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ACETYLENE-TERMINATED AROMATIC
AMIDE MONOMERS

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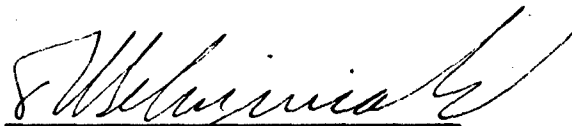
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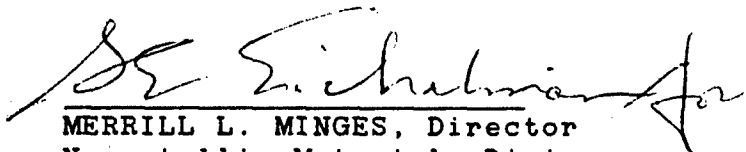


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FOREWORD

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SECTION I

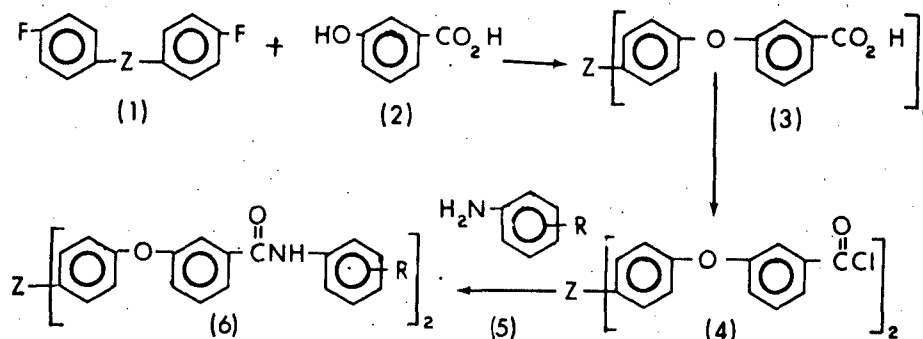
INTRODUCTION

Resin precursors that yield moisture resistant products without the evolution of volatiles during cure have potential in composite applications.¹ Considerable research has centered around the synthesis of acetylene-terminated (AT) materials for use where long-term thermo-oxidative stability at 350°F is required.² Unfortunately, the synthetic routes to many AT systems, particularly those with potential for good mechanical properties, have been tedious multi-step processes. Although the mechanical properties of only a few of these resins have been documented,³⁻⁵ a major drawback has been their lack of toughness.⁶ Toughness has been increased through increase in chain length between the terminal acetylene groups, but at the expense of the processing parameters and the use temperature.^{3,4,6}

This report describes a relatively simple synthetic route to a class of AT resin precursors that contain amide groups. Some of these compounds display thermal characteristics indicative of ready processability and have the potential to yield tough products. These semiflexible structures with molecular weights of 640-680amu would be expected to exhibit moderate thermo-oxidative stability upon curing and improved toughness compared to earlier AT systems based on shorter phenylene-R structures.^{3,4} In addition some of these monomers may have the necessary structural features to limit crosslinking during cure, thus minimizing the number of crosslinks in the cured resin network and preventing the brittleness that is characteristic of highly crosslinked resins.

RESULTS AND DISCUSSION

The synthesis of the AT resin precursors (6) is shown below. Compounds (1) underwent smooth nucleophilic displacement of fluoride ion by the phenolate formed from (2) to yield the diacids (3) in 85 percent ($Z=SO_2$) and 65 percent ($Z=CO$) yields. The carboxylate anion (the poorer nucleophile) apparently did interfere with the displacement. Hence it was unnecessary to use an ester of (2) in the reaction, as was previously employed in a similar situation.¹⁰ Conversion to the diacid chlorides (4) was readily effected through refluxing of the diacids in thionyl chloride followed by recrystallization of the crude diacid chlorides from tetrahydrofuran (THF). Yields of 90 percent ($Z=SO_2$) and 50 percent ($Z=CO$) were recorded. This method of synthesis of the requisite diacids compares very favorably with previously reported syntheses.^{11,12} The diacid with the sulfone moiety (3) ($Z=SO_2$) had been prepared via the action of m-cresol on bis(p-chlorophenyl)-sulfone in the presence of base, followed by oxidation of the methyl groups with aqueous potassium permanganate in pyridine.¹² Diacid (3) ($Z=CO$) has been reported as resulting from the nitro-displacement reaction of 4,4'-dinitrobenzophenone and m-hydroxybenzoic acid in the presence of base.¹¹ The ready availability of the compounds (1) ($Z=SO_2, CO$) and (2) offered a convenient alternate route to the diacids (3) ($Z=SO_2, CO$).



a, f
b, g
c, h
d, i
e, j

$$\begin{array}{l} o - C \equiv CH \\ o - C \equiv C Si(CH_3)_3 \\ m - C \equiv CH \\ p - C \equiv CH \\ p - C \equiv C Si(CH_3)_3 \end{array}$$

a - e
f - j

$$\begin{aligned} Z &= \text{SO}_2 \\ Z &= \text{CO} \end{aligned}$$

While the requisite m-aminophenylacetylene (5) ($R=m-C\equiv CH$) could be purchased from a commercial source, the ortho- and para-substituted analogs (5) ($R=o,p-C\equiv CH$) as well as their trimethylsilyl derivative (5) ($R=o,p-C\equiv CSi(Me)_3$) were prepared by the palladium-catalyzed ethynylation of 2-iodo- and 4-iodo-aniline with trimethylsilyl acetylene.¹³ This synthesis route had been previously reported for the synthesis of p-aminophenylacetylene and was preferable to the alternate methods of preparation based on the bromination and subsequent dehydrobromination of o-nitrocinnamic acid^{14,15} or the ethynylation of p-iodoaniline with 2-methyl-3-butyne-2-ol.¹⁶ Although the former approach was initially attempted for the preparation of o-aminophenylacetylene, it was abandoned because of experimental difficulties.

