High-Temperature Reactive Thermoplastic Aromatic Polyimides*

BRUCE A. REINHARDT and FRED E. ARNOLD, *Nonmetallic Materials Division, Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433*

Synopsis

A series of high molecular weight aromatic enyne polyimides were prepared by the condensation of various aromatic dianhydrides with (E)-1,3-bis(3-aminophenyl)-1-buten-3-yne. The polymers were soluble in common organic solvents and exhibited intrinsic viscosities as high as 0.43 (in DMAC at 30°C) with glass transition temperatures ranging from 200 to 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 and advances the glass transition temperature. Copolymers were also prepared using 1,3-bis(3-aminophenoxy)benzene and (E)-1,3-bis(3-aminophenyl)-1-buten-3-yne in an effort to obtain various percentages of enyne along the polymer backbone and, therefore, control the degree of crosslinking. The solvent resistance of selected copolymer compositions both in neat resin and thermoplastic composite form was evaluated.

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 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 related substances are detrimental to such systems.

From the above considerations it is evident that the ideal thermoplastic matrix material meet certain requirements. Thus, the material should have a low glass

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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.[1] Initially it was postulated that the enyne linkage when placed in a high-molecular-weight polymer backbond would thermally undergo an intramolecular cycloaddition (IMC)-type cure to form a phenylnaphthalene-type structure. When films of high-molecular-weight enyne polysulfone polymers were heated at 600°F (315.6°C) for 6 h under nitrogen, they became brittle and insoluble, indicating that 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 commerically available polysulfone polymers.[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.

EXPERIMENTAL

Monomers

3-Acetamidophenylacetylene (II). To a 250-ml three-neck flask fitted with a condenser, nitrogen inlet, outlet, and magnetic stirrer was added 150 ml acetic acid and 35 ml acetic anhydride. The mixture was heated to reflux under nitrogen and cooled under nitrogen. To the cooled mixture was added 15 g (0.114 mol) 3-aminophenylacetylene, and the homogeneous solution was heated at reflux 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 (mp 94–96°C).

ANAL. Calcd for $C_{10}N_9NO$: C, 75.47; H, 5.66; N, 8.81. Found: C, 75.12; H, 5.63; N, 8.73.

(E)-1,4-Bis(3-acetamidophenyl)-1-buten-3-yne (III). To 350 ml deoxygenated acetic acid was added 2.45 g cuprous acetate, whereupon a clear blue solution formed. The solution was brought to reflux, under nitrogen, and 14.35 g (0.09 mol) 3-acetamidophenylacetylene was added as a solid. The reaction mixture was maintained at reflux for 12 h 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%) (mp 234–237°C).

ANAL.   Calcd 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.

(E)-1,4-Bis(3-aminophenyl)-1-buten-3-yne (I).

To a solution made by dissolving 22 g KOH in 17 ml H_2O followed by dilution with 60 ml absolute ethanol was added 2.6 g (0.0084 mol) 1,4-bis(3-acetamidophenyl)-1-buten-3-yne and the mixture was refluxed for 1 h. After cooling to room temperature, the reaction mixture was poured into 300 ml 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 product (mp 105–106°C).

ANAL.   Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02. Found: C, 81.89; H, 5.81.

Polymers and Copolymers

The following are representative examples of the procedures used in the preparation of polymers and copolymers.*

Poly[(E)-(1,3-dioxo-2,5-isoindolinediyl)[oxy-1,4-phenylene-2,2,2-trifluoro-1-(tri-fluoromethyl)ethylidene]-1,4-phenyleneoxy-(1,3-dioxo-5,2-isoindolinediyl)-1,3-phen-ylene-1-buten-3-ynylene-1,3-phenylene]] (Va) (A = 1, B = 0).

