_2OCF_2$	312	0.47	-19	31.81 (32.02)	0.51 (0.56)	2.35 (2.51)
11.	$(CF_2)_2O(CF_2)_2O(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_4O(CF_2)_2OCF_2$	192	0.47	-29	30.70 (30.80)	0.45 (0.41)	2.10 (2.17)
12.	"	$CF_2O(CF_2CF_2O)m(CF_2)_5O(CF_2CF_2O)nCF_2$ m + n = 7	168	0.30	-58	26.91 (26.80)	0.28 (0.17)	1.31 (1.42)

(a) 0.2 g/dl, 25°C, HFIP

(b) Determined by differential scanning calorimetry, ΔT = 20°C/min

The thermal stability of the polymers were evaluated by thermogravimetric analysis (TGA) under both air and helium atmospheres. Onset of breakdown in an air atmosphere of the polymers reported here occurred in the 350-400°C (660-750°F) range, approximately 50°C lower than the previously reported FEB polymers (Reference 1). However, onset of breakdown in an inert atmosphere was in most cases not significantly lower. Representative TGA curves are shown in Figures 5 and 6.

The Tg's of the polymers were determined by differential scanning calorimetry and are given in Table I. As was expected, the polymers with higher fluorocarbon ether content generally exhibited lower Tg's. However, the Tg values for several of the polymers (Nos. 6 and 7) may be suspect due to the relatively low molecular weights of the samples. The lowest Tg obtained for a moderate to high molecular weight polymer was -58°C (-72°F) (No. 12). None of the polymers prepared exhibited crystalline melt temperature (Tm).

As in the case of the previously reported FEB polymers (Reference 1), slight deterioration of some of the polymer samples was noted upon prolonged exposure to a water-steam atmosphere. Similarly, a cured FEB polymer sample (No. 1) (compounded, cured, and evaluated by Warren Griffin, AFML/MBE) suffered some loss of mechanical properties after a 14-day exposure at 200°F and 95% humidity. Since components used in the formulation of the gum and the conditions used in the cure may have contributed to the instability of the vulcanizate, follow-on research is planned to incorporate crosslink sites into the polymer backbone. This will facilitate curing under milder conditions and deleterious effects on the base polymer should be minimized or eliminated during curing.

4. CONCLUSIONS

From the results presented in this report, it is concluded that high molecular weight FEB polymers varying in fluorocarbon ether content can be prepared by the polycondensation of fluorocarbon ether bis(o-aminophenol) monomers with fluorocarbon ether diimidate esters under appropriate reaction conditions.

Selection of monomers governed the Tg's of the resultant polymers. The polymers exhibited lower Tg's with increased fluorocarbon ether content, a minimum Tg of -58°C (-72°F) being achieved. Although the thermooxidative stability of these exceptionally low Tg polymers as determined by thermogravimetric analysis in air appears to be approximately 50 degrees lower than earlier higher Tg FEB polymers, potential long-term use at temperatures in excess of 500°F is still envisioned. This data strongly indicates great potential for achieving broader use temperature ranges than those currently available in present state-of-the-art materials. It appears likely that with additional research to improve curability and increase hydrolytic stability the FEB class of polymers will provide candidate materials for broad use temperature range seal applications in advanced Air Force systems.

SECTION III

EXPERIMENTAL

1. PREPARATION OF SOLVENTS AND INTERMEDIATES

Hexafluoroisopropanol obtained from PCR, Inc. or Pierce Chemical Company was dried over magnesium sulfate and redistilled.

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

1,14-Diiodoperfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane and 1,17-diiodoperfluoro-3,6,9,15-tetraoxaheptadecane were obtained from PCR, Inc. under Air Force contracts F33615-70-C-1403 and F33615-73-C-5042 (Reference 5).

2. PREPARATION OF MONOMERS

Dimethyl perfluoro-3,6-dioxaundecanediimidate was obtained in 99 + % purity from PCR, Inc. under Air Force contract F33615-70-C-1403 (Reference 5).

The other fluorocarbon ether diimidate ester monomers were obtained from Dr. C. Tamborski, AFML/MBP (Reference 3).