The target AT aromatic amides (6) were obtained in essentially quantitative yields through the triethylamine-promoted condensation of aromatic amines (5) and diacid chlorides (4) in THF. No purification was carried out since the materials were obtained in greater than 95 percent purity. A significant, difficult-to-remove impurity was THF trapped in the solid monomers. This synthesis reaction appeared to compare favorably in yield and purity of product with that described in recent reports on AT-aromatic amides.¹⁷

2. MONOMER CHARACTERIZATION

The AT-aromatic amides (6a-e) and (6f-j) were obtained as glassy white solids. Infrared spectra indicated absorptions corresponding to the N-H ($3300-3415cm^{-1}$), C=C-H ($3300-3310cm^{-1}$), C=C ($2100-2215cm^{-1}$), and C=O ($1645-1680cm^{-1}$) stretching vibrations.¹⁸ These absorptions are summarized in Table 1. The N-H stretching vibration moved to lower frequency as the ethynyl substitution changed from ortho, to meta, and then to para, presumably attributable to differences in intra- or intermolecular hydrogen bonding. Intermolecular packing apparently allowed strong intermolecular hydrogen bonding of the N-H group with C=O in the para isomers but only minimal intermolecular hydrogen bonding for the ortho isomers. However the ortho ethynyl function was in an ideal position for intramolecular hydrogen bonding with the N-H group. This interaction was manifested in the proton magnetic resonance spectra of all the ortho ethynyl compounds (6a,b,f,g) (see below).

Proton nuclear magnetic resonance spectra ($CDCl_3$, TMS) were consistent with the proposed structures. The spectral data for the individual monomers (6) are given in Table 2. Observed for the terminal ethynyl structures were singlets at 3.05-3.62ppm (2 protons) attributable to acetylenic protons, complex multiplets at 6.70-8.62ppm (24 protons) attributable to aromatic protons, and singlets at 8.49-8.82ppm (2 protons) indicative of the amide protons. The trimethylsilyl derivatives similarly exhibited

signals attributable to aromatic and amide protons as well as a singlet (18 protons) arising from the aliphatic methyl protons of the trimethylsilyl group. As was noted with the infrared spectral data, differences in spectra were observed between the ortho-, meta-, and para-substituted ethynyl compounds. The signals observed for the aromatic protons in the ortho-substituted monomers (6a,b,f,g) were particularly interesting. The conformation assumed by these compounds (presumably because of intramolecular hydrogen bonding of the N-H function with the ethynyl group) brought the aromatic ortho hydrogen atoms of the aniline moieties into the deshielding region of the carbonyl groups. Thus the signals for these hydrogens were observed (doublets) at fields lower than those of the complex aromatic multiplets.

TABLE 1
IR SPECTRA

Compound (6)	NH	C≡C-H	C≡C	C=O
a (film)	3415	3300	2100	1680
b (KBr)	3415	--	2160	1685
c (film)	3350	3310	2105	1660
d (KBr)	3300	3300	2115	1670
e (KBr)	3360	--	2170	1665
f (film)	3415	3300	2100	1680
g (KBr)	3410	--	2160	1690
h (film)	3360	3310	2100	1665
i (KBr)	3300	3300	2105	1645
j (KBr)	3355	--	2150	1660

$\nu(\text{cm}^{-1})$ given

Mass spectra of monomers (6) were consistent with the proposed structures in respect to fragmentation patterns. Mass peaks for the individual monomers are given in the Experimental Section. Only the trimethylsilyl compounds (6,b,e,g,j) and the ortho terminal ethynyl isomers (6a,f) exhibited parent ion peaks. The mass spectra of the para terminal ethynyl compounds (6d,i) could not be recorded even when the samples were heated to 500°C. Apparently efficient intermolecular packing prevented volatilization and/or allowed rapid resinification of these compounds. Infrared data indicated looser packing in the meta terminal ethynyl

monomers (6c,h). Even here only decomposition peaks were recorded in the mass spectrum. In the case of the ortho terminal ethynyl monomer (6a,f), the infrared and proton magnetic resonance spectra suggested that intermolecular packing was poor compared to the meta and para isomers (6c,d,h,i) in which intermolecular hydrogen bonding of the N-H function with the carbonyl group was observed. Intramolecular hydrogen bonding of the N-H function with the carbon-carbon triple bond in (6a,f) could readily occur instead, thus leading to weaker intermolecular forces and greater volatility.

TABLE 2
PMR SPECTRA

Compound (6)	Me ₃ Si	C=C-H	Ar-H	N-H
a	--	3.53(s,2)	7.08-8.16(m,22) 8.62(d,2,J=8c/s)	8.82(s,2)
b	0.00(s,18)	--	6.70-8.00(m,22) 8.48(d,2,J=8c/s)	8.80(s,2)
c	--	3.05(s,2)	6.83-8.07(m,24)	8.67(s,2)
d	--	3.12(s,2)	6.90-8.10(m,24)	8.49(s,2)
e	0.00(s,18)	--	6.64-7.90(m,24)	8.38(s,2)
f	--	3.62(s,2)	6.92-8.12(m,22) 8.61(d,2,J=8c/s)	8.82(s,2)
g	0.00(s,18)	--	6.66-7.90(m,22) 8.40(d,2,J=8c/s)	8.80(s,2)
h	--	3.05(s,2)	6.83-7.92(m,24)	8.75(s,2)
i(DMSO-d ₆)	--	4.10(s,2)	7.00-8.28(m,24)	not observed
j	0.00(s,18)	--	6.69-7.96(m,24)	8.36(s,2)

The solvent is chloroform-d unless indicated otherwise, and the chemical shifts are in parts per million from TMS for Compounds (6a,c,d,f,h,i) and in parts per million from the trimethylsilyl signal for Compounds (6b,e,g,j).

d = doublet, m = multiplet, s = singlet

Because of the trimethylsilyl groups, compounds (6b,e,g,j) were volatile enough for the parent ions to be observed as trace peaks. The energy required to volatilize these compounds, however, resulted in cleavage of the trimethylsilyl groups as had been recently reported for another complex ethynyl compound.¹⁹ The reactions of the trimethylsilyl groups liberated by the thermal process with the parent ion and other ion fragments resulted in complex mass spectra for (6b,e,g,j) when compared with the terminal ethynyl monomers (6a,c,d,f,h,i).