In a dry, 25-ml, three-necked flask equipped with a magnetic stirring bar, a ni-trogen inlet, a short-path distillation apparatus, and a stopper was placed 0.3999 g (1.707 mmol) (E)-1,4-bis(3-aminophenyl)-1-buten-3-yne (IK), 4 ml freshly distilled m-cresol, and two drops isoquinoline.[3] After the diamine had dissolved, 1.0727 g (1.707 mmol) 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoro-propane dianhydride[4] was added in several portions over a period of 30 min. The final portion of dianhydride was washed in with 4 ml m-cresol and 5 ml 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 toluene had been distilled, five additional milliliters toluene was added and the temperature raised slowly to 165°C for 1.5 h during which time the reaction mixture became very viscous. The reaction mixture was then cooled, diluted with 15 ml chloroform, and precipitated into 1200 ml 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 h, the polymer had an intrinsic viscosity of 0.51 in dimethylacetamide (DMAC) at 30°C.

All homopolymers and copolymers gave satisfactory elemental analyses.

Poly[[(E)-(1,3-dioxo-2,5-isoindolinediyl)[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy]-(1,3-dioxo-5,2-isoindolinediyl)-3-phenylene-1-buten-3-ynylene-1,3-phenylene]] (Vb) (A = 1, B = 0).

In a 25-ml, three-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) (E)-1,4-bis(3-aminophenyl)-1-buten-3-yne, 4 ml m-cresol, and two drops isoquinoline. After the diamine had dissolved, 0.9260 g (1.707 mmol) 1,4-bis(3-dicarboxyphenoxy)diphenylsulfone dianhydride[5] was added

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*Polymer and copolymer names provided by the courtesy of Dr. K. L. Loening, Director of No-menclature, Chemical Abstracts Service.

in portions over a period of 30 min. The final portion of dianhydride was washed in with 4 ml m-cresol and 5 ml 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 toluene was removed, five additional milliliters toluene was 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 2 h and then raised to 175°C for 1 h. The reaction mixture was cooled, diluted with 5 ml dimethylformamide (DMF), and precipitated into 1200 ml 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 h, the polymer had an intrinsic viscosity at 30°C of 0.35 in DMAC.

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, three-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) (*E*)-1,4-bis(3-aminophenyl)-1-buten-3-yne, 4 ml freshly distilled m-cresol, and two drops isoquinoline. After the diamine had dissolved, 0.7583 g (1.707 mmol) 2,2-bis(3,4-dicarboxy phenyl)hexafluoropropane dianhydride[6] was added in several portions over a period of 30 min. The final portion of dianhydride was washed in with 4 ml m-cresol and 5 ml 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 toluene was distilled, eight additional milliliters was 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 2 h. The reaction mixture was cooled, diluted with 10 ml chloroform, and precipitated into 1200 ml 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 h, the polymer had an intrinsic viscosity at 30°C of 0.42 in DMAC.

Poly[[(E)-(1,3-dioxo-x,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-trifuloro-1-(trifluoromethyl)ethylidene](1,3-dioxo-5,2-isoindolinediyl)-1,3-phenyleneoxy-1,3-phenyleneoxy-1,3-phenylene]] (VIIIa) (*A* = 0.25, *B* = 0.75).

In a dry 25 ml, three-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) (*E*)-1,4-bis(3-aminophenyl)-1-buten-3-yne, 3.4931 g (11.949 mmol) 1,3-bis(3-aminophenoxy)benzene, 6 ml freshly distilled m-cresol, and two drops isoquinoline. After both diamines had dissolved, 7.5832 g (17.070 mmol) 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride was added in several portions over a period of 30 min. The final portion of dianhydride was washed in with 4 ml m-cresol and 5 ml 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 toluene were

distilled, five additional milliters toluene was 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 2 h. The reaction mixture was cooled, diluted with 10 ml chloroform, and precipitated into 1200 ml rapidly stirred 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 h, the polymer had an intrinsic viscosity at 30°C of 1.42 in DMAC.

Copolymers

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 = 0.5, B = 0.5).

