New Thermal Cross-Linkers Based on Triazene: Cross-Linking of Fluorinated Polyimides and Aromatic Polymers

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ABSTRACT: Cross-linkers containing 3,3-dialkyl-1-phenylenetriazene ($-C_6H_4N{=}NNMe_2$) end groups have been prepared by diazotization of aromatic diamines and subsequent reaction of the diazotized products with an amine. Differential scanning calorimetry (DSC) of these cross-linkers exhibits decomposition peak temperatures (T_d) from 180 to 350 °C. Fluorinated polyimides and other aromatic polymers cross-linked with these cross-linkers at 400 °C exhibit high gel contents, increased glass transition temperature (T_g), improved resistance to organic solvents, and improved thermal stability. The dielectric constants of the fluorinated polyimides do not change significantly after cross-linking.

Introduction

Aromatic polyimides find increasing use in the fabrication of multilayer interconnection systems.[1] However, aromatic polyimides absorb moisture,[2] and they are insoluble in common organic solvents. One approach to solve these problems relies on the incorporation of flexible hexafluoroisopropylidene groups, $-(CF_3)_2C-$, into the polymer chain.[3] Aromatic polyimides containing hexafluoroisopropylidene groups exhibit lower dielectric constants which are less sensitive to moisture than the conventional aromatic polyimides[4] and are more susceptible to crazing upon exposure to organic solvents. The crazing fractures the copper circuitry metallized on the polymer surface.

It has been reported that cross-linking improves the resistance to microcracking[5] and solvent-induced crazing[6] of fluorinated polyimides. For example, reactive groups that cross-link at elevated temperature, such as acetylenic groups, have been incorporated into polyimides.[7] Magic-angle cross-polarization ^{13}C-NMR spectroscopy suggests that about 30% of the incorporated acetylene groups undergo cyclotrimerization in the cross-linking process.[8] The rest of the acetylene groups react to form vinyl, or other thermally unstable residues.[9] Reactive end groups based on polymerizable cycloaliphatics and alkenes also have been used to cross-link polyimides. These groups include norbornene,[10] maleimide,[11] allylphenyl,[12] and benzocyclobutene.[13] Unfortunately, the aliphatic residues produced from cross-linking reactions reduce the thermooxidative stabilities of the cross-linked polymers.[14] One approach to improve the thermooxidative stability relies on the replacement of these reactive end caps with [2.2]paracyclophane groups.[14a] Thermal polymerization of the [2.2]paracyclophane end caps produces a cross-linked network with fewer aliphatic sites. Polyimides can also be cross-linked through the trimerization of cyano pendants.[15] This approach requires a catalyst, a possible source of contamination in electronic devices. Finally, biphenylene units have been incorporated into aromatic polyimides as cross-linking sites.[16] The mechanism of cross-linking relies on the arylation of the aromatic nuclei on the polymer chains by the cross-linker, forming thermally stable aryl-aryl bonds. However, the multistep synthesis of the biphenylene end group requires expensive starting materials, and the overall yield is low (about 10%).[17]

The disadvantages of the above-mentioned approaches prompted us to develop new cross-linking reagents that are capable of cross-linking aromatic polyimides through the formation of thermally stable aryl-aryl bonds. Our previous work (Scheme I)[18] revealed that 3,3-dimethyl-1-phenylenetriazenes, $YC_6X_4N{=}NNMe_2$ (X = Y = H; X = F, Y = $-C_6F_4N{=}NNMe_2$), arylate aromatic nuclei at 270 °C without introducing aliphatic residue into the cross-linked network. Furthermore, the arylation does not require the presence of a catalyst. We also found that aryl ethers containing two or three 3,3-dimethyl-1-phenylenetriazene end groups ($-C_6H_4N{=}NNMe_2$) cross-link polyaromatics at elevated temperatures.[19] We report herein the synthesis and characterization of a series of bis(triazene) cross-linkers ($R_1R_2NN{=}NC_6H_4XC_6H_4N{=}NNR_1R_2$) and their use in cross-linking fluorinated polyimides and aromatic polymers.

Results and Discussion

Synthesis and Properties of Bis(triazenes). A general two-step, one-pot procedure for the synthesis of the bis(triazene) cross-linkers ($R_1R_2NN{=}NC_6H_4XC_6H_4N{=}NNR_1R_2$, **3**) is illustrated in Scheme II. An aryldiamine **1** is diazotized in aqueous tetrahydrofuran (THF) to afford a bis(diazonium) compound **2** which was subsequently reacted with a dialkylamine, an arylamine, or an alkylarylamine to give the bis(triazene) cross-linker **3**.