Analysis of the mass spectral data also indicated the presence of impurities arising from incomplete reaction of 4,4'-carbonyldi-(fluorobenzene) (1) (Z=CO and m-hydroxybenzoic acid (2) to yield 3-[4'-(p-fluorobenzoyl)phenoxy]benzene. Evidence for the minor impurities resulting from this incomplete reaction was seen in the spectra of (6g,h,j) in the form of parent ion peaks for the structures $F-\phi-CO-\phi-O\phi CON\phi R$ (7) ($R=m-C=CH, o, p-C=CSi(CH_3)_3$).

High-performance liquid chromatography (HPLC) indicated purity of greater than 96 percent for the terminal ethynyl monomers (6a,c,d,f,h,i) and a slightly lower level of purity for the trimethylsilyl monomers (6b,e,f,j). The number of components observed in the crude compounds (6) is listed in Table 3. Caution must be exercised in relating percent areas to percent purity as the relative absorbances of the components are not known. Based on the areas of the proton magnetic resonance signals, a purity of 95 percent or greater is indicated. The relatively large peak at 30.22 minutes (7 percent) in the chromatogram of (6e) may be due to hydrolysis of the trimethylsilyl groups during isolation [compare with: (6a) 30.09 min (97 percent)]. In some samples such as (6c), the main component appears at longer than usual retention times because different instruments are used to make the measurements.

The thermal characteristics of the monomers were investigated by means of differential scanning calorimetry (DSC) under a nitrogen atmosphere and thermogravimetric analysis (TGA) in air. Results of these test are summarized in Table 4 and a representative DSC scan is shown in Figure 1. With the exception of (6c,i), the initial Tg's of the terminal ethynyl monomers (6a,c,d,f,h,i) were well below the onset of cure and indicated an adequate processing "window." Onset of cure occurred in the 160-225°C range with maximum curing rates being recorded in the 225-260°C range. Ortho-substituted monomers (6a,f), upon heating to 450°C, exhibited Tg's of less than 200°C while the other monomers, upon similar treatment, either exhibited a significantly higher Tg (6c) or did not exhibit a Tg up to the onset of decomposition (6d,h,i). This substantial difference in the final Tg of the cured resins can be attributed to differences in substituent positions in the monomers and/or a lower extent of cure in the resins obtained from the ortho-substituted monomers (6a,f).

TABLE 3
HPLC RESULTS

Compound (6)	Solvent	Retention Time (min)	Area (%)
a	Methylene chloride	34.52	1.03
		35.93	97.68
		37.39	0.44
		41.78	0.84
b	Tetrahydrofuran	28.62	4.39
		30.32	95.16
		33.50	0.13
		34.54	0.30
c	Methylene chloride	33.78	0.66
		34.90	1.22
		36.56	97.90
		39.82	0.12
d	Tetrahydrofuran	30.09	96.69
		35.62	3.24
e	Tetrahydrofuran	29.25	91.78
		30.22	6.99
		33.89	1.03
f	Methylene chloride	32.38	0.92
		33.50	0.33
		34.73	96.39
		36.45	1.85
		41.52	0.21
		41.77	0.21
g	Methylene chloride	28.92	0.30
		30.74	96.87
		32.60	2.16
		36.22	0.62
h	Methylene chloride	33.18	0.32
		34.29	1.22
		35.88	96.00
		37.30	2.43
i	Tetrahydrofuran	30.12	97.46
		32.09	1.36
		35.62	1.15
j	Methylene chloride	30.83	97.22
		32.75	2.56
		34.21	0.16

4-500°A μ styragel, 1 ml/min solvent flow rate, 254 nm detector

TABLE 4
DSC DATA (°C)

Compound (6)	T _g (initial)	T ₁ (onset of exotherm)	T ₂ (peak of exotherm)	T _g (final)	T ₃ (onset of decomposition)
a	59	160	251	185	435
b	102	262	381	197	360
c	-	209	234	247	444
d	40	195	227	-	450
e	76	260	414	-	374
f	29	209	259	194	400
g	40	295	404	186	367
h	49	226	243	-	483
i	182	182	201	-	474
j	58	295	414	-	364

It is possible that crosslinking may have been limited because of electronic and/or steric interaction between the ortho- ethynyl- and amido- groups. As indicated by TGA (see below), the cured resins possibly suffered varying extents of decomposition upon heating to 450°C. Changes in structure attributable to decomposition may have had a significant effect on the final T_g of the cured resins.

In the case of the trimethylsilyl analogs (6b,e,g,j), cure temperatures were significantly higher owing to steric effects.⁵ As noted with the terminal ethynyl monomers, the ortho-substituted compounds (6b,g) also exhibited substantially lower T_g's upon heating to 450°C than the para-substituted compounds (6e,j). Since the final T_g would depend upon the degree of cure as well as resin precursor structure, the lower T_g's observed for the cured ortho-substituted monomers could be due to limited crosslinking. Unfortunately, the final T_g's for cured ortho-substituted monomers (6a,f,b,g) were not high enough to permit use at 350°F.