In a dry, 25 ml, three-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) (E)-1,4-bis(3-aminophenyl)-1-buten-3-yne, 0.2495 g (0.8534 mmol) 1,3-bis(3-aminophenoxy)benzene, 6 ml m-cresol, and two drops isoquinoline. After both diamines had dissolved, 0.7853 g (1.707 mmol) 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride was added in several portions over a period of 30 min. The final portion of dianhydride was washed in with 4 ml m-cresol and 5 ml 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 toluene was distilled, eight additional milliters toluene was 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 2 h. The reaction mixture was cooled, diluted with 12 ml chloroform, and precipitated into 1200 ml 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.

Characterization

Infrared spectra of the monomers, polymers, and copolymers were obtained on pressed KBr pellets or thin films with a Perkin–Elmer model 33 infrared spectrophotometer. Differential scanning calorimetry and thermal mechanical analysis data were obtained on a du Pont 990 thermal analyzer coupled with either a du Pont DSC or TMA cell. Isothermal aging studies were carried out with an automatic multisample apparatus, allowing weight loss to be obtained in the aging environment.

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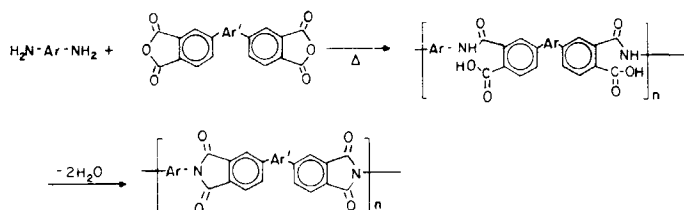
It was postulated that the enyne linkage could be most easily incorporated into the diamine component of the polymer-forming reaction.   The initial phase of the current work involved the synthesis of the diamine monomer I:
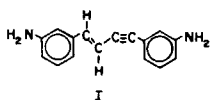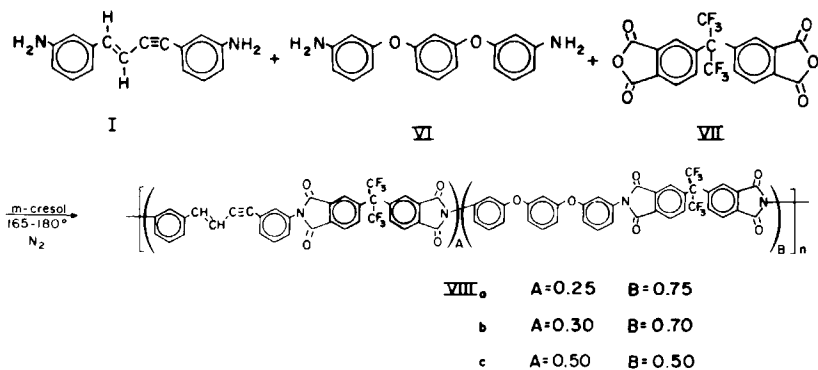

Monomer Synthesis

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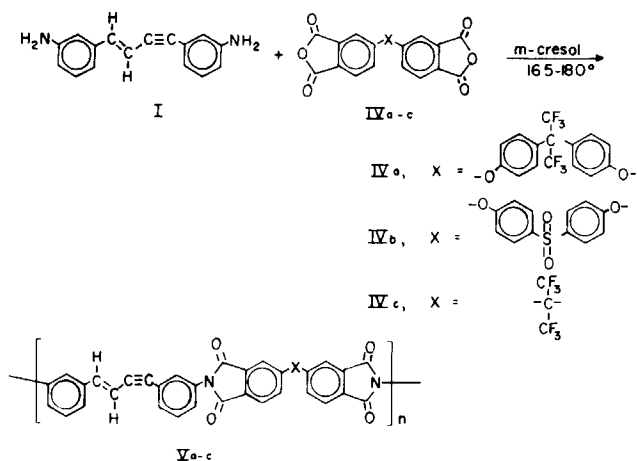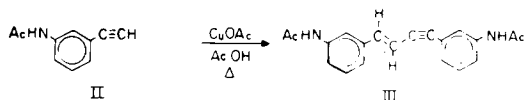

