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HIGH TEMPERATURE REACTIVE THERMOPLASTIC AROMATIC POLYIMIDES

B. A. Reinhardt
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Polymer Branch
Nonmetallic Materials Division

April 1980

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Final Report for Period October 1978 - December 1979

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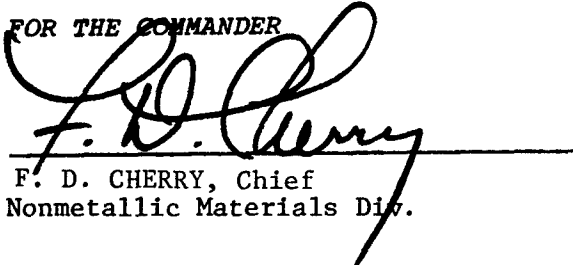


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A series of high molecular weight aromatic enyne polyimides were prepared by the condensation of various aromatic dianhydrides with (E)-33'-(1-buten-3-ynylene) dianiline (I). The polymers were soluble in low boiling solvents and exhibited intrinsic viscosities as high as 0.7 with glass transition temperatures ranging from 200°-265°C. The new thermoplastic materials have the capability to become lightly crosslinked when thermally treated during a stimulated high temperature thermoforming process. Thermal treatment diminishes the various solvent-induced problems inherent in linear polymeric materials, as		

20. ABSTRACT (Continued)

well as advances the glass transition temperature. Copolymers were also prepared using 1,3-bis(amino-phenoxy) benzene and (I) in an effort to obtain various percentages of enyne along the polymer backbone and therefore control the degree of crosslinking. Selected copolymer compositions are currently being evaluated as thermoplastic composite materials with improved solvent resistance.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFML Project Scientist. Co-authors were Mr. B. A. Reinhardt and Dr. F. E. Arnold, Materials Laboratory, (AFWAL/MLBP).

This report covers research conducted from October 1978 to December 1979.

The authors wish to thank Mr. E. J. Soloski for the determination of glass transition temperatures and isothermal aging studies of the polymer, as well as, Dr. E. G. Jones for mass spectra TGA analysis.

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SECTION I

INTRODUCTION

Thermoplastic matrix resins have attracted increased interest in recent years for use in fiber-reinforced composites. Thermoplastic processing techniques offer the possibility of reduced costs when compared to processing techniques used for conventional resin matrices. A major problem associated with thermoplastic composites is the high temperature which is required for processing. Temperatures in excess of 200-300°F above the glass transition temperature of the thermoplastic material are usually required to sufficiently decrease the bulk viscosity for the thermoforming process. The problem is compounded when the use temperature of the composite is extended since such higher use temperatures require thermoplastics with higher glass transition temperatures and consequently higher fabrication temperatures. The disadvantages of using very high processing temperatures (800-1000°F) include the unfavorable economics of high temperature tooling and the danger of thermal degradation of the polymer during fabrication. The use of thermoplastic resins as structural material in aircraft is also limited by the very low solvent creep and craze resistance exhibited by linear polymeric systems. Solvents normally found on aircraft or air fields such as hydraulic fluids, brake fluids, paint strippers, and the like, are potential hazards to such systems.

From the above considerations it is evident that the ideal thermoplastic matrix material meet certain requirements. Thus, the material should be one having a low glass transition temperature for favorable processing, and during fabrication its glass transition should increase so as to extend its use temperature. The thermoplastic material should also have the capability to become lightly crosslinked when thermally treated during fabrication so as to diminish the various solvent-induced problems inherent in linear materials.

A class of materials possessing the above properties were the enyne polysulfones previously synthesized in this laboratory (Reference 1). Initially it was postulated that the enyne linkage when placed in a high

molecular weight polymer backbone would thermally undergo an Intramolecular cycloaddition (IMC) type cure to form a phenyl naphthalene type structure. When films of high molecular weight enyne polysulfone polymers were heated at 600°F (315.6°C) for six hours under nitrogen they became brittle and insoluble indicating a facile interchain crosslinking reaction had occurred.

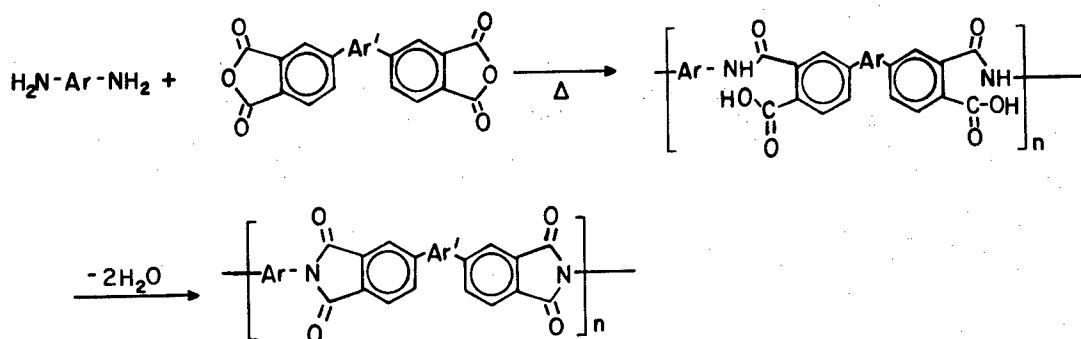
Composites formed from enyne polysulfone copolymers cured at 600°F showed improved solvent resistance to solvents at room and at elevated temperatures when compared to commercially available polysulfone polymers (Reference 2).

The objective of the current work was to extend the investigation of solvent-resistant thermoplastic materials by synthesizing a high molecular weight, soluble enyne polyimide copolymer with a glass transition temperature low enough to make thermal processing feasible. It was postulated that such a polymer could be thermally processed into laminates with increased solvent resistance.

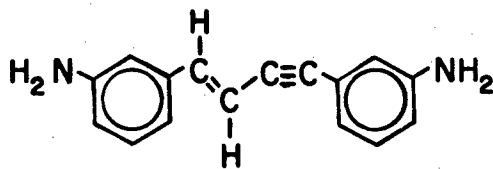
SECTION II

RESULTS AND DISCUSSION

Aromatic polyimide polymers are synthesized by the condensation of an aromatic diamine and an aromatic dianhydride to first form a polyamic acid which is then dehydrated to form the cyclic imide structure.



It was postulated that the enyne linkage could be most easily incorporated into the diamine component of the polymer forming reaction. The initial phase of the current work involved the synthesis of the diamine monomer I.

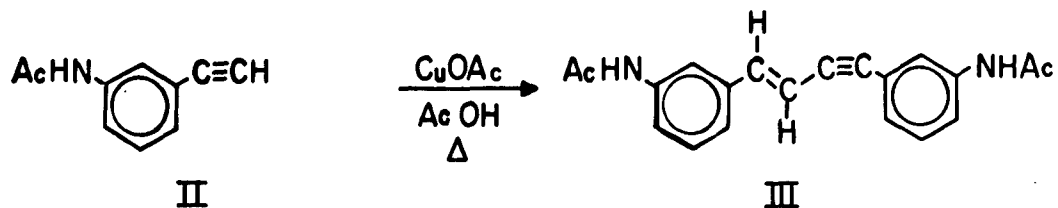


I

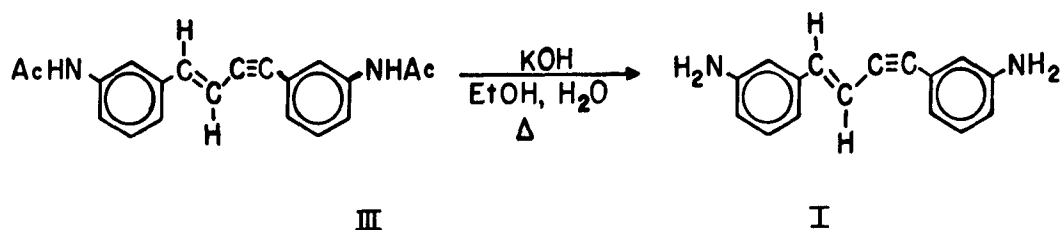
1. SYNTHESIS

A. Monomers

The enyne diamide III was synthesized in 86 percent yield via a Strauss coupling of m-acetamidophenylacetylene (II) using a cuprous acetate catalyst in refluxing acetic acid.