1,11-Bis(3-amino-4-hydroxyphenyl)perfluoro-3,9-dioxaundecane had been synthesized in an earlier phase of the current effort (Reference 1).

a. 1,14-Bis(3-amino-4-hydroxyphenyl)perfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane

To a solution of 4-iodophenyl acetate (7.86 g, 0.030 mole) and 1,14-diiodoperfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane (9.20 g, 0.010 mole) in 45 ml of N,N-dimethylformamide was added copper bronze (5.08 g, 0.080 g atom). This slurry was stirred under nitrogen at 115-117°C for 96 hours. The cooled reaction mixture was added to a stirred mixture of 150 ml of ether and 200 ml of water. The cuprous salts and excess copper were filtered off and the ether layer was washed repeatedly with water until free of the reaction solvent. The ethereal solution was evaporated to dryness to give a brown oil which was refluxed in 20 ml of acetic anhydride for 15 minutes. The excess acetic anhydride was distilled off and the residue was distilled under reduced pressure to give 3.40 g of 1,14-bis(4-acetoxyphenyl)-perfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane, b.p. 180-185°C/0.30 mm. This water-white oil was refluxed for an hour in a solution of 10 ml of concentrated hydrochloric acid in 100 ml of methanol. The solvent was evaporated under reduced pressure and the resultant tan oil was taken up in 600 ml of hexane. This solution was treated with charcoal, filtered, and reduced in volume to give 2.69 g (32% yield) of 1,14-bis(4-hydroxyphenyl) perfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane as a viscous water-white oil.

Analysis: Calc'd: C, 33.90; H, 1.19.
Found: C, 34.37; H, 1.42.

Molecular Weight (mass spectroscopy): Calc'd: 850. Found: 850.

To a solution of 1,14-bis(4-hydroxyphenyl)perfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane (2.60 g, 0.0030 mole) in 30 ml of glacial acetic acid was added 2.60 ml of concentrated nitric acid. The pale yellow solution was stirred at 43-45°C for four hours with care being taken to control any initial exotherms. The solution took on a deep red color which faded to pale orange as the reaction progressed to completion. The cooled reaction mixture was added to 200 ml of ice water and the product extracted twice with 250 ml portions of ether. The combined ether solutions were washed repeatedly with water and finally with dilute sodium bicarbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate and then reduced in volume to a viscous residue which was taken up in hot heptane. Distillation yielded 2.05 g (73% yield) of 1,14-bis(3-nitro-4-hydroxyphenyl)perfluoro-5,10-dimethyl-3,6,9,12-tetraoxatetradecane as a pale yellow oil, b.p. 180-184°C/0.15 mm.

Analysis: Calc'd: C, 30.59; H, 1.07; N, 2.97.

Found: C, 30.51; H, 0.89; N, 2.80.

Molecular Weight (mass spectroscopy): Calc'd: 940. Found: 940.

A solution of 1,14-bis(3-nitro-4-hydroxyphenyl)perfluoro-5, 10-dimethyl-3,6,9,12-tetraoxatetradecane (1.80 g, 0.0020 mole) in 150 ml of methanol was deoxygenated by passing nitrogen through the boiling solution for 15 minutes. Concentrated hydrochloric acid (10 ml) and 10% Pd/C(0.20 g) were added to the cooled solution and the catalytic reduction was run at room temperature and 50 psi of hydrogen for six hours. The catalyst was filtered off and the water-white residue was slurried in a water-ether mixture. After careful neutralization with solid sodium bicarbonate, the product dissolved in the ether layer which was washed several times with water, dried over magnesium sulfate and evaporated to dryness. The soluble portion of the residue was taken up in 1800 ml of boiling hexane, the solution treated with charcoal and reduced in volume to 600 ml to give upon cooling 0.92 g (50% yield) of slightly off-white product, m.p., 55-58°C.

Analysis: Calc'd: C, 32.75; H, 1.37; N, 3.18.

Found: C, 33.09; H, 1.49; N, 3.01.

Molecular Weight (mass spectroscopy): Calc'd: 880. Found: 880.

b. 1,17-Bis(3-amino-4-hydroxyphenyl)perfluoro-3,6,9,15-tetraoxaheptadecane

4-Iodophenyl acetate (7.86 g, 0.030 mole), 1,17-diiodoperfluoro-3,6,9,15-tetraoxaheptadecane (9.68 g, 0.010 mole), and copper bronze (5.08 g, 0.080 g atom) were stirred together under nitrogen at 113-117°C for 48 hours. The cooled reaction was added to 200 ml of ether. The cuprous salts and excess copper were filtered off and washed on the frit with ether. The ethereal solution was washed several times with water to remove the reaction solvent, dried over anhydrous magnesium sulfate, and reduced in volume under reduced pressure to yield a brown oil. The oil was refluxed with 10 ml of acetic anhydride for 20 minutes and the excess acetic anhydride then distilled off under reduced pressure. Distillation of the residue yielded 4.53 g of 1,17-bis(4-acetoxyphenyl) perfluoro-3,6,9,15-tetraoxaheptadecane, b.p. 184-189°C/0.10 mm.

The diacetate ester was hydrolyzed by refluxing for 30 minutes in a solution of 5 ml of concentrated hydrochloric acid in 100 ml of methanol. The solution was reduced in volume under reduced pressure to give a light tan oil which was taken up in 250 ml of hexane. Treatment of the solution with charcoal, followed by removal of the hexane under reduced pressure yielded 3.93 g (39% yield) of 1,17-bis(4-hydroxyphenyl)perfluoro-3,6,9,15-tetraoxaheptadecane as a bright yellow oil.