Table I summarizes the overall yields, melting points, and exothermic decomposition peak temperatures (T_d) of a series of bis(triazene)cross-linkers (**3a-i**) prepared in our study. These bis(triazene) cross-linkers are stable at ambient temperature and are soluble in polar solvents such as THF, *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), and cyclohexanone. The T_d of a bis(triazene) compound depends on the nature of R_1 and R_2 attached to the triazene group ($-N{=}NNR_1R_2$). Differential scanning calorimetry (DSC) of bis(triazene) **3d**, in which $R_1 = R_2 = Me$, exhibits a T_d of 263 °C, whereas bis(triazene) **3h**, which is identical to **3d** except $R_1 = R_2 = Et$, exhibits a T_d of 350 °C. However, when a phenyl substituent is introduced, such as in bis(triazene) **4i** where $R_1 = H$ and $R_2 = C_6H_5$, the T_d is reduced to 180 °C. The T_d of a bis(triazene) also depends on the nature of X in the central aryl segment ($-C_6H_4XC_6H_4-$). For example, changing X from O (as in bis(triazene) **3a**) to SO_2 (as in bis(triazene) **3b**), the T_d increases from 269 to 290 °C. The compatibility of a bis(triazene) cross-linker with the polymer that is going to be cross-linked, can also be tailored by changing the molecular structure of $-C_6H_4XC_6H_4-$.

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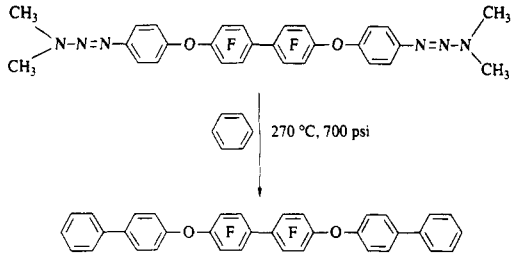
Scheme I
Arylation of Benzene with a Bis(triazene) Compound



Scheme II
General Procedure for the Preparation of Bis(triazene) Cross-Linkers

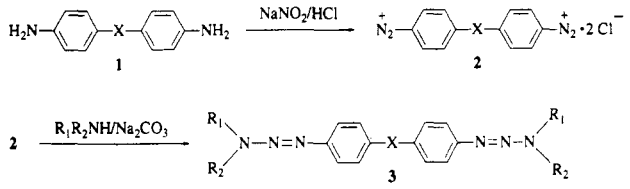
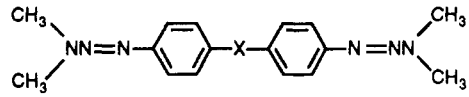
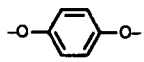
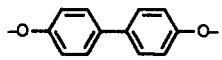
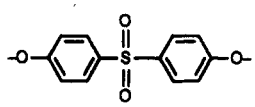
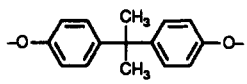
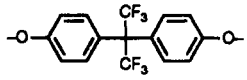
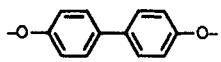
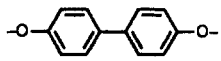


Table I
Overall Yield (%), Melting Point (°C), and Exothermic Decomposition Peak Temperature (T_d, °C) of Bis(triazenes) 3

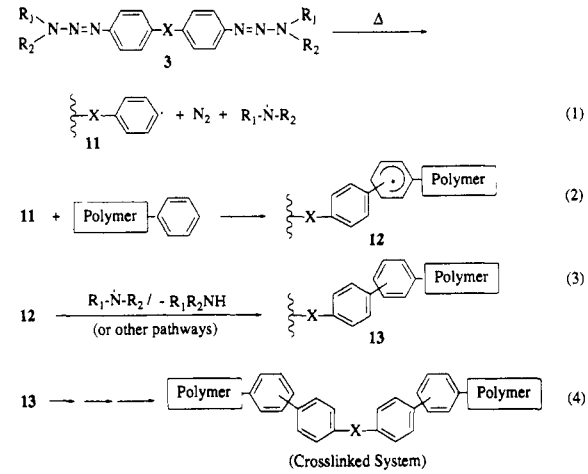


3

3	X	R_1	R_2	yield	mp	T_d
a	-O-	CH_3	CH_3	59	53–55	269
b		CH_3	CH_3	48	209–211	290
c		CH_3	CH_3	91	140–43	277
d		CH_3	CH_3	77	167–69	263
e		CH_3	CH_3	57	159–60	288
f		CH_3	CH_3	63	74–76	279
g		CH_3	CH_3	68	125–28	283
h		CH_3CH_2	CH_3CH_2	67	105–8	350
i		H	C_6H_5	61	155–57	180