Hydrolysis of III using a 28% aqueous ethanolic KOH solution gave a 50% yield of the free diamine I:

VIII a	A=0.25	B=0.75
b	A=0.30	B=0.70
c	A=0.50	B=0.50

Polymer Synthesis

The enyne containing polyimides 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%, and tough, transparent films could be cast from 2% solution of the chloroform-soluble polymers. Intrinsic viscosities of the polymers ranged from 0.24 to 0.51 in DMAC at 30°C.

The DSC thermogram ($\Delta = 20°C/min$) of polymers Va–b show initial basline shifts characteristic of a glass transition at 212 and 243°, respectively, an exotherm beginning at approximately 250°, and an exotherm maxima between 340 and 350°C. Polymer Vc showed no baseline 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 baseline shift was taken as the temperature of either a glass transition or polymerization exotherm. Pelletized samples of the polymers cured for 6 h at 265°C for polymers Va and Vb and at 315°C for Vc showed glass transitions close to the cure temperatures.

Thermal data for all homopolymers are summarized in Table I. When film samples of polymers Va–c were heated at 316° under nitrogen for 2 h, they became brittle and insoluble, indicating that a facile interchain reaction was occurring producing a material with a high crosslink density.

Copolymer Synthesis

It had been demonstrated previously with enyne polysulfone polymers[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. 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 homo-

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TABLE I
Thermal Analytical and Viscosity Data for Enyne Polyimides

Polymer	X	$[\eta]^a$	T_g^b	T_i^c	T_g cured
$\underline{V_a}$	(structure)	0.51	212	255	245[d]
$\underline{V_b}$	(structure)	0.24	NONE OBSERVED	265	325[d]
$\underline{V_c}$	(structure)	0.45	NONE OBSERVED	270	315[e]

[a] Intrinsic viscosity measured in DMAC (0.5%).
[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 6 h.
[e] T_g measured by DSC and TMA for polymer samples cured at 316°C (650°F) for 6 h.

polymers, 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 (Fig. 1). Pelletized samples of the copolymers cured at 316°C (600°F) for 6 h under nitrogen showed by DSC and TMA analyses
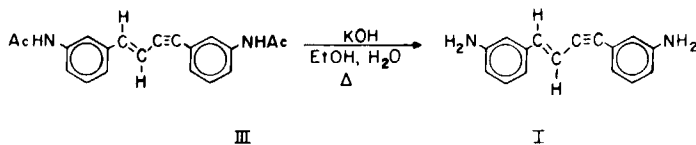
a 40° advancement in T_g (Figs. 2 and 3) above the T_g of the uncured polymers. Thermal analysis and viscosity data for the copolymers are summarized in Table II. Film samples of the copolymers when heated under nitrogen at 315.6°C for 3 h retained a high degree of flexibility indicative of a decreased 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,[1] where the flexibility of the cured copolymers increased as the amount of enyne content was reduced.
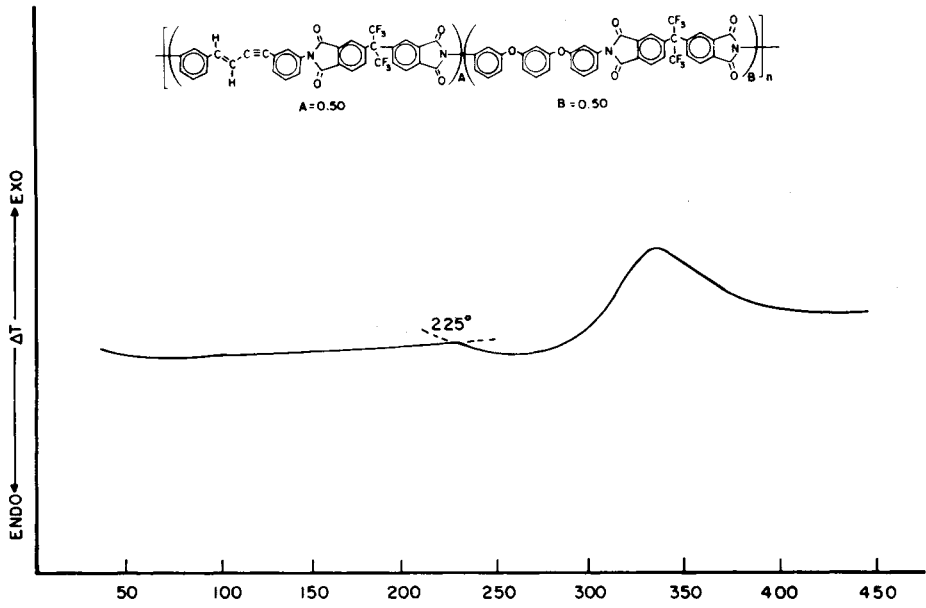
Fig. 1. DSC thermogram of enyne polyimide copolymer (50%).