Analysis: Calc'd: C, 33.35; H, 1.12.
Found: C, 33.17; H, 1.66.

Molecular Weight (mass spectroscopy): Calc'd: 900. Found: 900.

A stirred solution of 1,17-bis(4-hydroxyphenyl)perfluoro-3,6,9,15-tetraoxaheptadecane (3.90 g, 0.0039 mole) in 50 ml of glacial acetic acid was treated at room temperature with 3.70 ml of concentrated nitric acid. The pale yellow solution was stirred at 43-45°C for five hours with care being taken to control any initial exotherms. The solution took on a deep red color which faded to yellow as the reaction progressed to completion. The cooled reaction mixture was added to 250 ml of ice water and the product extracted several times with 200 ml of ether. The combined ether solutions were washed several times with 200 ml portions of water and then with dilute sodium bicarbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate and reduced in volume to a viscous oil which was taken up in hot hexane. Distillation yielded 3.10 g (79% yield) of 1,17-bis(3-nitro-4-hydroxyphenyl)perfluoro-3,6,9,15-tetraoxaheptadecane as a pale yellow oil, b.p. 190-192°C/0.10 mm.

Analysis: Calc'd: C, 30.32; H, 0.82; N, 2.83.
Found: C, 30.75; H, 0.85; N, 2.72.

Molecular Weight (mass spectroscopy): Calc'd: 990. Found: 990.

1,17-Bis(3-nitro-4-hydroxyphenyl)perfluoro-3,6,9,15-tetraoxaheptadecane (3.00 g, 0.0030 mole) was dissolved in 180 ml of methanol and the solution deoxygenated by passing nitrogen through the boiling solution for 15 minutes. Concentrated hydrochloric acid (20 ml) and 10% Pd/C (0.30 g) were cautiously added to the cooled solution and catalytic reduction to the desired product took place overnight at 50 psi of hydrogen. The catalyst was filtered off and the clear white solution evaporated to dryness under reduced pressure to yield the slightly off-white dihydrochloride salt. It was stirred vigorously in a water-ether mixture which was treated carefully with solid sodium bicarbonate. The ether layer was washed several times with water, dried over magnesium sulfate, and evaporated to dryness. The residue was recrystallized twice from approximately 1400 ml of heptane (charcoal) to yield 1.41 g (50% yield) of slightly off-white product, m.p. 92-95°C.

Analysis: Calc'd: C, 32.28; H, 1.30; N, 3.01.
Found: C, 32.82; H, 1.59; N, 3.13.

Molecular Weight (mass spectroscopy): Calc'd: 930. Found: 930.

3. PREPARATION OF POLYMERS

Typical preparative techniques for the polymers are as follows:

a. [Poly 2,5-benzoxazolediyl(tetrafluoroethylene)oxy(decafluoropentamethylene)oxy(tetrafluoroethylene)-5,2-benzoxazolediyl(octafluorotetramethylene)oxy(octafluorotetramethylene)oxy(octafluorotetramethylene)] (No. 1)

To a mixture of dimethyl perfluoro-6,11-dioxahexadecane diimidate (0.748 g, 0.0010 mole) and 1,11-bis(3-amino-4-hydroxyphenyl)perfluoro-3,9-dioxaundecane (0.698 g, 0.0010 mole) was added 5 ml of redistilled hexafluoroisopropanol. Glacial acetic acid (0.25 g, 0.0041 mole) was added with stirring to the resultant clear amber solution. The polycondensation reaction was allowed to proceed for 13 days at 50-55°C at which time the viscous solution was poured into 300 ml of methanol. The precipitated gum was washed several times with methanol and then taken up in 15 ml of Freon 113. The filtered solution was added to 250 ml of methanol and the product dried at 100°C (0.01 mm Hg) for 16 hours to yield 1.05 g (77% yield) of light amber polymer (inherent viscosity = 0.40 in HFIP at 25°C).

Analysis:	Calc'd:	C, 31.18;	H, 0.44;	N, 2.08.
	Found:	C, 31.59;	H, 0.68;	N, 2.04.

b. [Poly 5,2-benzoxazolediyl(difluoromethylene)oxy(tetrafluoroethylene oxy(octafluorotetramethylene)-2,5-benzoxazolediyl(tetrafluoroethylene)oxy (decafluoropentamethylene)oxy(tetrafluoroethylene)oxy(tetrafluoroethylene) oxy(tetrafluoroethylene)] (No. 11)

Dimethyl perfluoro-3,6-dioxaundecane diimidate (0.249 g, 0.00050 mole) and 1,17-bis(3-amino-4-hydroxyphenyl)perfluoro-3,6,9,15-tetraoxaheptadecane (0.465 g, 0.00050 mole) were dissolved in 3 ml of redistilled hexafluoroisopropanol. Glacial acetic acid was added to the clear, pale yellow solution and the reaction was run at 50-55°C for eight days. The resultant viscous solution was slowly added to 150 ml of cold methanol (-78°C) and the precipitated polymer was washed several times with cold methanol. The polymer was redissolved in 5 ml of Freon 113, the solution filtered, and the polymer reprecipitated in cold methanol. Several washings with methanol followed by drying at 180°C (0.05 mm Hg) gave 0.45 g (68% yield) of light amber polymer (inherent viscosity = 0.47 in HFIP at 25°C).