Mechanism of Cross-Linking. A mechanism of cross-linking, which is similar to that proposed for the phenylation of benzenes with 3,3-dimethyl-1-phenylenetriazene,[20] is outlined in Scheme III. The triazene end groups of **3** decompose at elevated temperature to form σ-radicals **11**, nitrogen gas, and a dimethylaminyl radical (reaction 1). Radicals **11** homolytically substitute aromatic nuclei of the polymer chains (reaction 2) to form σ-complexes **12**. The σ-complexes **12** then aromatize by reacting with the dimethylaminyl radicals, or through other pathways, to form **13** (reaction 3) which produces a cross-linked system through the repetition of reactions 1–3.

Scheme III
Proposed Mechanism for the Cross-Linking of Polyaromatics by Bis(triazenes)



Cross-Linking Efficiency. The gel content of a cross-linked system is an indication of the cross-linking efficiency of a bis(triazene) cross-linker. The gel contents of fluorinated polyimide **4** (structure in Table II) cured with a series of bis(triazene) cross-linkers (**3a–g**) at 400 °C were determined after extraction with NMP for 24 h and are summarized in Table III. Under the same curing conditions, control samples of **4** containing no cross-linker gave 0% gel content. Heating blends of polyimide **4** with **3a–g** at 200 °C for 60 min also showed no evidence of cross-linking.

Polyimide **4** cured with **3d** and **3g** at 400 °C exhibited gel contents of 93% and 85%, respectively. By contrast, polyimide **4** cured with **3a** at 400 °C exhibited a gel content of 0%. Thermal gravimetric analysis (10 °C/min under N_2) of polyimide **4** indicates its weight loss at 400 °C is less than 3%. The bis(triazenes), however, exhibit various extents of weight loss at their T_d's. According to our proposed mechanism, a bis(triazene) decomposes to form σ-radical species for cross-linking. Provided that the radical species are nonvolatile and that the rate of homolytic substitution is fast, a bis(triazene) should exhibit weight loss at T_d not exceeding the stoichiometric amounts of dimethylamine and nitrogen gas. On the basis of these assumptions, the calculated weight losses at T_d for **3a**, **3d**, and **3g** are 46%, 30%, and 23%, respectively (Table III). TGA and DSC data of **3d** and **3g** indicate that their weight losses at T_d are 34% and 28%, respectively. These results suggest that most of the radical species generated by the decomposition of **3d** and **3g** remain in the system to cross-link the polymer, producing high gel contents. In contrast, the TGA and DSC data of **3a** indicate the weight loss at T_d is 70% (Table III). This high weight loss at T_d suggests that the radical species generated by **3a** volatilizes considerably, resulting in inefficient cross-linking.

As shown in Table III, bis(triazene) **3f**, which contains aliphatic hydrogen atoms, exhibits 38% weight loss at T_d. This is close to the calculated value of 28%. Polyimide **4** cured with **3f** at 400 °C, however, gives a gel content of 16%. It is possible that a considerable fraction of the radicals generated in the **4**/**3f** system are consumed by hydrogen atom abstraction from the isopropylidene groups of **3f**. Such a reaction would lead to reduced cross-linking as observed. We also find that polyimide **4** cured with sulfone-containing bis(triazenes), such as **3b** and **3e**, exhibits low gel contents.

A series of polyimides (**5–8**) and other polyaromatics (**9** and **10**) have been cross-linked with **3d** (Table IV). All

Table II
Chemical Structures of Polymers

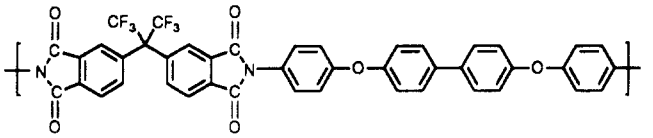
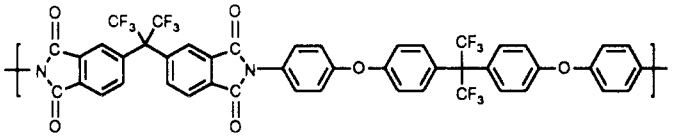
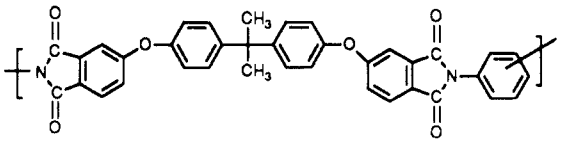
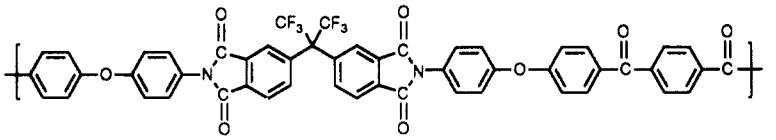
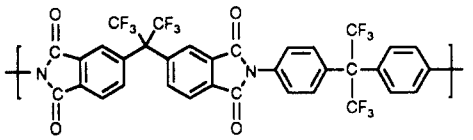
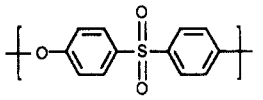
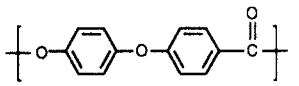
polymer	structure
4	
5	
6	
7	
8	
9	
10	