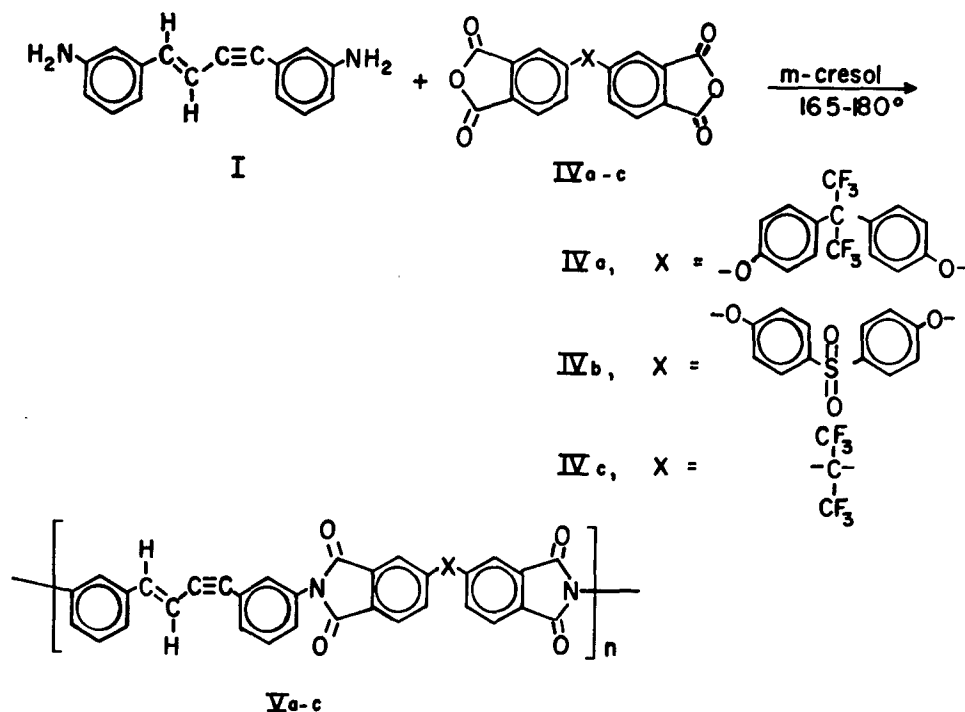


Hydrolysis of III using a 28 percent aqueous ethanolic KOH solution gave a 50 percent yield of the free diamine I.



B. Polymers

The enyne containing polyamides Va-c were prepared by the addition of an aromatic dianhydride IV to a solution of the enyne diamine I in m-cresol at 165° containing a few drops of isoquinoline.



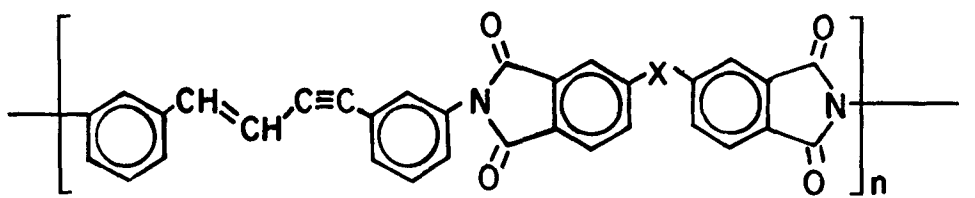
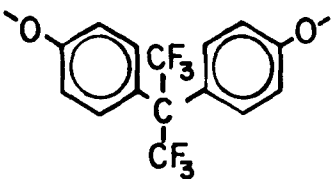
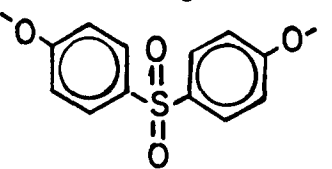
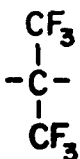
The polymers Va-c after precipitation into methanol were soluble in chloroform or DMAC in concentrations greater than 20 percent and tough, transparent films could be cast from 2 percent solutions of the chloroform soluble polymers. Intrinsic viscosities of the polymers ranged from 0.24 to 0.51 in DMAC at 30°.

The DSC thermogram ($\Delta = 20^\circ\text{C}/\text{min}$) of polymers Va, b show initial base line shifts characteristic of a glass transition at 212° and 243° respectively, an exotherm beginning at approximately 250° and an exotherm maxima between 340-350°C. Polymer Vc showed no base line shift characteristic of a glass transition, with an exotherm onset at 270° and an exotherm maxima at 325°. In all cases, the extrapolated onset of the DSC base line shift was taken as the temperature of either a glass transition or polymerization exotherm. Pelletized samples of the polymers cured for six hours at 265°C for polymer Va and 315°C for polymers Vb and c showed glass transitions close to the cure temperatures. Thermal data for all homopolymers are summarized in Table 1. When film samples of polymers Va-c were heated at 316° under nitrogen for two hours they became brittle and insoluble indicating that a facile interchain reaction was occurring producing a material with a high crosslink density.

C. Copolymers

It had been demonstrated previously with enyne polysulfone polymers (Reference 1) that high molecular weight copolymers could be synthesized which were soluble in common organic solvents, easily processible, and could be lightly crosslinked at high temperatures to afford materials with increased solvent resistance. It was postulated that the same enyne linkage could be incorporated into an imide containing backbone. Aromatic enyne imide copolymers VIIIa-c employing 1,3-bis-(aminophenoxy) benzene VI and 2,2-bis [4-(3,4-dicarboxyphenoxy)phenyl] hexafluoropropane dianhydride (VII) as comonomers with the diamine I were prepared by the reaction scheme illustrated below.

TABLE 1
THERMAL ANALYTICAL AND VISCOSITY DATA FOR
ENYNE POLYIMIDES

					
Polymer	X	(n) ^a	T _g ^b	T _i ^c	T _g cured
<u>V_a</u>		0.51	212	255	245 ^d
<u>V_b</u>		0.24	NONE OBSERVED	265	325 ^d
<u>V_c</u>		0.45	NONE OBSERVED	270	315 ^e

a. Intrinsic viscosity measured in DMAC (0.5%).

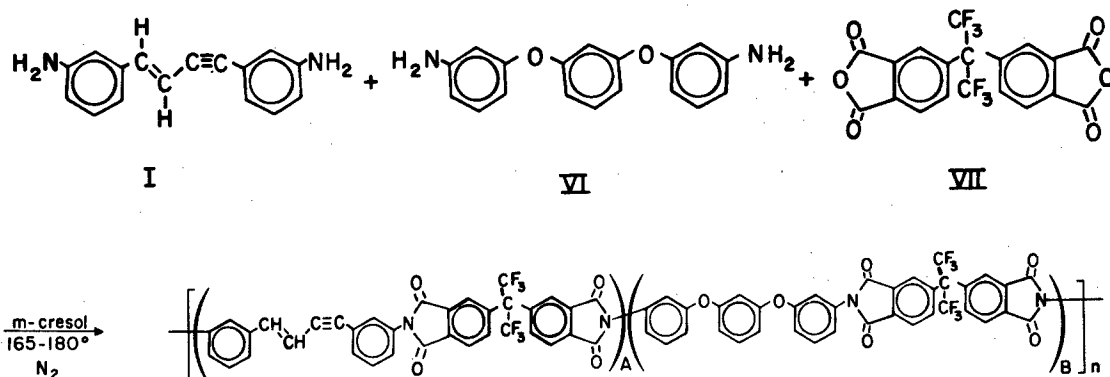
Predicted T_g base on Fox-Flory or Copolymer Equation.

b. Measured by DSC and TMA.

c. Temperature at which curing exotherm begins.

d. T_g measured by DSC and TMA for polymer samples cured at 265°C for six hours.

e. T_g measured by DSC and TMA for polymer samples cured at 316°C (650°F) for six hours.



VIII_a	A=0.25	B=0.75
b	A=0.30	B=0.70
c	A=0.50	B=0.50

The copolymers were isolated by precipitation of the reaction mixtures into methanol. The intrinsic viscosities of the copolymers ranged from 0.42 to 1.42 in DMAC. The solubilities of the copolymers were improved when compared to the homopolymers and tough transparent films could be cast from chloroform of any of the copolymers.

The DSC thermogram of the copolymers showed baseline shifts characteristic of a glass transition between 217° and 253°C with the polymerization exotherm beginning at approximately 270°C (Figure 1). Pelletized samples of the copolymers cured at 316°C (600°F) for six hours under nitrogen showed by DSC and TMA analyses a 40 degree advancement in T_g (Figures 2 and 3) above the T_g of the uncured polymers. Thermal analysis and viscosity data for the copolymers are summarized in Table 2. Film samples of the copolymers when heated under nitrogen at 315.6°C for three hours retained a high degree of flexibility indicative of a decreased crosslink density compared to the higher enyne linkage containing homopolymer. These results are analogous with those obtained in the study of the enyne containing polysulfones where the flexibility of the cured copolymers increased as the amount of enyne content was reduced.