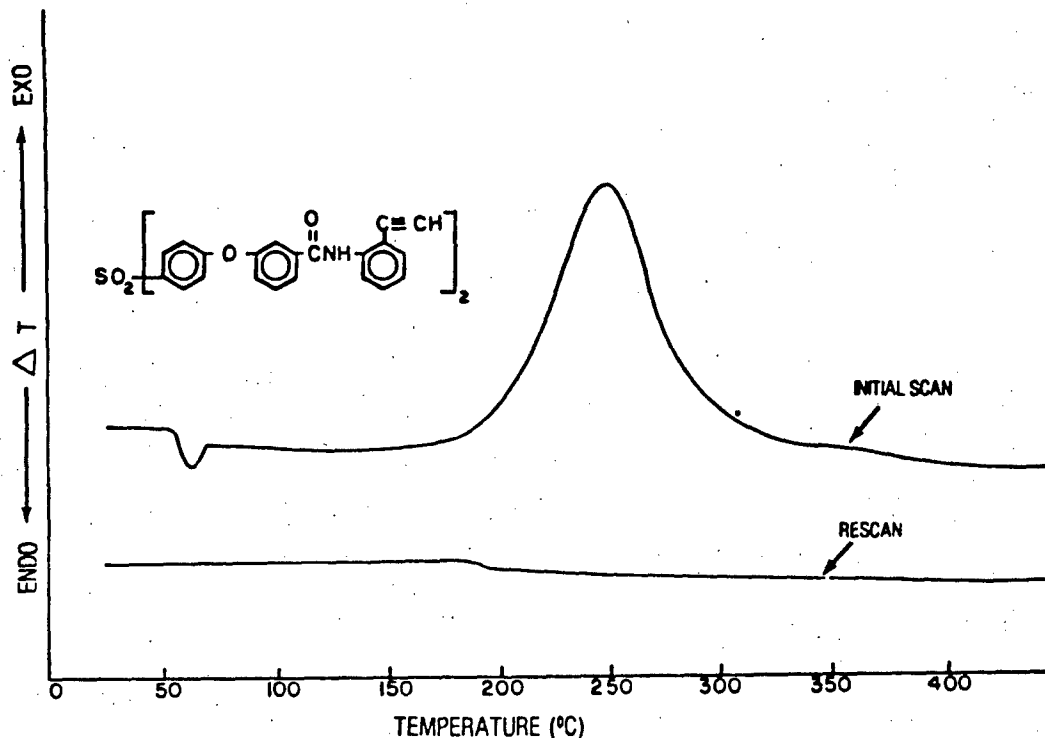


Figure 1. DSC in Nitrogen ($\Delta T=50^{\circ}\text{C}/\text{min}$) of Monomer 6a.

The thermo-oxidative stabilities of the cured resins were evaluated by TGA. Onset of weight loss in an air atmosphere for the terminal ethynyl monomers (6a,c,d,f,h,i) occurred in the $400\text{--}485^{\circ}\text{C}$ range with essentially no weight residues being present at 700°C . For the sulfonyl compounds (6a,c,d), weight loss took place in two steps, the initial weight loss corresponding to extrusion of sulfur dioxide after resinification.²⁰ In contrast, the carbonyl compounds (6f,h,i) underwent a continuous weight loss after onset of decomposition. In the case of the trimethylsilyl-terminated monomers (6b,e,g,j), onset of weight loss occurred below 375°C with the initial weight loss being attributable to breakdown of the trimethylsilyl groups. This ready decomposition essentially precludes the use of the trimethylsilyl-terminated monomers as high temperature resin precursors. The extrapolated values for onset of weight loss are summarized in Table 4. Representative TGA curves for the resins derived from the carbonyl monomers (6) ($\text{Z}=\text{SO}_2$) and sulfonyl monomers (6) ($\text{Z}=\text{CO}$) are shown in Figures 2 and 3,² respectively.

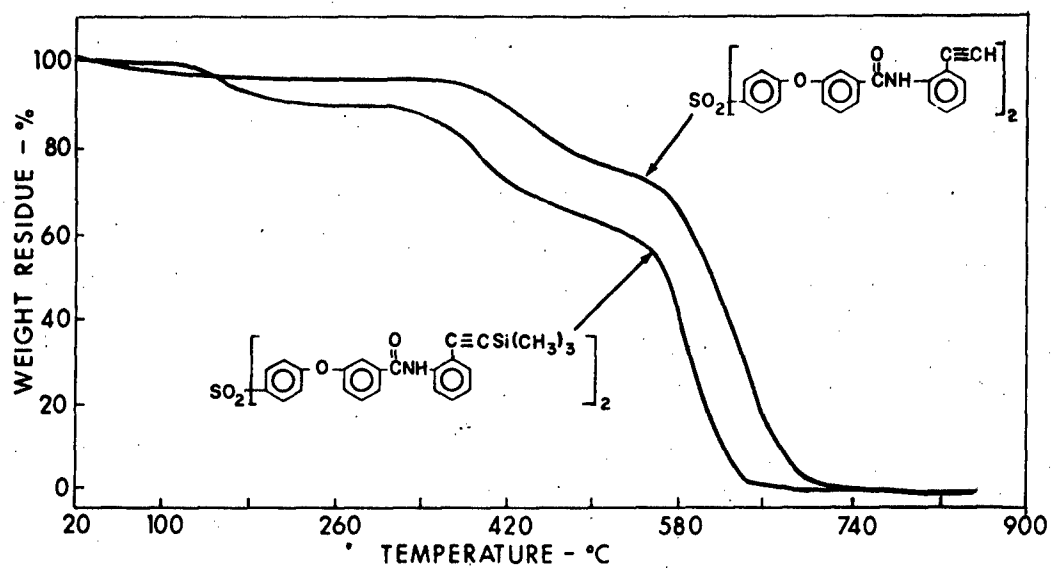


Figure 2. TGA in Air ($\Delta T = 10^\circ\text{C/min}$) of Resins from Monomers (6a,b).