Table III
Weight Losses at T_d of 3 and Gel Contents of Fluorinated Polyimide 4 Cross-Linked with 20 wt % 3

	weight loss at T_d		
cross-linker 3	calcd	measd	% gel content
a	46	70	0
b	40	48	65
c	37	50	55
d	30	34	93
e	27	28	21
f	28	37	16
g	23	28	85

Table IV
Gel Contents of Polymers Cured with Bis(triazene) 3d

polymer	wt % of **3d**	% gel content	polymer	wt % of **3d**	% gel content
4	20	93	8	20	1
5	20	81	9	15	98
6	20	83	10	10	64
7	30	57			

the cured polymer thin films (10–20 μm thick) are flexible and are insoluble in polar organic solvents such as NMP and DMAc. In general, fluorinated polyimides and the other polyaromatics cured with **3d** exhibit high gel contents.

Polyimide 8 cured with **3d** exhibits an exceptionally low gel content of 1% (Table IV). Aryl σ-radicals, such as 11 which we propose are responsible for cross-linking via homolytic substitution (Scheme III), are known to be electrophilic.[21] We propose that the electron-withdrawing group, $(CF_3)_2C$, deactivates the aryl rings in 8 toward radical attack. As a result, cross-linking in the 8/**3d** system

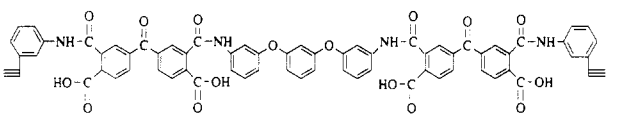


Figure 1. Acetylene-terminated amic acid oligomer.

is inefficient. The same effect is observed in polyimides 7 and 10 which contain electron-withdrawing carbonyl groups.

Dielectric Constant and Solvent-Induced Stress Crazing. Initially we studied the dielectric constants of polyimides 4 and 5 cured with bis(triazene) cross-linkers **3d** and **3g**. We selected 4 and 5 for our studies because they have low dielectric constants at 0% relative humidity (RH) and exhibit high gel contents after cross-linking. Furthermore, they contain no aliphatic moiety and are therefore thermooxidatively stable.

It was reported that fluorinated polyimides cured with an acetylene-terminated oligomer of amic acid (see Figure 1 for the molecular structure of the acetylene-terminated oligomer) exhibited improved resistance to organic solvents.[6] We wanted to compare this acetylene-terminated oligomer with **3d** and **3g** in their effects on the dielectric constants of polyimides 4 and 5. Thin films of polyimides 4 and 5 cured with 20 wt % of the acetylene-terminated oligomer, **3d**, and **3g** were prepared. The dielectric constants of these films were measured at 0% and 60% RH, and the results are summarized in Table V.

Polyimides contain polar groups (permanent dipoles) which absorb moisture.[2c] As the relative humidity of the environment increases, the moisture content of the polymer increases, resulting in increased dielectric constants. The dielectric constants of 4 and 5 cured without a cross-

Table V
Dielectric Constants of Polyimide Films Prepared with and without Cross-Linkers, Measured at 10 kHz on 10–20-μm Films

cross-linker	polyimide 4			polyimide 5		
	0% RH	60% RH	Δε, %	0% RH	60% RH	Δε, %
none	2.82	3.21	14	2.72	3.03	10
acetylene-terminated amic acid oligomer (20 wt %)	2.97	3.57	20	2.82	3.38	21
3d (20 wt %)	2.82	3.30	14	2.80	3.11	11
3g (20 wt %)	2.84	3.21	14	2.75	3.07	11