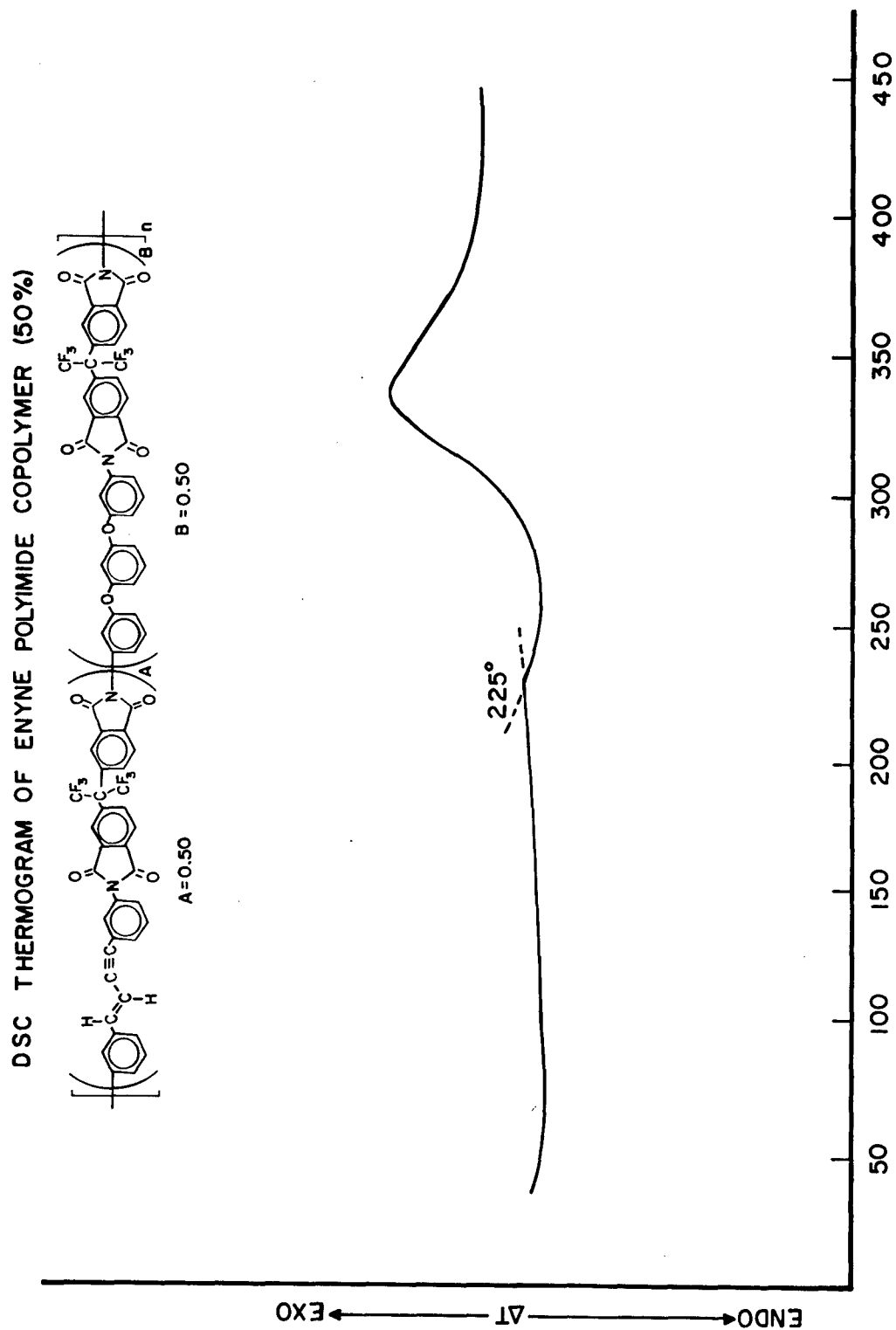


Figure 1. DSC Thermogram of Enyne Polyimide Copolymer (50%)

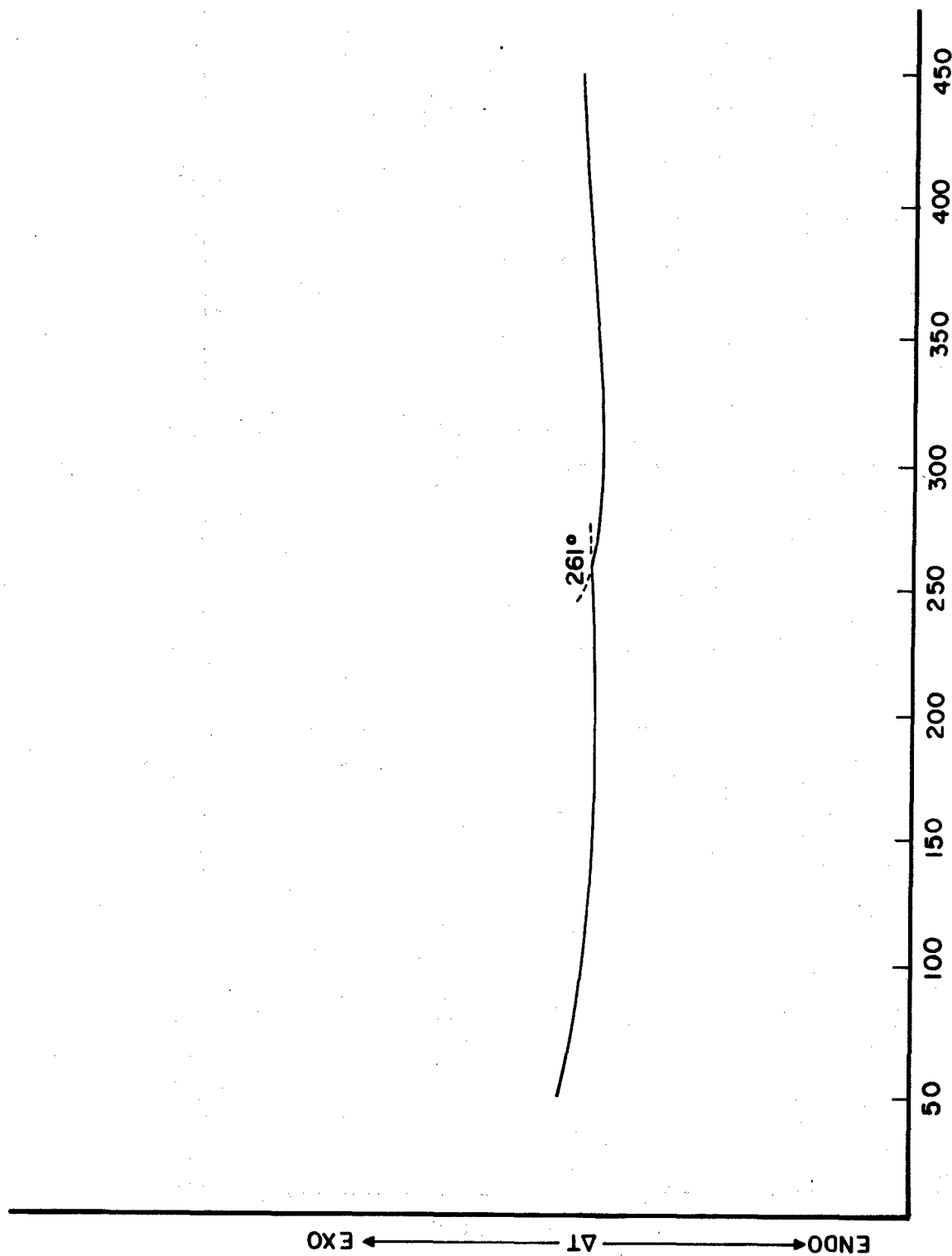


Figure 2. DSC Thermogram of Enyne Polyimide Copolymer (50%) After Curing Six Hours at 315.6°C (600°F) N₂

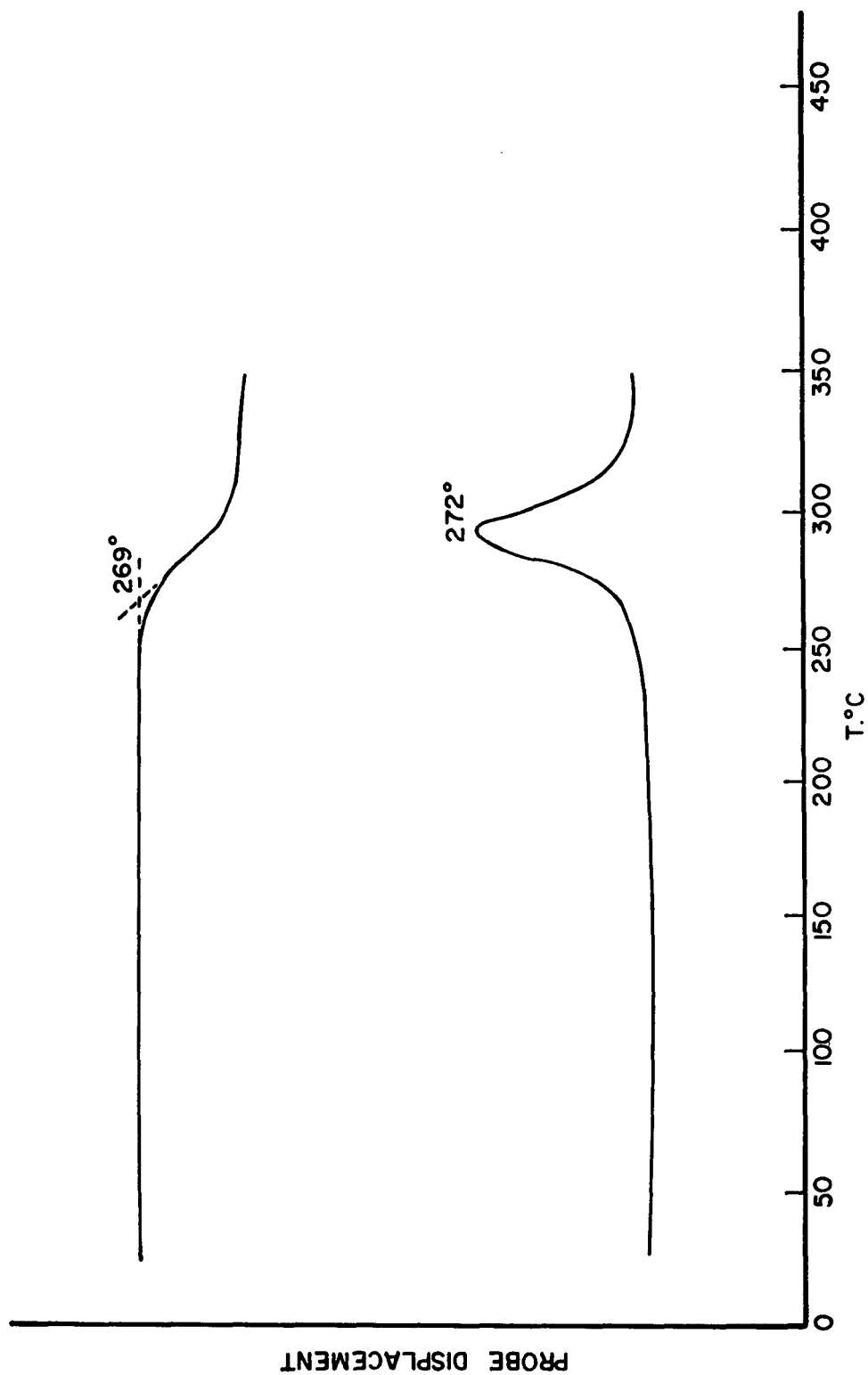
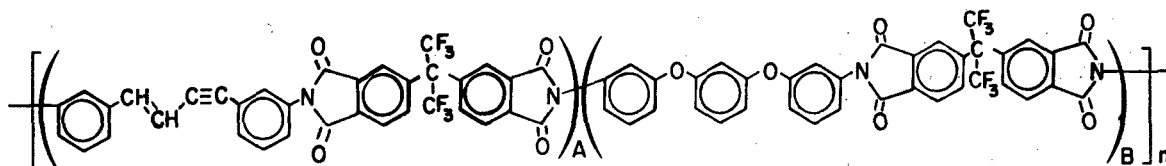