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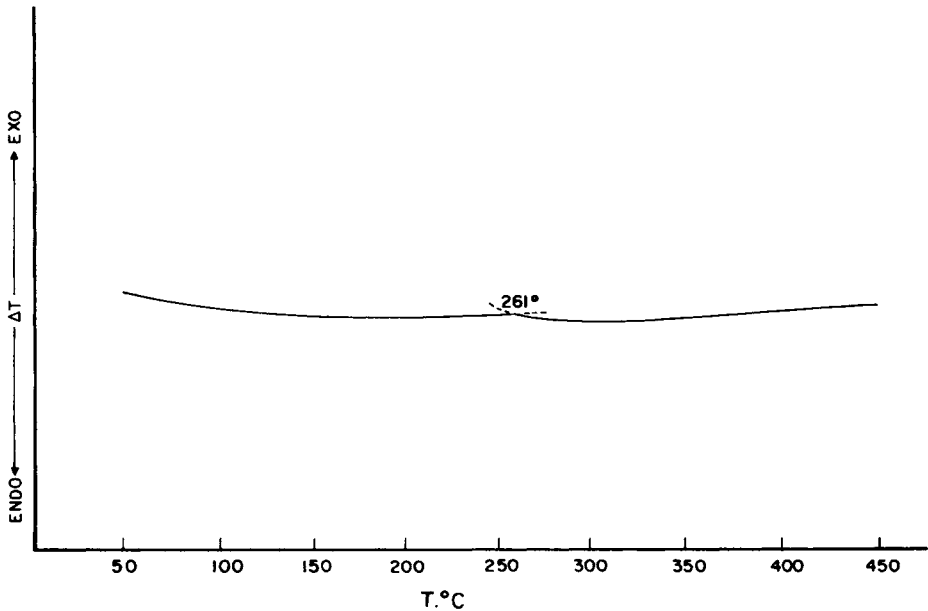