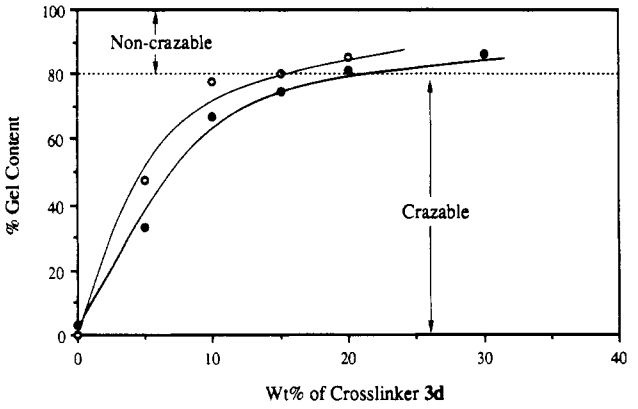


Figure 2. Effect of the gel content on solvent-induced stress crazing of fluorinated polyimides: (○) polyimide 4; (●) polyimide 5.

linking reagent exhibit an increase of about 10% as the RH increased from 0% to 60%. According to the proposed cross-linking mechanism, the cross-linkages (σ-radical species) generated by **3d** and **3g** contain no polarizable, hydrophilic groups. When **4** and **5** are cross-linked with **3d** or **3g**, no additional polar group is introduced into system. As a result, when the RH increases from 0% to 60%, their dielectric constants also exhibit an increase of about 10%. In contrast, the dielectric constants of **4** and **5** cured with the acetylene-terminated oligomer exhibit an increase of about 20% over the same RH range. The larger increase in dielectric constants is probably due to additional imide groups introduced by the acetylene-terminated oligomer. Furthermore, polyimides **4** and **5** cured with the acetylene-terminated oligomer exhibit higher dielectric constants at 0% RH than those cured with **3d** and **3g**.

We found that the solvent-induced stress crazing of polyimides **4** and **5** depends on their gel contents. The correlation between the concentration of cross-linker **3d**, gel contents, and solvent-induced stress crazing is shown in Figure 2. Increased cross-linker concentration results in an increase of the gel content. When the gel content reaches a threshold of about 80%, the cured polymer thin films no longer solvent stress craze.

It is believed that polymer thin films cured at high temperature exhibit residual stress.[22] Solvent swelling releases the residual stress, leading to crazing upon drying. Chemical cross-linking prevents the cured polymer from swelling and, thus, improves the resistance to solvent-induced crazing.

Thermal Stability. The glass transition temperatures (T_g) and TGA data of polyimides **4** and **5** cured with 20 wt % **3d** or **3g** are summarized in Table VI. The T_g's of the cross-linked polymers increase by 10–68 °C after cross-linking. Although the TGA onset temperature decreases by about 5% after cross-linking, there is no significant change for the temperature at 5% weight loss, whereas polyimides **4** and **5** cured with 20 wt % **3d** or **3g** exhibit improved TGA weight loss at 700 °C (in air) and the isothermal weight loss at 400 °C (3 h in air) by about 50%.

Experimental Section

The reported melting points of all compounds are uncorrected. The dielectric constants of free-standing polymer films were measured at 10 kHz according to the method reported by Mercer and Goodman.[23] Elemental analyses were performed by Galbraith Laboratories, Inc.

The ^{1}H-NMR spectra were recorded on a Varian XL-300 spectrometer. All chemical shifts are expressed in ppm downfield from internal tetramethylsilane. The IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed with a Perkin-Elmer 7700 thermal analyzer at 10 °C/min under a nitrogen atmosphere. Catalytic hydrogenation was performed with a Parr 3911 hydrogenation apparatus (Parr Instrument Co.). Gel permeation chromatography (GPC) was performed with a Hewlett-Packard 1090 liquid chromatograph instrument fitted with four Polymer Labs PL gel columns (100-, 500-, 10^3-, and 10^4-Å pore diameters) using THF as eluent and polystyrene standards.

Polyimide **5** was obtained from Ethyl Corp. under the trade name of Eymyd HP-40. Polyimide **6** was obtained from General Electric under the trade name of Ultem 1000. Polyimide **8** was obtained from Hoechst under the trade name of Sixef-44. Poly(aryl ether sulfone) (**9**) was obtained from ICI under the trade name of Victrex PES 4100. The acetylene-terminated amic acid oligomer was obtained from National Starch & Chemical Corp. under the trade name of Thermid LR-600. The authors thank the following inventors for their generous donations of polymers: R. H. Whiteley for poly(ether ketone imide) (**7**)[24] and V. Jansons for poly(aryl ether ketone) (**10**).[25] All other chemicals were used as received without further purification.