Analysis:	Calc'd:	C, 30.70;	H, 0.45;	N, 2.10.
	Found:	C, 30.80;	H, 0.41;	N, 2.17.

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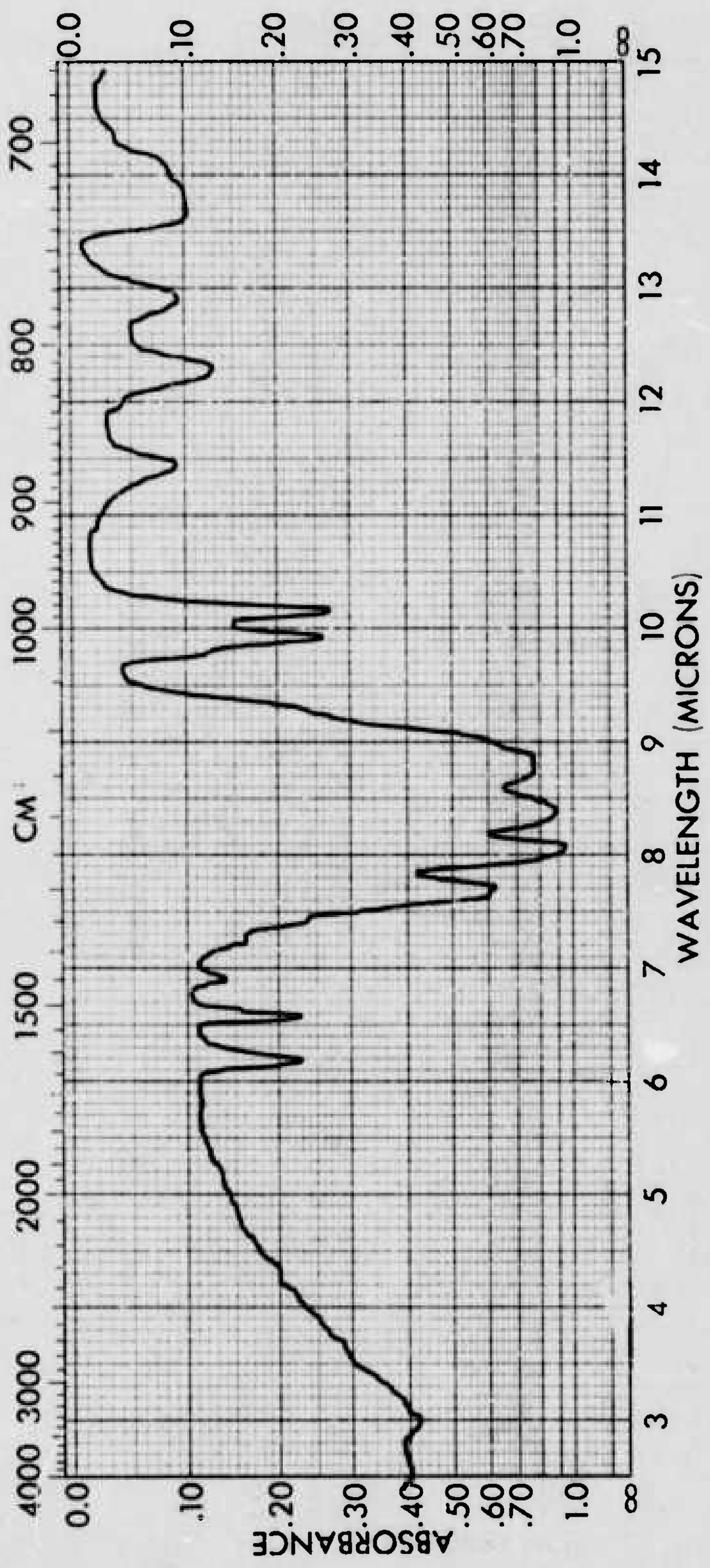

Figure 1. Infrared Spectrum of Monomer II (KBr Pellet)