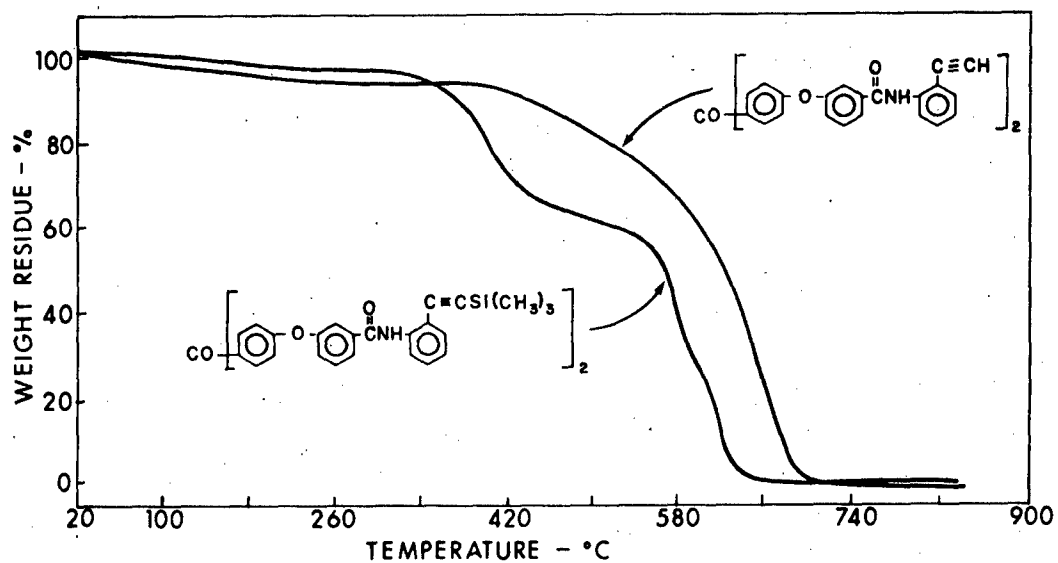


Figure 3. TGA in Air ($\Delta T = 10^\circ\text{C/min}$) of Resins from Monomers (6f,g).

SECTION III

CONCLUSIONS

A simple synthetic route to the resin precursors (6) has been established. Intermediates could be readily purified by recrystallization and distillation; no purification was necessary in the final synthetic step that yielded (6).

Based on thermal analytical data, the terminal ethynyl monomers upon curing yielded thermo-oxidatively stable resins. They generally exhibited a substantial difference between monomer Tg and onset of curing, indicative of an adequate processing "window." Upon programmed heating to 450°C, the resinified monomers, with the exception of the ortho-ethynyl structures (6a,f), exhibited adequate Tg's for 350°F applications. The ortho-ethynyl substituted structures had relatively low Tg's, possibly inadequate for use at 350°F, that could be attributable to the individual monomer structures and/or a lesser extent of crosslinking resulting from electronic and steric interaction between the ortho-ethynyl- and amido- groups. Further processing and testing of mechanical properties would be necessary to determine if these monomers led to any advantages in mechanical properties such as toughness over earlier AT resins.

The trimethylsilylethynyl-terminated monomers exhibited significantly higher cure temperatures than the ethynyl-terminated structures and also lower thermo-oxidative stability under TGA which precludes their use in high-temperature composite applications.

SECTION IV

EXPERIMENTAL

1. INSTRUMENTS USED

Beckman IR 33 Spectrophotometer, Varian EM360 ^1H NMR Spectrometer, Finigan 4021 Mass Spectrometer (ionizing voltage 70 eV), Waters Associates 244 High-Performance Liquid Chromatograph (HPLC), DuPont Differential Scanning Calorimeter 910 (DSC, samples run under nitrogen), and DuPont Thermo Gravimetric Analyzer 951 (TGA, samples run in air).

2. MONOMERS

3,3'-[Sulfonylbis(p-phenyleneoxy)]dibenzoic acid (3,Z=SO₂)

A mixture of m-hydroxybenzoic acid (Aldrich; 6.50g, 47.1mmol), 4,4'-sulfonyldi(fluorobenzene) (Aldrich; 5.98g, 23.5mmol), and 26g of anhydrous K₂CO₃ in 100mL of anhydrous dimethyl sulfoxide (DMSO) (distilled from CaH₂ under vacuum) was stirred by paddle and maintained under N₂ at 120°C for 24 hours.

After cooling, a solution was obtained by pouring the reaction slurry into ca. 300mL of H₂O. Approximately 100mL of conc. HCl was then added slowly to the cooled (ice bath) solution. Upon the addition of conc. HCl, a white precipitate formed which was filtered off after being allowed to stand in the cold bath for 1/2 hour. The lumpy residue was broken up and washed with copious amounts of H₂O. Recrystallization from an acetic acid-water solution gave 3,3'-[sulfonylbis(p-phenyleneoxy)]-dibenzoic acid as white crystals (which were dried overnight at 60°C [0.1mm Hg]; 9.65g, 83 percent; mp. 217.5-220°C). A sample of the product with m.p. 219-220°C could not be purified further by recrystallization from acetic acid-water solutions.