Figure 3. TMA Penetration Curve of Enyne Polyimide Copolymer (50%)
After Curing Six Hours at 315.6°C (600°F) N₂

TABLE 2

THERMAL ANALYTICAL AND VISCOSITY DATA FOR ENYNE POLYIMIDE COPOLYMERS



Polymer	%A	%B	$[\eta]^a$	Tg pred ^b	Tg ^c	Ti ^d	Tg cured ^e	W ^f
Vc	100	0	0.45	418°	observed	270	315	87
VIII a	25	75	0.42	217	208	220	229	89
VIII b	30	70	1.42	227	212	270	236	91
VIII c	50	50	0.70	253	225	270	269	89

- Intrinsic viscosity measured in DMAC (0.5%).
- Predicted Tg base on Fox-Flory or Copolymer Equation.
- Measured by DSC and TMA.
- Temperature at which curing exotherm begins.
- Tg measured by DSC and TMA for polymer samples cured at 316°C (650°F) for six hours.
- Isothermal Aging - weight retained after 200 hours at 315.6°C (600°F).

Isothermal aging studies on copolymer samples containing from 25 to 100 percent enyne at 315.6°C (600°F) in air showed only 5 to 12 percent weight losses after 200 hours (Figure 4). When the temperature of these samples was raised to 343°C (650°F) the samples retained between 60 and 80 percent of their weight after 120 hours (Figure 5).

Isothermal aging studies on samples of homopolymer and a copolymer with an enyne content of 30 percent were carried out in air at 700°F (371°C). These samples showed a weight retention of 10 to 30 percent after 200 hours (Figure 6).

Mass spectra TGA analysis was carried out on polymer VIIIb from room temperature to 900°C using a 4.2°C/minute heating rate. The onset of degradation appears to be at 440°C with the major degradation product being carbon monoxide. The peaks corresponding to maxima in carbon monoxide production at 560°C and 630°C. The second most abundant product is hydrogen fluoride displaying a maxima at 560°C. Other products and their maxima are as follows: HCN (680°C), CO₂ (560° and 610°), and H₂O (560° and 650°). The sample retained 53 percent of its weight during the run to 900°.

Comparison of isothermal and mass spectra TGA studies carried out on enyne polysulfones with those carried out on enyne polyimides indicate that the enyne linkage is much more thermooxidatively stable in enyne polyimides than in enyne polysulfones (Figure 7). The current data indicate that the presence of the enyne linkage in the polysulfone backbone enhances the thermooxidative decomposition of the polymer, reducing the temperature of the onset of degradation by 100° when compared to an aromatic polysulfone of similar structure but with no enyne linkage. In contrast, enyne polyimides show little difference in thermal oxidative stability when compared to their aromatic polyimide analogs containing no enyne linkages.

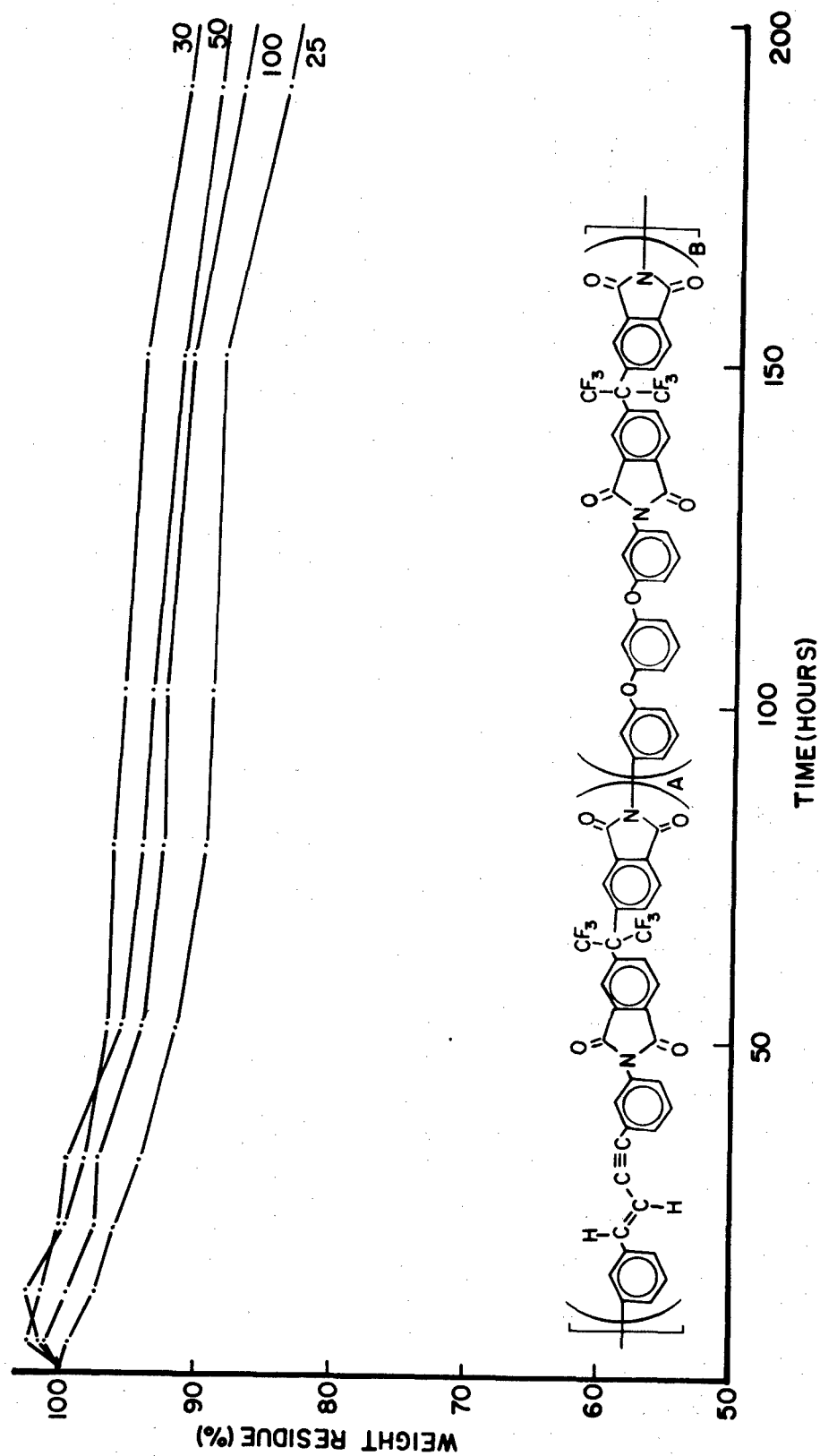


Figure 4. Isothermal Aging Curves for Enyne Polyimide Polymers in Air at 315.6°C (600°F)