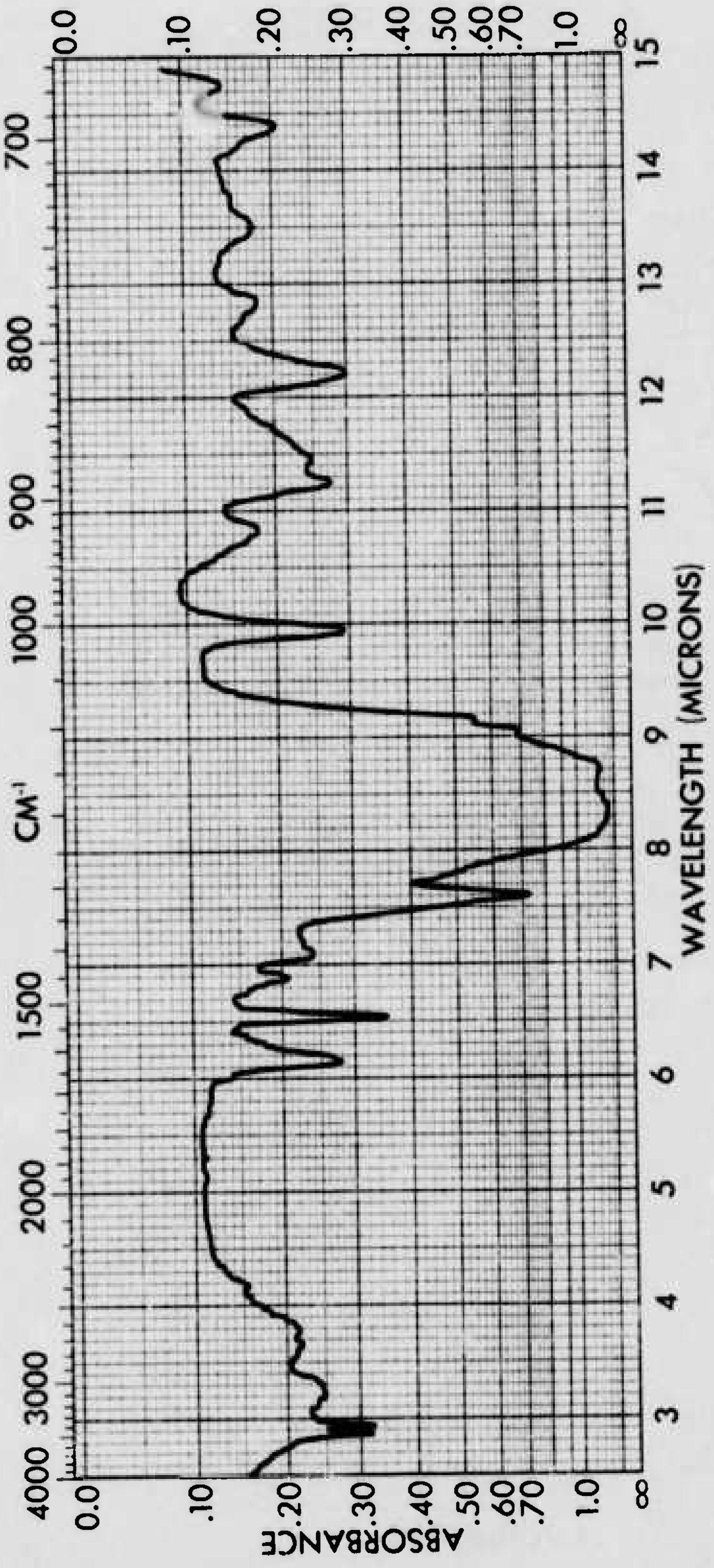

Figure 2. Infrared Spectrum of Monomer III (KBr Pellet)