General Procedure for Cross-Linking Polymers. Typically, 2.4 g of the linear polymer, together with 0.6 g (20 wt %) of the bis(triazene) cross-linker, was dissolved in 12 mL of NMP or DMAc. The solution was filtered and degassed under reduced pressure before use. Thin films (10–20 μm) of the polymer were obtained by spin-casting the resulting solution onto a 4 in. × 4 in. Pyrex glass plate. The coated plate was then soft-baked for 30 min each at 100 and 200 °C to remove most of the solvent. The resulting polymer film was finally cured at 400 °C for 30 min. The final high-temperature treatment is necessary to decompose the bis(triazene) cross-linker and to cross-link the polymer. All films were void and bubble free when prepared under these conditions. Free-standing, flexible films were obtained by releasing the cured polymers from their substrates after soaking the coated plates in water at 90 °C for 4–16 h.

Since polymer **10** is insoluble in NMP or DMAc, a mixture of dichloromethane and 1,1,1,3,3,3-hexafluoroisopropyl alcohol (1:1, v/v) was used as the solvent.

Determination of the Gel Content. Free-standing films (0.2–0.5 g) were first rinsed with water and acetone and then dried at 200 °C for 30 min. The dried samples, with the exception of polymer **10**, were extracted with NMP in a Soxhlet apparatus for 24 h. The insoluble fraction was removed, cooled to room temperature, rinsed with acetone, and then dried in a vacuum oven at 100 °C for 16 h. The gel content is defined as the weight ratio of the cross-linked polymer isolated after extraction to that of the polymer prior to extraction.

Free-standing films of the cured polymer **10** (0.2–0.5 g) were stirred in 100 mL of concentrated sulfuric acid at 150 °C over a period of 24 h. The insoluble fraction was filtered and was then extracted with boiling water in a Soxhlet apparatus for 5 h. The gel content was determined after vacuum drying the insoluble fraction at 100 °C for 16 h.

Table VI
DSC and TGA Data of Polyimides 4 and 5 Cured with 20 wt % Bis(triazenes) 3d and 3g

	polyimide 4			polyimide 5		
	none	3d	3g	none	3d	3g
T_g (°C)	272	340	305	258	277	268
onset wt loss in air (°C)	544	506	510	525	510	501
temp at 5% wt loss in air (°C)	518	515	514	520	514	510
max wt loss at 700 °C in air (%)	85	34	36	89	39	42
isothermal wt loss at 400 °C for 3 h (%)	15.8	8.7	7.6	9.4	4.9	4.3

Determination of Solvent-Induced Stress Crazing. An aliquot of the polyimide/cross-linker solution in NMP was coated onto a 4 in. × 4 in. Pyrex glass plate by spin-casting. The resulting thin polyimide coating (10–20 μm) then was soft-baked and cured as described in the general procedure for cross-linking polymers. A second coating of the polyimide/cross-linker solution was applied to the polyimide-coated glass plate in such a way that only part of the first coating was covered. The resulting plate was soft-baked for 30 min each at 100 and 200 °C. After cooling to room temperature, the underlying layer of polymer, especially along the overlapping edges, was examined under an optical microscope for cracks. If solvent-induced stress crazing occurs, cracks are readily visible underneath the top polyimide layer.

Fluorinated Polyimide 4. Polyimide 4 was prepared according to the procedure reported by Jones et al.[26] (T_g = 260 °C, M_n = 11 570, and M_w = 22 740).

2,2-Bis[4-(4-nitrophenoxy)phenyl]hexafluoropropane. To a 500-mL three-necked flask equipped with a mechanical stirrer and a reflux condenser were added 17.15 g (51.0 mmol) of 4,4′-(hexafluoroisopropylidene)diphenol (Aldrich Chemical Co.), 17.57 g (111.5 mmol) of 1-chloro-4-nitrobenzene, 27.83 g (201.4 mmol) of potassium carbonate, and 130 mL of DMAc. The mixture was heated to reflux for 16 h with constant stirring and then stirred overnight at room temperature. To the reaction mixture was added with stirring 300 mL of distilled water. The precipitate was filtered, washed with water, and recrystallized from ethanol to yield 29.0 g (98%) of the product, mp 158–161 °C (lit.[27] mp 158–60 °C). IR (KBr): 1590, 1510, 1340, 1240, 1170, 975, 880, 760, 650 cm^{-1}.