Calculated for C₂₆H₁₈O₈S: C, 63.66; H, 3.69; S, 6.53

²⁶₁₈Found: C, 63.58; H, 3.67; S, 6.48

IR (KBr): 3700-2120 (m,br,OH), 1735 (sh),
1695 (s,CO)

3,3'-[Carbonylbis(p-phenyleneoxy)]dibenzoic acid (3,Z=CO)

Using the procedure for the synthesis of the related sulfonyldiacid (3,Z=SO₂), the crude carbonyldiacid was obtained by heating a mixture of m-hydroxybenzoic acid (13.0g, 94.2mmol), 4,4'-carbonyldi(fluorobenzene) (10.27g, 47.1mmol), and anhydrous K₂CO₃ (52.0g) in 190mL of anhydrous DMSO at 120°C for 48 hours under N₂.

The crude product was boiled in ca. 400mL of glacial acetic acid, and the boiling solution was filtered to remove suspended solids. The residue thus obtained weighed 2.4g (m.p. 263-265°C). On cooling the filtrate yielded 13.3g (m.p. 257-261°C) of white crystals. This lower melting material was treated as before with ca. 200mL of glacial acetic acid to give a residue (4.7g, m.p. 261-262°C) and white crystals (7.0g, m.p. 260-262°C). All samples were dried at 80°C (0.1mm Hg). The combined purer fractions weighed 14.1g (65 percent).

Calculated for $C_{27}H_{18}O_2$: C, 71.36; H, 3.99

Found: C, 70.93; H, 4.03

IR (KBr): 3770-2200 (s,br,OH), 1690 (s,CO)

3,3'-[Sulfonylbis(p-phenyleneoxy)]dibenzoyl chloride (4,Z-SO₂)

A suspension of 3,3'-[sulfonylbis(p-phenyleneoxy)]dibenzoic acid (16.2g, 33.0mmol) in 130mL of thionyl chloride (Aldrich, Gold Label) was refluxed under N₂ for 4 hours. The suspension dissolved as the reaction progressed. Excess thionyl chloride was removed by distillation at atmospheric pressure initially, followed by the application of a vacuum. The glassy residue was difficult to crystallize. However, after standing 48 hours in a dry box, the residue readily crystallized from a solution of anhydrous tetrahydrofuran (THF) (distilled from sodium/benzophenone) and heptane. 3,3'-[sulfonylbis(p-phenyleneoxy)]dibenzoyl chloride was obtained as white crystals (which were dried overnight at 50°C [0.1mm Hg]; 15.8g, 90 percent; m.p. 113-116°C). (Recrystallization raised the melting point to 116-116.5°C), which could not be improved further by recrystallization.

Calculated for $C_{26}H_{16}Cl_2O_4S$: C, 59.21; H, 3.05; Cl, 13.44; S, 6.08

Found: C, 59.01; H, 2.91; Cl, 13.42; S, 6.10

IR (KBr): 1765 (sh), 1745 (s,CO)

3,3'-[Carbonylbis(p-phenyleneoxy)]dibenzoyl chloride (4,Z=CO)

By a procedure identical with that described for the related sulfonyldiacid chloride (4, Z-SO₂), the title diacid chloride was obtained in 47 percent yield (m.p. 137-140°C) by treatment of the corresponding diacid with thionyl chloride.

Calculated for $C_{27}H_{16}O_4Cl_2$: C, 66.00; H, 3.28; Cl, 14.43

Found: C, 66.23; H, 3.34; Cl, 14.25

IR (KBr): 1760 (sh), 1755 (sh), 1750 (C=O)

2-Trimethylsilylethynylaniline (5,R=o-C≡C-SiMe₃)

2-Iodoaniline (Aldrich; 26.0g, 118.7mmol) was added to 100mL of anhydrous diethylamine (distilled under N₂ from calcium hydride). The solution was cooled (ice bath) after stirring (magnetic bar) for a few minutes under a stream of nitrogen.

Cuprous iodide (0.2g, 1.0mmol), dichlorobis(triphenylphosphine) palladium(II) (1.60g, 2.3mmol), and ethynyltrimethylsilane (Silar; 17.0mL, 122.7mmol) were then added to the reaction vessel. The reaction mixture was stirred under N₂ for 16 hours at room temperature. At the end of this period a substantial quantity of light-yellow oil (presumably diethylamine hydriodide) had settled to the bottom of the flask. A small quantity of white precipitate was also present. Most of the volatiles were removed by vacuum distillation at room temperature. Pentane (ca. 250mL) was then added to the residue. The insolubles were isolated by filtration and washed with pentane. The filtrate was washed with copious amounts of water, dried (MgSO₄), and evaporated to an oil which was distilled under vacuum to give an almost colorless distillate of 2-trimethylsilylethynylaniline. The initial distillate (5.11g, b.p. 86-91°C @ 0.25mm Hg) had one major component with only traces of impurities (GC).

In the latter fraction (14.38g, b.p. 91-95°C @ 0.25mm Hg) these impurities were barely discernible. The total yield was 87 percent. IR (neat): 3500, 3400 (s, NH), 2160 (s, -C≡C-), 1620 (s), 1255 (s, SiMe), 875 (s), 840 (s, SiMe), 760 (s, sh), 747 (s). NMR (CDCl₃): 0.00 (s, SiMe), 3.92 (s, br, NH), 6.20-7.17 (m, 4Ar-H). MS (most prominent peaks): M⁺ (86.4), [M-CH₃]⁺ (100).

2-Ethynylaniline (5, R=o-C≡C-H)

2-Trimethylsilylethynylaniline (13.5g) was dissolved in 200mL of methanol and stirred overnight under nitrogen in the presence of anhydrous potassium carbonate (4.0g). The methanol was then removed by vacuum pump at room temperature. Water was added to the residual material, and the water extracted with pentane. The organic solution was dried (MgSO₄), and evaporated to an oil. 2-Ethynylaniline was isolated as a colorless oil by vacuum distillation (7.0g, 84 percent; b.p. 45°C @ 0.35mm Hg). IR (neat): 3490, 3395 (s, NH), 3300 (s, -C≡C-H), 2100 (m, -C≡C-), 1620 (s), 750 (s). NMR (CDCl₃): 3.40 (s, -C≡C-H), 4.20 (s, br, NH₂), 6.57-7.60 (m, 4Ar-H).