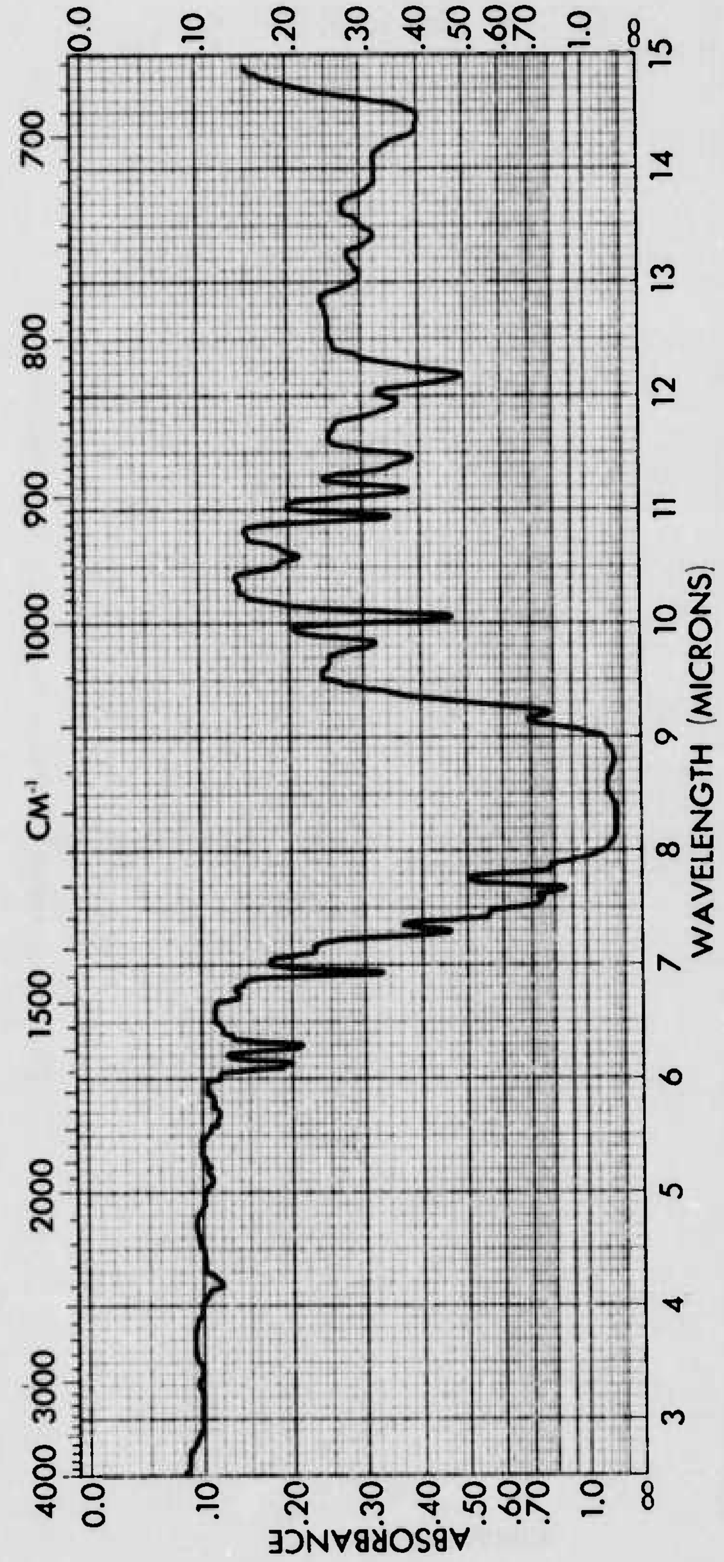

Figure 3. Infrared Spectrum of Polymer (No. 11) (Film)