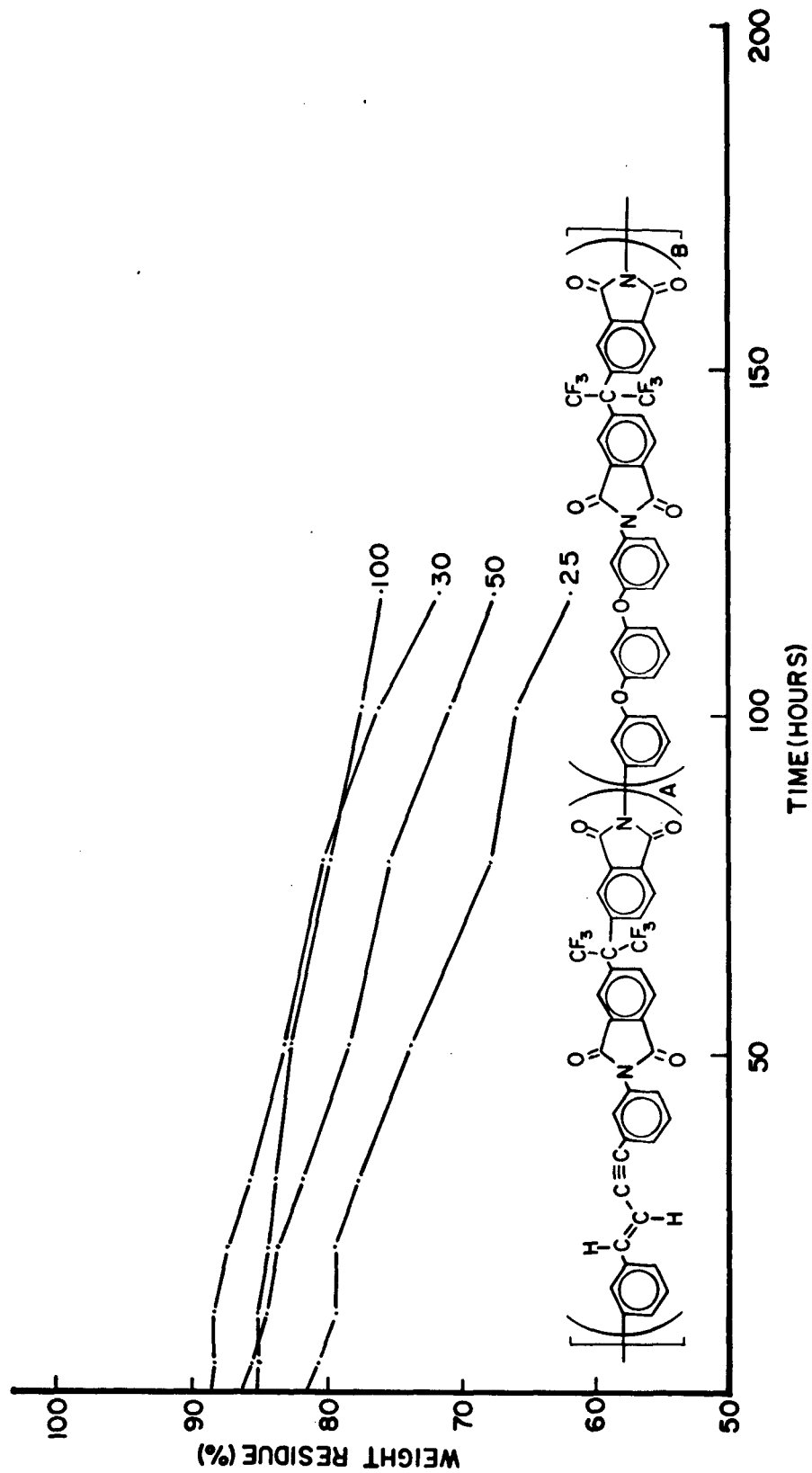


Figure 5. Isothermal Aging Curves for Enyne Polyimide Polymers in Air at 343.3°C (650°F)

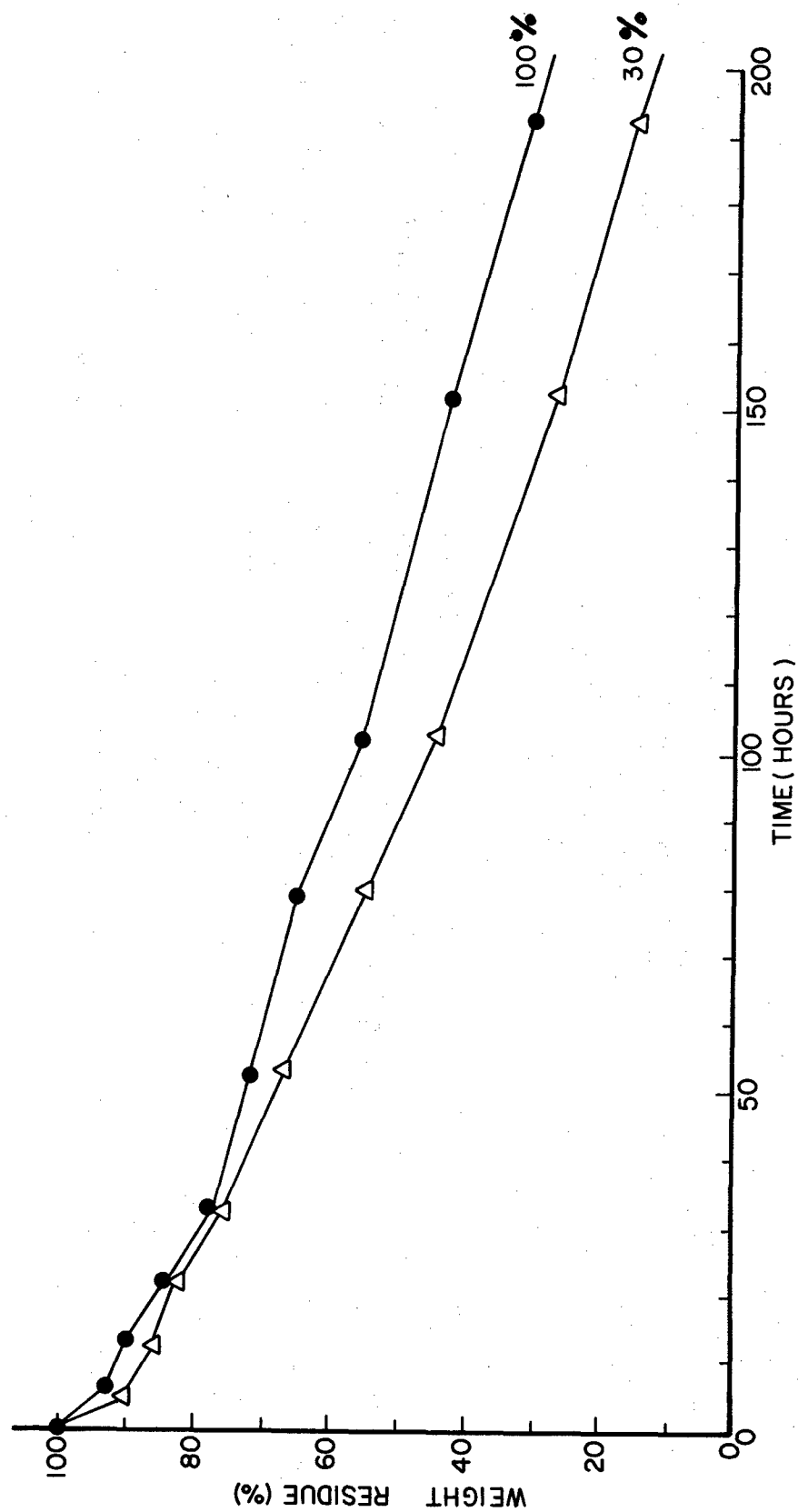
ISOTHERMAL AGING CURVES FOR SELECTED ENYNE POLYIMIDE POLYMERS IN AIR
AT 371°C (700°F).

Figure 6. Isothermal Aging Curves for Selected Enyne Polyimide Polymers in Air at 371°C (700°F)

COMPARISON OF ISOTHERMAL AGING CURVES OF ENYNE POLYIMIDE 50% COPOLYMER
AND ENYNE POLYSULFONE 50% COPOLYMER IN AIR AT 600°F (315.6°C).