2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane Dihydrochloride. To a solution of 23.75 g (41.0 mmol) of 2,2-bis[4-(4-nitrophenoxy)phenyl]hexafluoropropane in a mixture of 60 mL of ethanol, 60 mL of THF, and 40 mL of ethyl acetate was added 1.0 g of a platinum catalyst on activated charcoal (0.5% Pt). Hydrogenation was carried out under 60 psi for 16 h at room temperature. The reaction mixture was filtered and the solvent removed under reduced pressure at about 35 °C. The residue was redissolved in 200 mL of anhydrous THF, and anhydrous hydrogen chloride gas was passed through the solution. The reaction mixture was chilled and the precipitate filtered, washed with more anhydrous THF, and vacuum dried to give 23.6 g (97.2%) of the product, mp 270 °C dec. IR (KBr): 2900, 1500, 1250, 1177 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 7.0–7.8 (m, 16 H, ArH), 10.25 (b, 6 H, ammonium). Anal. Calcd for $C_{27}H_{22}Cl_2F_6N_2O_2$: C, 54.84; H, 3.75; Cl, 11.99; F, 19.28; N, 4.74. Found: C, 54.06; H, 3.93; Cl, 12.23; F, 19.57; N, 4.67.

To a solution of 10.0 g of the dihydrochloride in 150 mL of water was added with stirring 50 mL of 1 N NaOH. The insoluble diamine was filtered, washed with plenty of water, suction air dried, and vacuum dried at room temperature to give 6.6 g of the free diamine, mp 148–151 °C (lit.[27] mp 150–2 °C).

General Procedure for the Preparation of Bis(triazene) Cross-Linkers: 1,1′-(oxydi-1,4-phenylene)bis[3,3-dimethyl-1-triazene] (3a). To a stirred solution of 3.60 g (12.4 mmol) of 4-aminophenyl ether (Aldrich Chemical Co.) in 160 mL of tetrahydrofuran (THF) in a 500-mL three-neck flask equipped with a mechanical stirrer, a thermometer, and an addition funnel was added slowly a solution of 7.0 mL (86.7 mmol) of 12 N hydrochloric acid in 80 mL of water. The reaction solution was then chilled at −5 °C with stirring. To this vigorously stirred mixture was added dropwise over a period of 30 min a solution of 3.50 g (50.8 mmol) of sodium nitrite in 50 mL of water. Stirring was continued at −5 to 0 °C for an additional 60 min. At the end of the reaction, THF was removed under reduced pressure at 25 °C. The remaining aqueous solution was chilled at 0 °C and neutralized to pH 6–7 with an ice-cold, saturated solution of sodium carbonate. This neutralized solution was immediately poured into a 1-L beaker containing a freshly prepared solution of 5.0 g (61.3 mmol) of dimethylamine hydrochloride and 11.0 g (94.34 mmol) of sodium carbonate in 150 mL of ice water. The mixture was stirred vigorously with a mechanical stirrer for 10 min and then extracted with four 50-mL portions of dichloromethane. The combined extracts were washed twice with distilled water, dried over anhydrous magnesium sulfate, and decolorized with activated charcoal. After filtration, the solvent was removed under reduced pressure at 35 °C and the oily residue was recrystallized from acetone to give 2.93 g (59%) of **3a**, mp 53–5 °C (lit.[28] mp 45 °C). IR (KBr): 1585, 1492, 1231, 1083 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.30 (s, 12 H, CH_3), 6.91–7.60 (m, 8 H, aromatic). Anal. Calcd for $C_{16}H_{20}N_6O$: C, 61.52; H, 6.45; N, 26.90. Found: C, 61.98; H, 6.68; N, 26.93.

1,1′-(Sulfonyldi-1,4-phenylene)bis[3,3-dimethyl-1-triazene] (3b). The general procedure was followed except 3.50 g (14.1 mmol) of 4-aminophenyl sulfone (Aldrich Chemical Co.) dissolved in 160 mL of methanol was used. Recrystallization of the crude product from a dichloromethane/hexanes mixture (1:20, v/v) afforded 2.32 g (48%) of **3b**, mp 209–11 °C (lit.[28] mp 198 °C). IR (KBr): 1476, 1148, 1108 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.32 (s, 12 H, CH_3), 7.40–8.10 (m, 8 H, aromatic). Anal. Calcd for $C_{16}H_{20}N_6O_2S$: C, 53.32; H, 5.59. Found: C, 53.33; H, 5.61.

1,1′-[[1,4-Phenylene]bis(oxy-4,1-phenylene)]bis[3,3-dimethyl-1-triazene] (3c). The general procedure was followed except 3.6 g (12.4 mmol) of 1,4-bis(4-aminophenoxy)benzene (Chriskev Co.) was used. Recrystallization of the crude product from a mixture of acetone/hexanes (1:30, v/v) afforded 4.56 g (91%) of **3c**, mp 140–3 °C. IR (KBr): 1448, 1222, 1084 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.29 (s, 12 H, CH_3), 6.82–7.48 (m, 12 H, aromatic). Anal. Calcd for $C_{22}H_{24}N_6O_2$: C, 65.33; H, 5.98; N, 20.78. Found: C, 65.02; H, 6.13; N, 21.13.