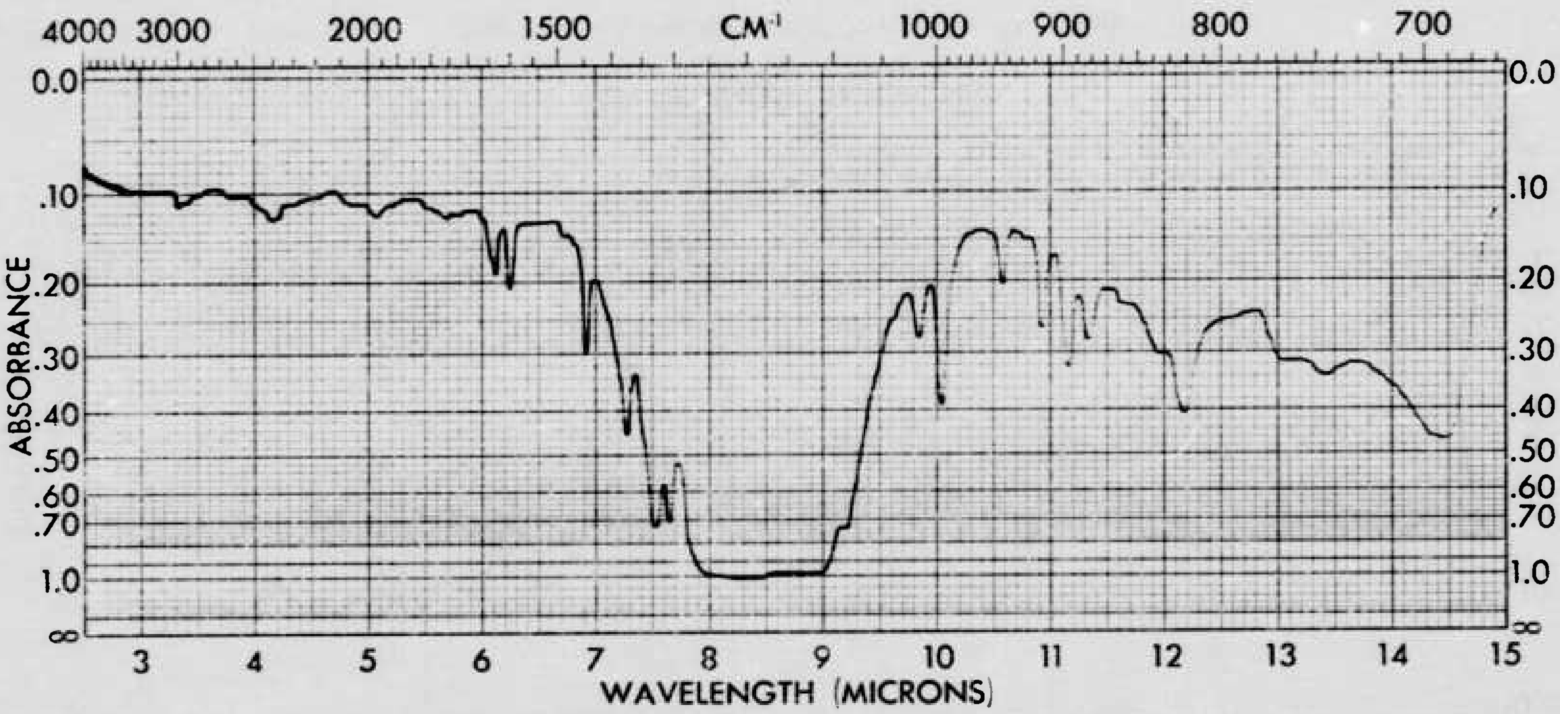

Figure 4. Infrared Spectrum of Polymer (No. 12) (Film)