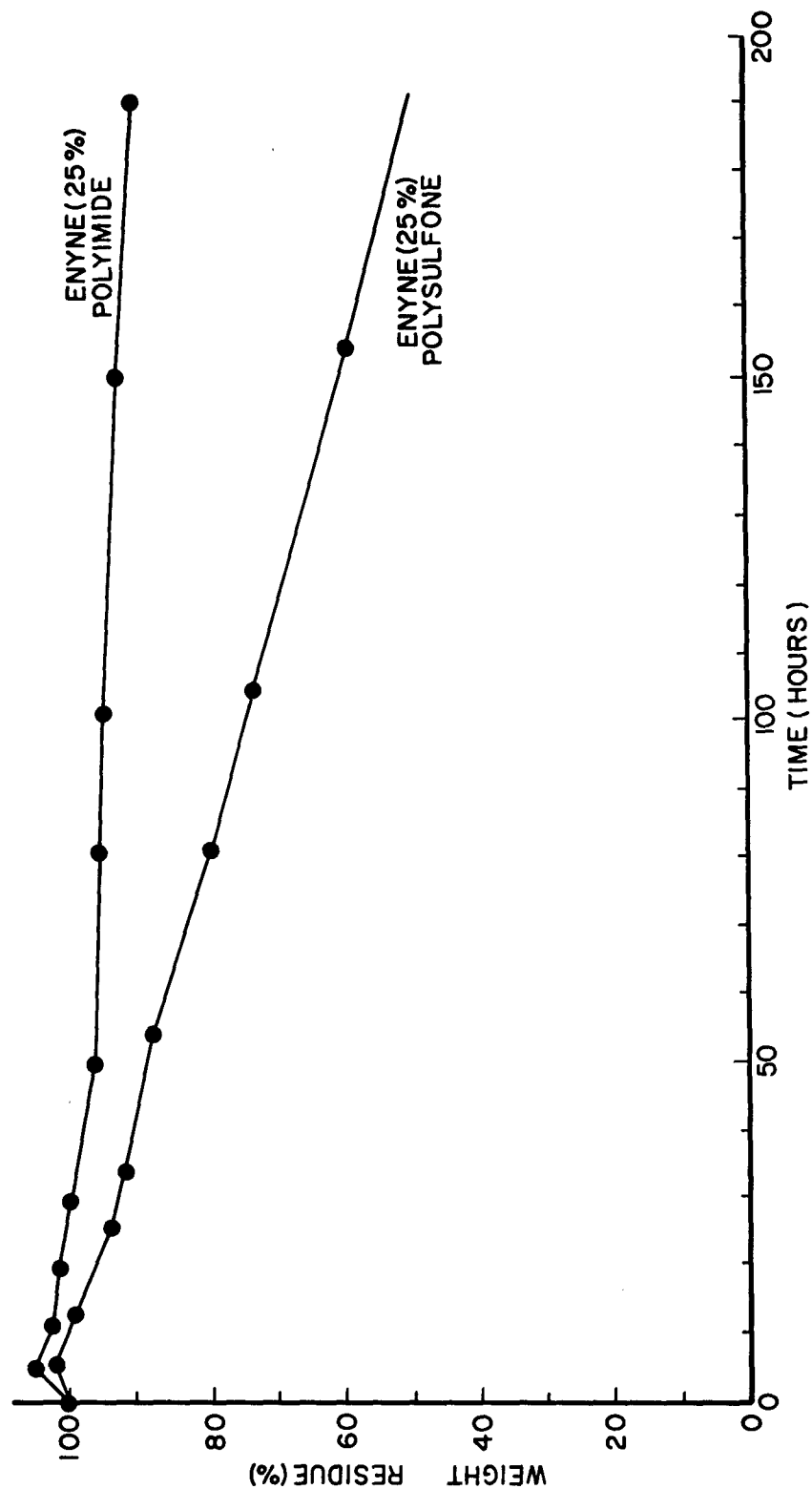


Figure 7. Comparison of Isothermal Aging Curves of Enyne Polyimide (50%) Copolymer and Enyne Polysulfone (50%) Copolymer in Air at 315.6°C (600°F)

2. COPOLYMER SOLVENT RESISTANCE

Films of the 30 percent enyne polyimide copolymer cast from methylene chloride were pressed into resin bars at 93°C and 35 KN. These resin bars, after curing, were tested in a constant stress apparatus (Reference 3) while being exposed to methylethyl ketone solvent. After 1.5 hours at a stress of 3.4 MPa, the samples showed no signs of rupture or crazing. In contrast, when a commercially available thermoplastic polysulfone resin bar was tested at a stress of 3.4 MPa, rupture occurred within one second after contact with methyl-ethyl ketone (Reference 4). Further studies of the solvent resistance properties of enyne polyimide copolymers are now underway.

SECTION III

EXPERIMENTAL

1. MONOMERS

A. 3-Acetamidophenylacetylene (II)

To a 250-ml 3-neck flask fitted with a condenser, nitrogen inlet, outlet and magnetic stirrer was added 150 ml of acetic acid and 35 ml of acetic anhydride. The mixture was heated to reflux under nitrogen and cooled under nitrogen. To the cooled mixture was added 15 g (0.114 mole) of 3-amino-phenylacetylene and the homogeneous solution was refluxed overnight. The cooled reaction mixture was transferred to a 500 ml one-neck flask, and the acetic acid was removed by a rotor-evaporator under high vacuum. Water (200 ml) was added to the residual oil to crystallize the solid product. The material was isolated by filtration and washed with water and then air dried. Recrystallization from carbon tetrachloride with 200 g/10 g solid plus charcoal yielded 14.4 g (79% yield) of a white crystalline product (m.p. 94-96°C)

Analysis calculated for $C_{10}H_9NO$: C, 75.47; H, 5.66; N, 8.81

found : C, 75.12; H, 5.63; N, 8.73

B. (E)-1,4-Bis-(3-acetamidophenyl)-buta-1-ene-3-yne (III)

To 350 ml of deoxygenated acetic acid was added 2.45 g of cuprous acetate whereupon a clear blue solution formed. The solution was brought to reflux, under nitrogen, and 14.35 g (0.09 mole) of 3-acetamidophenyl-acetylene was added as a solid. The reaction mixture was maintained at reflux for 12 hours and cooled to room temperature. Isolation of the material was carried out by precipitation of the reaction mixture into distilled water (2500 ml) and collection by filtration. The light tan material was air dried and recrystallized from isopropanol to give 13.8 g of product (86.6%) (m.p. 234-237°C).

Analysis calculated for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80

found : C, 75.44; H, 5.46; N, 8.49

C. (E)-1,4-Bis-(3-aminophenyl)-buta-1-ene-3-yne (I)

To 50 ml of a 28 percent aqueous ethanol solution was added 2.6 g (.0084 mole) of 1,4-bis-(3-acetamidophenyl)-buta-1-ene-3-yne and the mixture was refluxed for one hour. After cooling to room temperature, the reaction mixture was poured into 300 ml of distilled water and extracted with three 100 ml portions of methylene chloride. Removal of the methylene chloride under reduced pressure provided a light yellow material. Recrystallization of the material from a one-to-one mixture of benzene/hexane gave 1 g (50% yield) of produce (m.p. 105-106°C).

Analysis calculated for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02

found : C, 81.89; H, 5.81

2. POLYMERS AND COPOLYMERS

A. Poly [(E)-(1,3-dioxo-2,5-isoindolinediyl) [oxy-1,4-phenylene-2,2,2-trifluoro-1-(trifluoromethyl) ethylidene]-1,4-phenyleneoxy-(1,3-dioxo-5,2-isoindolinediyl)-1,3-phenylene-1-buten-3-ynylens-1,3-phenylene]] (Va)

a = 1, b = 0

In a dry, 25 ml, 3 necked flask equipped with a magnetic stirring bar, a nitrogen inlet, a short-path distillation apparatus, and a stopper was placed 0.3999 g (1.707 mmol) of (E)-3,3'-(1-buten-3-ynylene) dianiline, 4 ml of freshly distilled m-cresol, and two drops of isoquinoline. After the diamine had dissolved, 1.0727 g (1.707 mmol) of 2,2-bis [4-(3,4-dicarboxyphenoxy) phenyl]-hexafluoropropane dianhydride was added in several portions over a period of 30 minutes. The final portion of dianhydride was washed in with 4 ml of m-cresol and 5 ml of toluene. The reaction mixture was heated slowly to 80°C during which time all solids went into solution. The temperature of the reaction mixture was raised to 140°C at which time the toluene began to distill. After approximately 4 ml of toluene had been distilled, five additional ml of toluene were added and the temperature raised slowly to 165°C for 1-1/2 hours during which time the reaction mixture became very viscous. The reaction mixture was then cooled, diluted with 15 ml of chloroform and precipitated into 1200 ml of rapidly stirring methanol. The resulting white polymer was filtered, air

dried and reprecipitated from chloroform-methanol. After drying at 130°C (0.4 mm Hg) for 18 hours, the polymer had an intrinsic viscosity of 0.51 in dimethylacetamide (DmAc) at 30°C.

Analytical data for the homopolymer and copolymers are summarized in Table 3.

B. Poly [[(E)-(1,3-dioxo-2,5-isoindolinediyl) [oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy]-(1,3-dioxo-5,2-isoindolinediyl)-1,3-phenylene-1-buten-3-ynylene-1,3-phenylene]] (Vb)

a = 1, b = 0

In a 25 ml, 3 necked reaction flask, equipped with a short path distillation apparatus, a magnetic stirring bar, a nitrogen inlet, and a stopper was placed 0.3999 g (1.707 mmol) of (E)-3,3'-(1-buten-3-ynylene) dianiline, 4 ml of m-cresol and two drops of isoquinoline. After the diamine had dissolved, 0.9260 g (1.707 mmol) of 1,4-bis(3,4-dicarboxyphenoxy) diphenyl-sulfonyl dianhydride was added in portions over a period of 30 minutes. The final portion of dianhydride was washed in with 4 ml m-cresol and 5 ml of toluene. The reaction mixture was heated slowly to 80°C during which time all the suspended solids dissolved. The temperature was raised to 140°C at which time toluene began to distill. After approximately 4 ml of toluene were removed, five additional ml of toluene were added and the temperature raised slowly to 165°C during which time almost all the remaining toluene distilled. The temperature was held at 165°C for two hours and then raised to 175°C for one hour. The reaction mixture was cooled, diluted with 5 ml of dimethylformamide (DMF), and precipitated into 1200 ml of rapidly stirring methanol. The white fibrous polymer was filtered, air dried, and reprecipitated from DMF-methanol. After drying at 120°C (0.4 mm Hg) for 18 hours, the polymer had an intrinsic viscosity at 30°C of 0.35 in DmAc.