N,N'-2-Ethynylphenyl-3,3'-[Sulfonylbis(p-phenyleneoxy)-dibenzamide (6a)]

A solution of 3,3'-[sulfonylbis(p-phenyleneoxy)]dibenzoyl chloride (6.0g, 11.4mmol) in 50mL of anhydrous THF (distilled under N₂ from sodium/benzophenone) was added dropwise under N₂ to a cooled solution (ice bath) of 2-ethynylaniline (3.0g, 25.6mmol) in 12mL of anhydrous triethylamine (distilled under N₂ from calcium hydride) and 20mL of anhydrous THF. A white precipitate of triethylamine hydrochloride appeared as the addition progressed. After all the acid chloride was added, the reaction mixture was stirred for 3

hours at room temperature. Water was then added, and the aqueous phase extracted with methylene chloride. The methylene chloride solution was washed with water, thoroughly with cold (ice bath) 2N HCl, water, and aqueous NaHCO₃, in that order. After drying the organic layer with MgSO₄, a colorless oil resulted upon removal of the solvent at 40°C by rotary evaporator. A glassy-white foam appeared when residual solvents were removed by vacuum pump at room temperature. The foam was broken up and maintained under vacuum for 24 hours at room temperature. The title compound thus obtained weighed 7.5g (95 percent). The product, however, was contaminated with residual THF (NMR) which could not be removed by vacuum at room temperature. Warming the compound during vacuum drying was not attempted in order to avoid possible polymerization via the terminal ethynyl groups.

Calculated for C₄₂H₂₈N₂O₂S: C, 73.24; H, 4.09; N, 4.06; S, 4.65
Found: C, 72.49; H, 4.05; N, 4.24; S, 4.53

Compounds (6b-j) were obtained using similar procedures. Aqueous acid or base was not allowed to contact compounds containing the trimethylsilyl group. IR, ¹H NMR, HPLC, and DSC data are recorded in Tables 1-4. Elemental analysis for (6b-j) was not obtained owing to difficulties in removing the last traces of solvents and also because of the presence of other minor components (Table 4). Mass spectral data for (6) are listed below [m/e (percent) given]. Major peaks are given; many low intensity peaks are not included. Trace peaks are listed without percent intensity figures.

(6a): 688 (8.9) [M]⁺, 573 (15.8), 572 (44.3) [M-NH-φ-o-C≡C-H]⁺, 454 (3.9) [M-2NH-φ-o-C≡C-H-2H]⁺, 286 (9.4), 228 (77.3), 203 (8.9), 197 (10.8), 196 (26.1), 168 (37.9), 152 (12.3), 140 (12.8), 139 (46.3), 118 (10.3), 117 (100) [NH₂-φ-o-C≡C-H]⁺.

(6b): 976 [M-2H+2Me Si]⁺, 975, 961 [976-CH]⁺, 905 [M+Me Si]⁺, 904, 903, 902³, 889 [904-CH]⁺, 888 [903-CH]⁺, 853³, 833, 832, 831 [M-H]⁺, 830 [M-2H]⁺, 818, 817, 816 [831-CH]⁺, 804 (5.9), 790, 758 [831-Me Si]⁺, 745, 733, 717 [790-Me Si]⁺, 699, 688, 661, 645³ (3.95) [M-NH-φ-o-C≡C-SiMe₃+H]⁺, 619, 454 (9.0) [M-2NH-φ-o-C≡C-SiMe₃-2H]⁺, 147 (36.6) [Me Si-SiMe H]⁺ or [Me SiOSiMe]⁺, 117, (16.6) [NH-φ-o-C≡C-H]⁺, 73 (100) [Me Si]⁺.³ Trace peaks also scattered throughout the lower m/e³ region of the spectrum.

(6c): 214 (18.8), 141 (34.6), 115 (22.9), 77 (64.6) [6₆H₅]⁺, 64 (100) [SO₂]⁺.

(6d): The sample was heated to 500°C. No ions were observed.