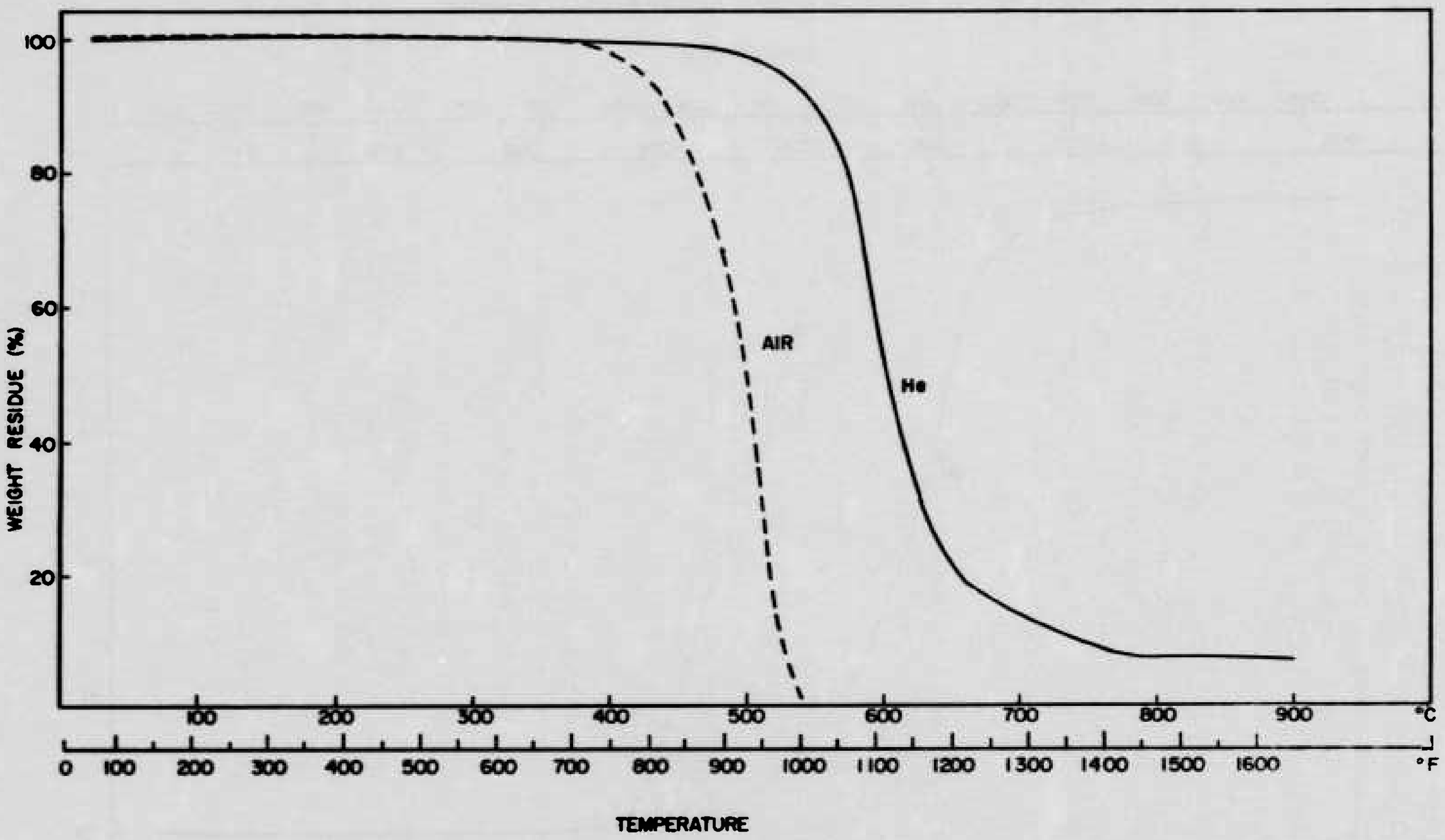

Figure 5. TGA Curve of Polymer (No. 11) in Air and in Helium (ΔT = 3°C/Min)

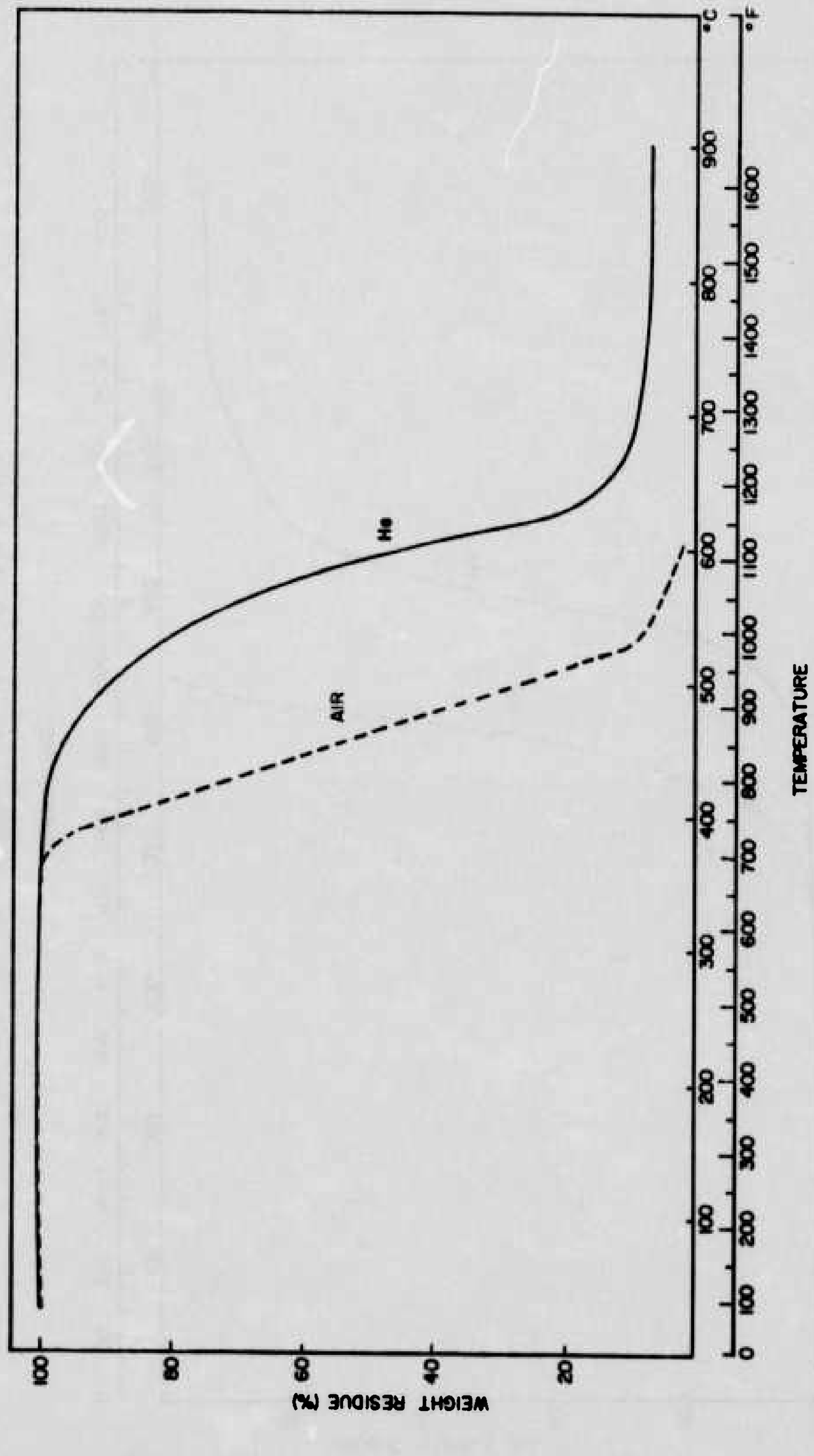

Figure 6. TGA Curve of Polymer (No. 12) in Air and in Helium (ΔT = 3°C/Min)

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