TABLE 3
ELEMENTAL ANALYSIS FOR ENYNE POLYIMIDE
POLYMERS AND COPOLYMERS

<u>POLYMER</u>	<u>CALCULATED %</u>	<u>FOUND %</u>
Va	C 68.28	67.91
	H 2.93	2.57
	N 3.39	3.23
Vb	C 71.34	71.24
	H 3.27	3.19
	N 3.78	3.54
	S 4.33	5.02
Vc	C 65.61	65.42
	H 2.15	2.51
	N 4.54	4.36
<u>COPOLYMER</u>		
VIIIa	C 63.87	63.60
	H 2.57	2.20
	N 4.08	4.39
VIIIb	C 63.96	62.80
	H 2.57	1.95
	N 4.10	4.43
VIIIc	C 64.34	64.36
	H 2.55	2.19
	N 4.16	4.46

- C. Poly [[(E)-(1,3-dioxo-2,5-isoindolinediyl)[2,2,2-trifluoro-1-(trifluoromethyl) ethylidene] (1,3-dioxo-5, 2-isoindolinediyl)-1,3-phenylene-1-buten-3-ynylene-1,3-phenylene]] (Vc)

$$A = 1, B = 0$$

In a dry, 25 ml, 3 necked flask, equipped with a magnetic stirring bar, a nitrogen inlet, a short-path distillation apparatus, and a stopper was placed 0.3999 g (1.707 mmol) of (E)- 3,3'-(1-buten-3-ynylene) dianiline, 4 ml of freshly distilled m-cresol and two drops of isoquinoline. After the diamine had dissolved, 0.7583 g (1.707 mmol) of 2,2-bis(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride was added in several portions over a period of 30 minutes. The final portion of dianhydride was washed in with 4 ml m-cresol and 5 ml of toluene. The mixture was heated slowly to 80°C during which time all the solids dissolved. The stopper was replaced with an addition funnel and the temperature of the reaction mixture raised to 140°C at which time the toluene began to distill. After approximately 4 ml of toluene were distilled, eight were added and the temperature raised slowly to 175°C during which time almost all the remaining toluene distilled. The temperature was held at 175°C for two hours. The reaction mixture was cooled, diluted with 10 ml of chloroform and precipitated into 1200 ml of rapidly stirring methanol. The white fibrous polymer was filtered, air dried, and reprecipitated from chloroform-methanol. After drying at 130°C (0.4 mm Hg) for 18 hours, the polymer had an intrinsic viscosity at 30°C of 0.42 in DmAc.

3. COPOLYMERS

- A. Poly [[(E)-(1,3-dioxo-2,5-isoindolinediyl) [2,2,2-trifluoro-1-(trifluoromethyl) ethylidene] (1,3-dioxo-5,2-isoindolinediyl)-1,3-phenylene-1-buten-3-ynylene-1,3-phenylene]-co-[1,3-dioxo-2,5-isoindolinediyl) [2,2,2-trifluoro-1-(trifluoromethyl) ethylidene]-(1,3-dioxo-5,2-isoindolinediyl)-1,3-phenyleneoxy-1,3-phenyleneoxy-1,3-phenylene]] (VIIIC)

$$A = .5, B = .5$$

In a dry, 25 ml, 3 necked flask, equipped with a magnetic stirring bar, a short path distillation apparatus, a nitrogen inlet, and a stopper was placed 0.2000 g (0.8535 mmol) of (E)-3,3'-(1-buten-3-ynylene) dianiline, 0.2495 g (0.8534 mmol) of 1,3-bis-aminophenoxybenzene, 6 ml of m-cresol

and two drops of isoquinoline. After both diamines had dissolved, 0.7853 g (1.707 mmol) of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride was added in several portions over a period of 30 minutes. The final portion of dianhydride was washed in with 4 ml of m-cresol and 5 ml of toluene. The mixture was heated slowly to 80°C during which time all the solids dissolved. The temperature of the reaction mixture was raised to 140°C at which time the toluene began to distill. After approximately 4 ml of toluene were distilled, eight additional ml of toluene were added and the temperature raised slowly to 175°C during which time almost all the remaining toluene distilled. The temperature was held at 180°C for two hours. The reaction mixture was cooled, diluted with 12 ml of chloroform and precipitated into 1200 ml of rapidly stirring methanol. The white fibrous polymer additional ml of toluene were added and the temperature raised slowly to 165°C during which time almost all the remaining toluene distilled. The temperature was held at 165°C for two hours. The reaction mixture was cooled, diluted with 10 ml of chloroform and precipitated into 1200 ml of rapidly stirring methanol. The white fibrous polymer was filtered, air dried and reprecipitated from chloroform-methanol. After drying at 120°C (0.4 mm Hg) overnight, the polymer had an intrinsic viscosity at 30°C of 0.45 in DmAc.

- B. Poly [[(E)-(1,3,dioxo-5,2-isoindolinediyl) [2,2,2,-trifluoro-1-(trifluoromethyl)ethylidene] (1,3,-dioxo-5,2-isoindolinediyl)-1,3-phenylene-1-buten-3-ynylene-1,3-phenylene]-co-[1,3-dioxo-2,5-isoindolinediyl) [2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-(1,3-dioxo-5,2-isoindolinediyl)-1,3-phenyleneoxy-1,3-phenyleneoxy-1,3-phenylene]] (VIIIa)

$$A = .25, \quad B = .75$$

In a dry, 25 ml, 3 necked flask, equipped with a magnetic stirring bar, a nitrogen inlet, a short-path distillation apparatus, and a stopper was placed 1.1998 g (5.121 mmol) of (E)-3,3'-(1-buten-3-ynylene) dianiline, 3.4931 g (11.949 mmol) of 1,3-bis-amino-phenoxybenzene, 6 ml of freshly distilled m-cresol and two drops of isoquinoline. After both diamines had dissolved, 7.5832 g (17.070 mmol) of 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride was added in several portions over a period of 30 minutes. The final portion of dianhydride was washed in

with 4 ml of m-cresol and 5 ml of toluene. The mixture was heated slowly to 80°C during which time all solids dissolved. The stopper was replaced with an addition funnel and the temperature of the reaction mixture raised to 140°C at which time the toluene began to distill. After approximately 4 ml of toluene were distilled, five additional ml of toluene were added and the temperature raised slowly to 175°C during which time almost all the remaining toluene distilled. The temperature was held at 175°C for two hours. The reaction mixture was cooled, diluted with 10 ml of chloroform and precipitated into 1200 ml of rapidly stirring methanol. The white fibrous polymer was filtered, air dried and reprecipitated from chloroform-methanol. After drying at 130°C (0.4 mm Hg) for 18 hours, the polymer had an intrinsic viscosity at 30°C of 1.42 in DmAc.

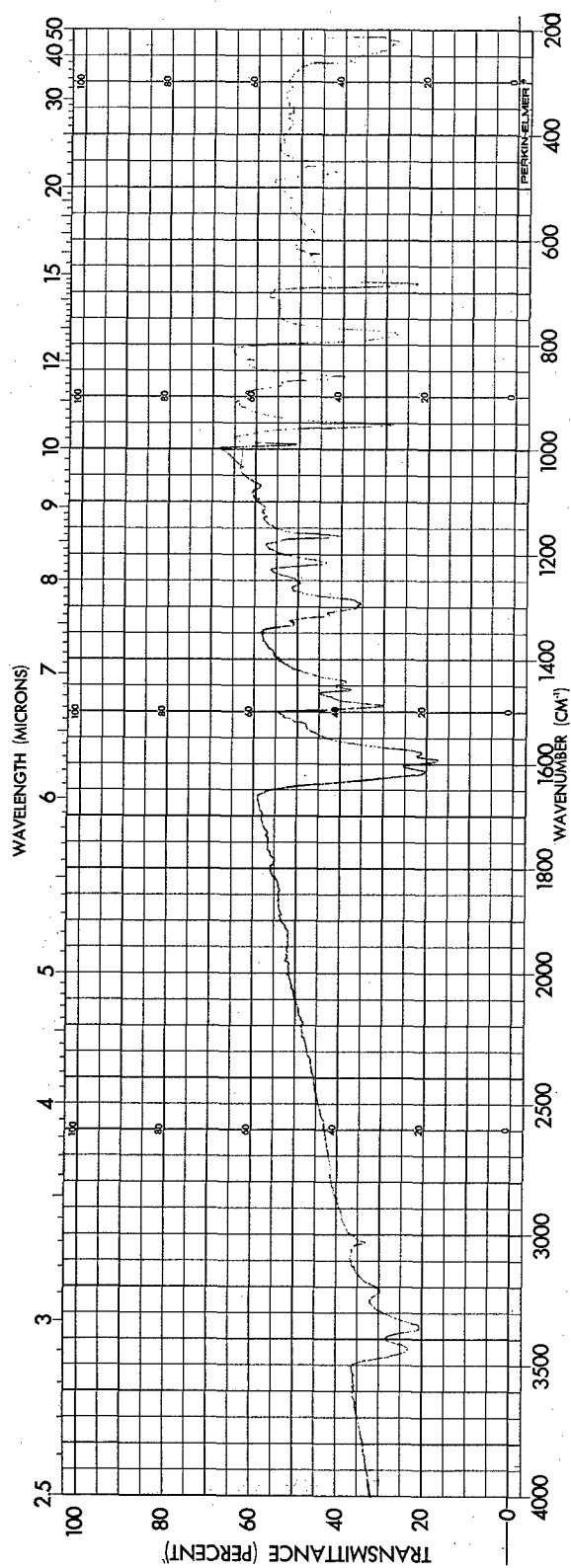


Figure 8. IR Spectrum of Enyne Diamine Monomer (I)