Fig. 2. DSC thermogram of enyne polyimide copolymer (50%) after curing 6 h at 315.6°C (600°F) N₂.
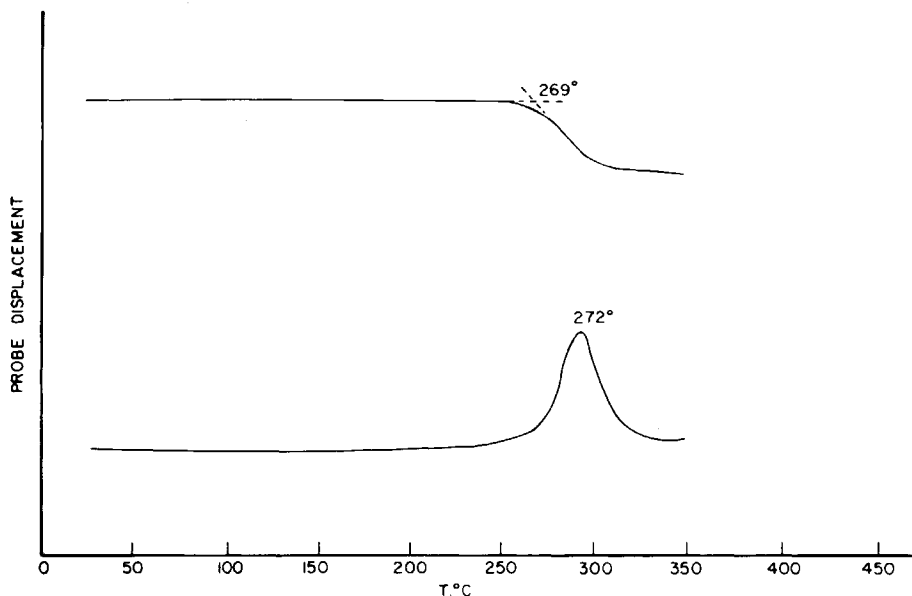
Fig. 3. TMA penetration curve for enyne polyimide copolymer (50%) after curing 6 h at 315.6°C (600°F) N₂.

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

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 thermo-oxidatively stable in enyne polyimides than in enyne polysulfones (Fig. 7). The current data indicate that the presence of the enyne linkage in the polysulfone backbone enhances the thermo-oxidative decomposition of the polymer, reducing the temperature of the onset of degradation

TABLE II
Thermal Analytical and Viscosity Data for Enyne Polyimide Copolymers

Polymer	% A	% B	[η]ᵃ	Tg predᵇ	Tgᶜ	Tᵢᵈ	Tg curedᵉ	Wᶠ
Xc	100	0	0.45	418°	observed	270	315	87
VIIIa	25	75	0.42	217	208	220	229	89
VIIIb	30	70	1.42	227	212	270	236	91
VIIIc	50	50	0.70	253	225	270	269	89

ᵃ Intrinsic viscosity measured in DMAC (0.5%).
ᵇ Predicted T_g base on Fox–Flory or copolymer equation.[9]
ᶜ Measured by DSC and TMA.
ᵈ Temperature at which curing exotherm begins.
ᵉ T_g measured by DSC and TMA for polymer samples cured at 316°C (650°F) for 6 h.
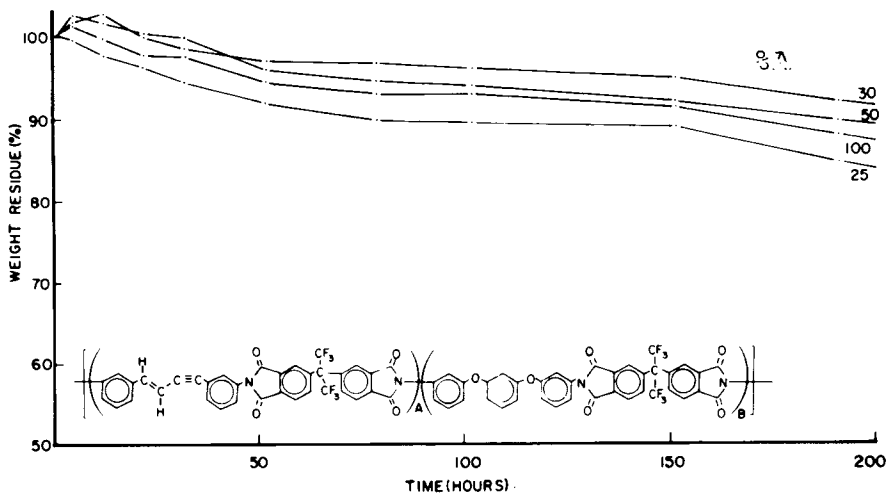ᶠ Isothermal aging—weight retained after 200 h at 315.6°C (600°F).

Fig. 4. Isothermal aging curves for enyne polyimide copolymers in air at 315.6°C (600°F).

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.