- (6e): 189 (20.6) $[\text{NH}-\phi-\text{p}-\text{C}\equiv\text{CSiMe}]^+$, 174 (25.9) $[\text{M}-\text{CH}]^+$, 101 (25.2) $[\text{EtN}]^+$, 86 (100) $[\text{M}^3-\text{CH}]^+$, 58 (30.8) $[\text{86}^3-\text{CH}]^+$. On heating further: 976 (2.6) $[\text{M}^3-2\text{H}+\text{MeSi}]^+$, 975 (5.9) $[\text{M}^3\text{H}+2\text{MeSi}]^+$, 960, (1.7) $[\text{975}-\text{CH}]^+$, 906, 905, 903 (4.1) $[\text{M}^3-2\text{H}+\text{MeSi}]^+$, 888 $[\text{903}-\text{CH}]^+$, 831 (2.4) $[\text{M}-\text{H}]^+$, 806, 804 (3.4), 791 (2.5) $[\text{718}-\text{MeSi}]^+$, 789 (2.3) $[\text{716}+\text{MeSi}]^+$, 727, 725, 718 $[\text{906}-\phi-\text{p}-\text{C}\equiv\text{C}-\text{SeMe}]^+$, 716, 701 $[\text{716}-\text{CH}]^+$, 699, 630, 628 (2.2) $[\text{701}-\text{MeSi}]^+$, 627, 626, 625, 554 $[\text{627}-\text{MeSi}]^+$, 553 $[\text{626}-\text{MeSi}]^+$, 528 (3.2), 530, 529, 527, 526, 456 (1.8) $[\text{M}^3-2\text{NH}-\phi-\text{p}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 454 (6.0) $[\text{456}-2\text{H}]^+$, 147 (34.0) $[\text{Me}_3\text{SiSiMe}_3+\text{H}]^+$ or $[\text{Me}_3\text{SiOSiMe}_2]^+$, 73 (100) $[\text{Me}_3\text{Si}]^+$.
- (6f): 652 (6.0) $[\text{M}]^+$, 536 (19.2) $[\text{M}-\text{NH}-\phi-\text{o}-\text{C}\equiv\text{C}-\text{H}]^+$, 418 (M-2NH- $\phi-\text{C}\equiv\text{C}-\text{H}-2\text{H}]^+$, 328 (6.7), 268 (11.6), 241 (5.9), 238 (10.0), 222 (9.4), 210 (77.9), 203 (16.5), 197 (16.2), 196 (28.8), 168 (22.9), 167 (5.7), 166 (6.0), 165 (7.3), 152 (10.3), 141 (8.8), 140 (9.4), 139 (29.0), 120 (27.0), 117 (30.7) $[\text{NH}_2-\phi-\text{o}-\text{C}\equiv\text{C}-\text{H}]^+$, 116 (9.8), 43 (100).
- (6g): 189 (32.8) $[\text{NH}-\phi-\text{o}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 174 (46.2) $[\text{M}-\text{CH}]^+$, 101 (25.4) $[\text{EtN}]^+$, 86 (100) $[\text{M}^3-\text{CH}]^+$, 58 (26.6) $[\text{86}^3-\text{CH}]^+$, 508 (2.5), 507 (6.5) $[(7), \text{R}=\text{o}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 492 (5.1) $[\text{M}-\text{CH}]^+$, 320 (8.5), 319 (40.8) $[\text{M}-\text{NH}-\phi-\text{o}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 123 (100) $[\text{F}^3-\phi-\text{p}-\text{CO}]^+$. On further heating: 867 $[(6g)-2\text{H}+\text{MeSi}]^+$, 852 $[\text{867}-\text{CH}]^+$, 835, 795 $[\text{Me}-\text{H}]^+$, 780 $[\text{795}-\text{CH}]^+$, 724 $[\text{M}-\text{MeSi}+\text{H}]^+$, 608 $[\text{M}-\text{NH}-\phi-\text{o}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 418 $[\text{M}-2\text{NH}-\phi-\text{o}-\text{C}\equiv\text{C}-\text{SiMe}-2\text{H}]^+$, 147 (15.3) $[\text{MeSiSiMe}_3+\text{H}]^+$ or $[\text{Me}_3\text{SiOSiMe}_2]^+$, 117 (29.0) $[\text{NH}_2-\phi-\text{o}-\text{C}\equiv\text{C}-\text{H}]^+$, 73 (100) $[\text{Me}_3\text{Si}]^+$.
- (6h): 436 (2.7), 435 (12.7) $[(7), \text{R}=\text{m}-\text{C}\equiv\text{C}-\text{H}]^+$, 434 (4.0), 328 (1.3), 320 (10.7), 319 (53.6) $[\text{M}-\text{NH}-\phi-\text{m}-\text{C}\equiv\text{C}-\text{H}]^+$, 291 (1.5) $[\text{319}-\text{CO}]^+$, 238 (3.5), 235 (2.1), 123 (100) $[\text{F}-\phi-\text{p}-\text{CO}]^+$. On heating further: 411 (1.9), 410 (6.0), 393 (2.6), 366 (4.4), 317 (3.0), 274 (1.9), 273 (8.4), 259 (2.2), 242 (4.5), 241 (25.7), 197 (100), 141 (29.4), 121 (36.4), 115 (27.8), 100 (64.8).
- (6i): The sample was heated to 500°C. No ions were observed.
- (6j): 189 (52.7) $[\text{NH}-\phi-\text{p}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 174 (100) $[\text{M}-\text{CH}]^+$, 101 (26.2) $[\text{EtN}]^+$, 86 (100) $[\text{M}^3-\text{CH}]^+$, 58 (20.3) $[\text{86}^3-\text{CH}]^+$. On heating further: 551, 509, 508 (5.3), 507 (13.4) $[(7), \text{R}=\text{p}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 494, 493 $[\text{508}-\text{CH}]^+$, 492 (7.5) $[\text{507}-\text{CH}]^+$, 320 (20.0), 319 (90.3) $[\text{M}-\text{NH}-\phi-\text{p}-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 299 (4.9), 285 (4.2), 264 (6.3), 246 (8.1), 239 (12.7), 237 (9.5), 236 (20.0), 199 (24.0) $[\text{F}-\phi-\text{p}-\text{CO}-\phi]^+$, 123 (100) $[\text{F}-\phi-\text{p}-\text{CO}]^+$, 940, 925 $[\text{940}-\text{CH}]^+$, 869 $[\text{943}-\text{H}-\text{MeSi}]^+$, 868 (1.0) $[\text{941}-\text{MeSi}]^+$, 867 $[\text{940}-\text{MeSi}]^+$, 854, 853 $[\text{868}-\text{CH}]^+$, 767, 796 (1.0) $[(6j)]^+$, 771 $[\text{625}+2\text{MeSi}]^+$, 420 (1.0) $[\text{M}-2-\text{p}-\phi-\text{C}\equiv\text{C}-\text{SiMe}]^+$, 418 (1.0) $[\text{M}-2\text{H}]^+$, 147 (42.3) $[\text{Me}_3\text{SiSiMe}_3+\text{H}]^+$ or $[\text{Me}_3\text{SiOSiMe}_2]^+$, 73 (100) $[\text{Me}_3\text{Si}]^+$.

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