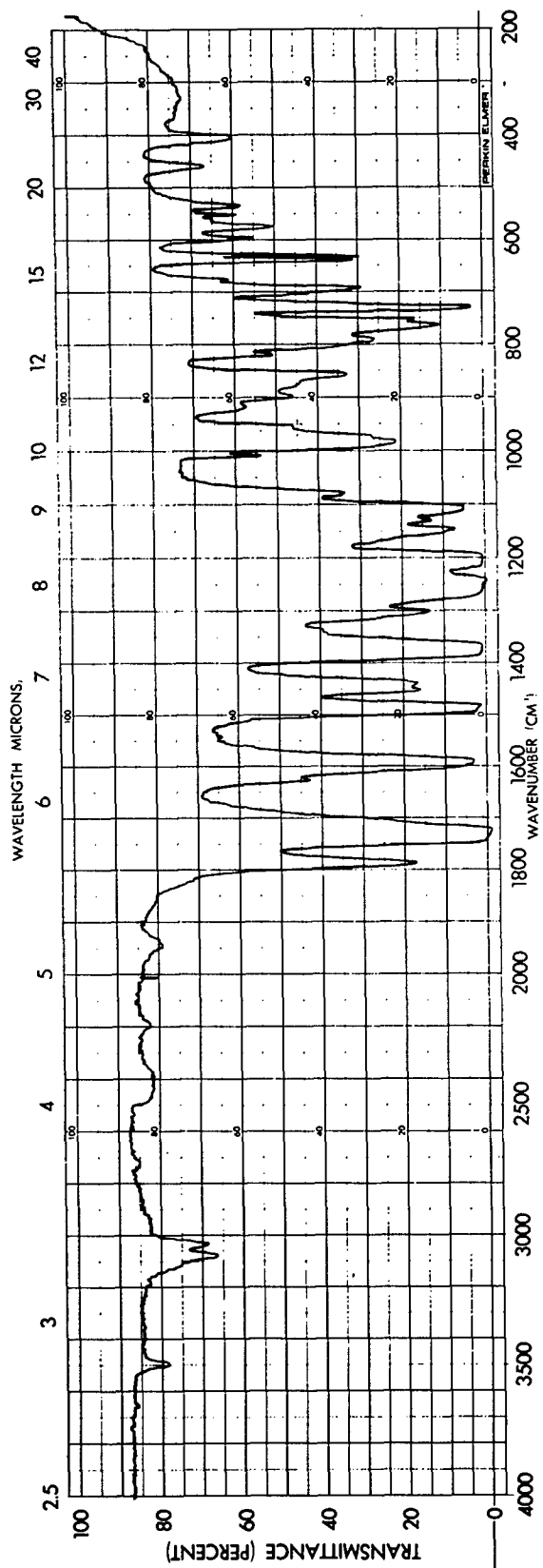


Figure 9. IR Spectrum of Enyne (25%) Copolymer VIIa

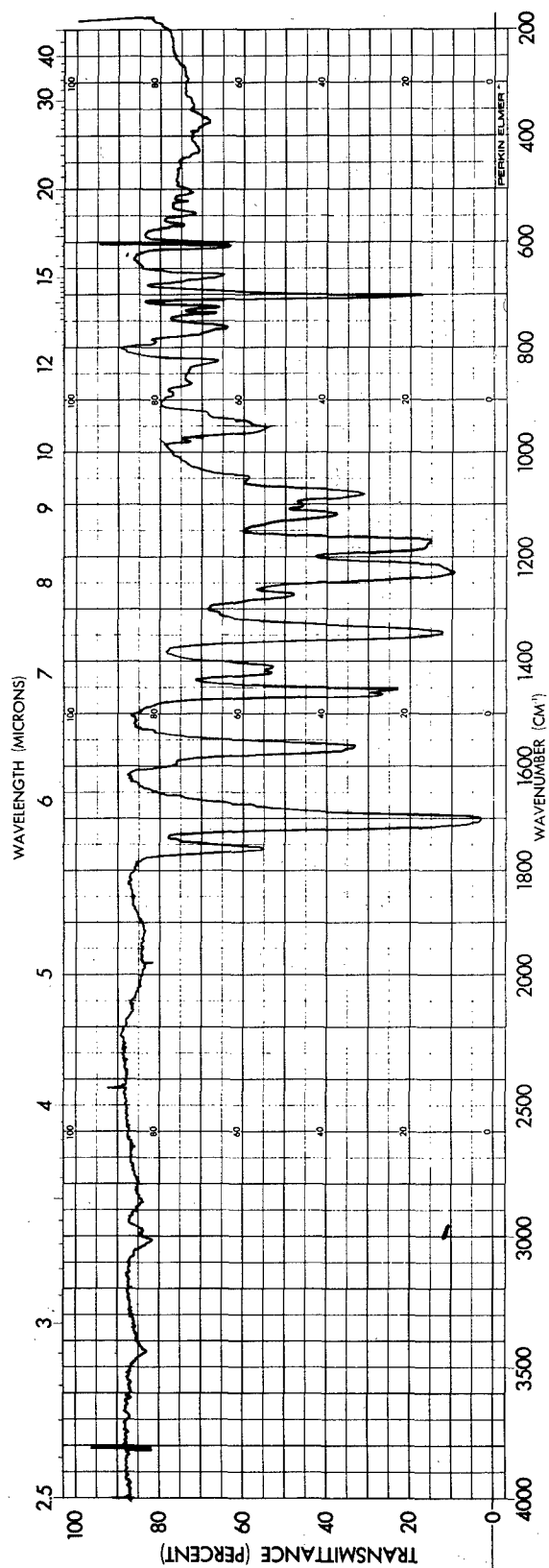


Figure 10. IR Spectrum of Enyne (30%) Copolymer VIIIb

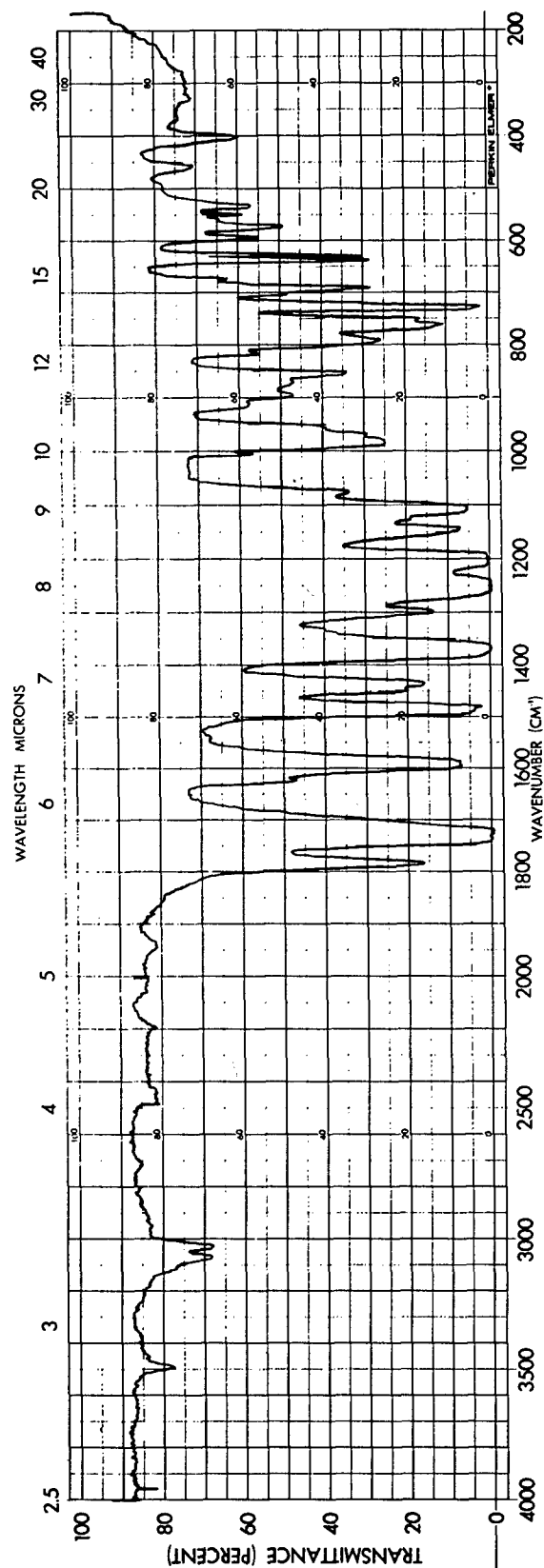


Figure 11. IR Spectrum of Enyne (50%) Copolymer VIIIC

SECTION IV

CONCLUSIONS

The goals set forth in the introduction of this report have been realized with the synthesis of high molecular weight enyne polyimide polymers and copolymers which are soluble in methylene chloride and have glass transition temperatures low enough for thermal processing. Preliminary data indicate that the enyne imides can be lightly crosslinked to form materials with a high degree of thermal oxidative stability and increased solvent resistance.

Further work is being carried out to determine both neat resin and composite properties of the 30 percent enyne polyimide copolymer. Additional solvent susceptibility studies will be carried out on enyne polyimide composites to determine their potential for use as matrix resins in Air Force aircraft applications.

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