Mass spectra TGA analysis was carried out on polymer VIIIb from room temperature to 900°C using a 4.2°C/min heating rate. The onset of degradation appears to be at 440°C, with the major degradation product being carbon monoxide production at 560 and 630°C. The second most abundant product is hydrogen fluoride displaying a maximum at 560°C. Other products and their maxima are as follows: HCN, 680°C; CO_2, 560 and 610°C; and H_2O, 560 and 650°C. The sample retained 53% of its weight during the run to 900°C.

A study was undertaken to evaluate the enyne polyimide copolymers as neat resins and as thermoplastic graphite composites for improved solvent and craze
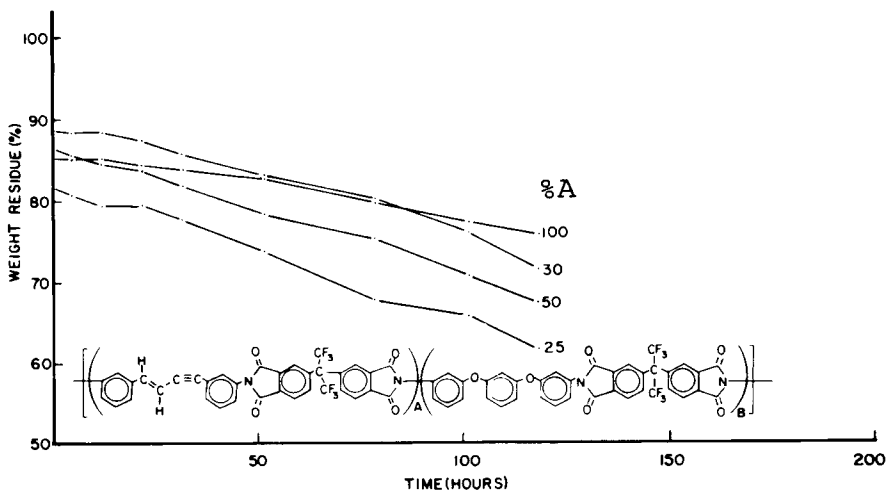

Fig. 5. Isothermal aging curves for enyne polyimide copolymers in air at 343.3°C (650°F).
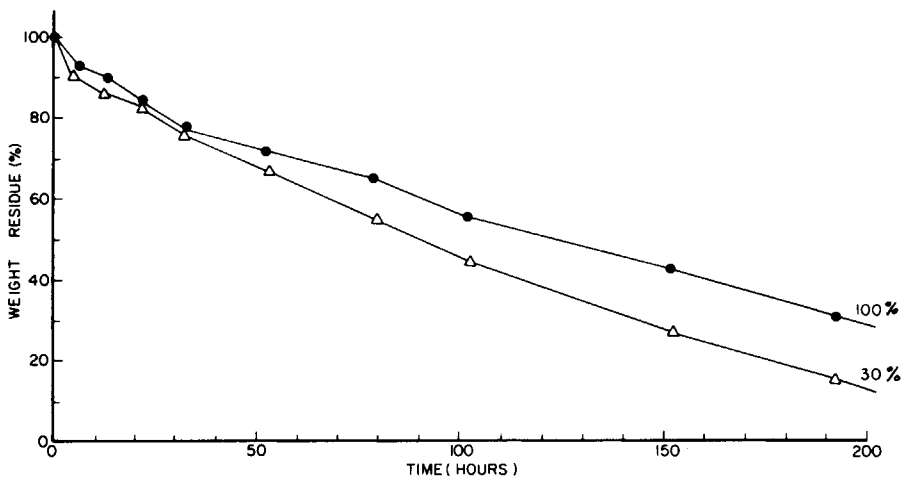
Fig. 6. Isothermal aging curves for selected enyne polyimide polymers in air at 371°C (700°F).

resistance. The copolymer neat resin properties were evaluated in the following manner: Films of the 30% 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 contant-stree apparatus[7] while being exposed to methyl ethyl ketone solvent. After 1.5 h 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 1 s after contact with methyl ethyl ketone.[8] Similar tests were carried using the same resin with methylene chloride and acetone as solvents. The enyne polyimide copolymer showed excellent resistance to all solvents tested (Table III).

The enyne polyimide copolymers were also evaluated as to their potential use as matrix resins for advanced composite materials. The 30% enyne polyimide
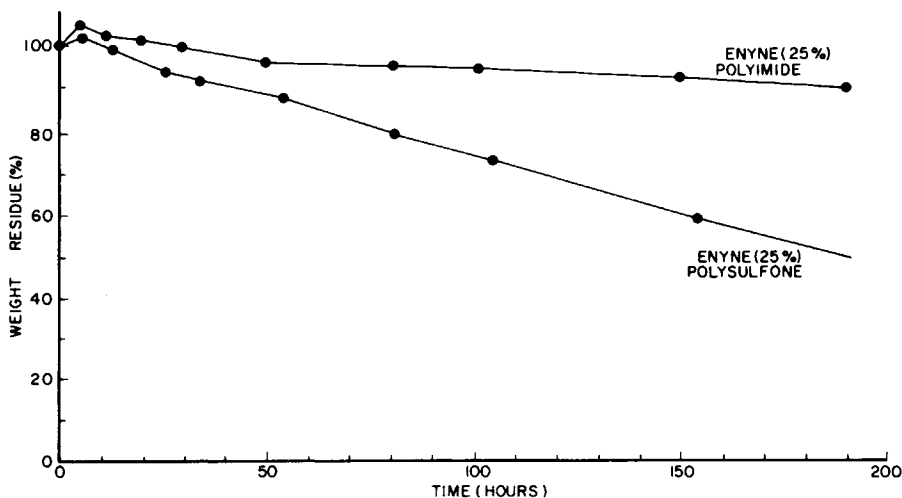

Fig. 7. Comparison of isothermal aging curves of enyne polyimide (25%) copolymer and enyne polysulfone (25%) copolymer in air at 315.6°C (600°F).

TABLE III
Comparison of Solvent Resistance of a Commercial Aromatic Polysulfone and Enyne Polyimide
Copolymer (30%)[a]

SOLVENT	STRESS (M Pa)	RUPTURE TIME	
		COM. POLYSULFONE	ENYNE IMIDE
MEK*	3.45	1 s	
MEK	3.45	2-15 s	>36 h
MEK	13.8	- - - -	>2.25 h
MEK	27.6	- - - -	33-42 min
CH_2Cl_2*	3.45	3 min	- - -
CH_2Cl_2*	6.90	10 s	- - -
CH_2Cl_2	3.45	17 min	>77 min
CH_2Cl_2	6.9	- - - -	>120 min
CH_2Cl_2	13.8	- - - -	5 min

[a] From G. E. Husman and J. T. Hartness, 24th National SAMPE Symposium, 24(1), 26 (1979).

copolymer was fabricated into a graphite-reinforced laminate. Short-beam shear strengths of cured laminates before and after exposure to various solvents at room and elevated temperatures were compared to an unmodified polybiphenyl sulfone laminate.

The enyne polyimide copolymer laminate at room temperature had an initial short-beam shear strength of 85.0 MPa. After immersion for 30 days in methyl ethyl ketone, the short-beam shear strength was reduced by 18% to 69.3 MPa. At 177°C, a similar specimen retained 64% of its original short-beam shear strength. These data, when compared to a 40% retention at room temperature for the unmodified polybiphenyl sulfone laminate,[4] show a substantial improvement in solvent resistance for the enyne imide copolymer. The laminates were also tested for resistance to methylene chloride. Specimens of the enyne polyimide resin retained 34 and 30% of their short-beam shear strengths at room temperature and 177°C, respectively. A commercial polysulfone laminate would be soluble in methylene chloride; therefore, the increased solvent resistance of the enyne imide laminate is evident.

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