1,1′-[[1,1′-Biphenyl]-4,4′-diylbis(oxy-4,1-phenylene)]bis[3,3-dimethyl-1-triazene] (3d). The general procedure was followed except 15.0 g (40.7 mmol) of 4,4′-bis(4-aminophenoxy)-biphenyl (Chriskev Co.) was used. Recrystallization of the crude product from a mixture of CH_2Cl_2/acetone (1:5, v/v) gave 15.05 g (77%) of **3d**, mp 167–9 °C. IR (KBr): 1492, 1250, 1067 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.32 (s, 12 H, CH_3), 6.86–7.66 (m, 16 H, aromatic). Anal. Calcd for $C_{28}H_{28}N_6O_2$: C, 69.98; H, 5.87; N, 17.49. Found: C, 70.74; H, 5.87; N, 16.29.

1,1′-[[Sulfonyldi-1,4-phenylene]bis(oxy-4,1-phenylene)]-bis[3,3-dimethyl-1-triazene] (3e). The general procedure was followed except 3.90 g (9.1 mmol) of 2,2-bis[4-(4-aminophenoxy)-phenyl] sulfone (Chriskev Co.) was employed. Recrystallization of the crude product from a mixture of CH_2Cl_2/acetone (1:5, v/v) afforded 2.84 g (57%) of **3e**, mp 159–60 °C. IR (KBr): 1468, 1239, 1189, 1104 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.29 (s, 12 H, CH_3), 6.81–8.02 (m, 16 H, aromatic). Anal. Calcd for $C_{28}H_{28}N_6O_4S$: C, 61.75; H, 5.18; N, 15.43. Found: C, 62.03; H, 5.35; N, 15.39.

1,1′-[[2,2-Propylidenedi-1,4-phenylene]bis(oxy-4,1-phenylene)]bis[3,3-dimethyl-1-triazene] (3f). The general procedure was followed except 3.6 g (16.0 mmol) of 2,2-bis[4-(4-aminophenoxy)phenyl]propane (Chriskev Co.) was used. Recrystallization of the crude product from a mixture of acetone/hexanes (1:20, v/v) gave 3.13 g (63%) of **3f**, mp 74–6 °C. IR (KBr): 1493, 1246, 1078 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.61 (s, 6 H, CCH_3), 3.29 (s, 12 H, NCH_3), 6.72–7.53 (m, 16 H, aromatic). Anal. Calcd for $C_{31}H_{34}N_6O_2$: C, 71.24; H, 6.56; N, 16.08. Found: C, 71.62; H, 6.97; N, 15.82.

1,1′-[[2,2-Hexafluoropropylidenedi-1,4-phenylene]bis(oxy-4,1-phenylene)]bis[3,3-dimethyl-1-triazene] (3g). The general procedure was followed except 10.06 g (17.0 mmol) of 2,2-

bis[4-(4-aminophenoxy)phenyl]hexafluoropropane dihydrochloride was used. Recrystallization of the crude product from a mixture of CH_2Cl_2/acetone (1:5, v/v) afforded 10.57 g (68%) of **3g**, mp 125–8 °C. IR (KBr): 1495, 1247, 1198, 1086 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 3.20 (s, 12 H, CH_3), 6.82–7.53 (m, 16 H, aromatic). Anal. Calcd for $C_{31}H_{28}F_6N_6O_2$: C, 59.05; H, 4.48; N, 13.33. Found: C, 58.50; H, 4.53; N, 12.67.

1,1′-[[1,1′-Biphenyl]-4,4′-diylbis(oxy-4,1-phenylene)]bis[3,3-diethyl-1-triazene] (3h). The general procedure was followed except 5.00 g (13.6 mmol) of 4,4′-bis(4-aminophenoxy)biphenyl (Chriskev Co.) was used. The intermediate bis(diazonium) salt was reacted with 4.48 g (61.3 mmol) of diethylamine. The reaction afforded 7.50 g (67%) of **3h** after recrystallization from a mixture of dichloromethane/acetone (1:10, v/v), mp 105–8 °C. IR (KBr): 1600, 1495, 1240, 1087 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 1.43 (t, 12 H, CH_3), 3.90 (q, 8 H, NCH_2), 6.90–7.89 (m, 16 H, ArH). Anal. Calcd for $C_{32}H_{36}N_6O_2$: C, 71.62; H, 6.76; N, 15.66. Found: C, 72.04; H, 6.69; N, 14.79.

1,1′-[[1,1′-Biphenyl]-4,4′-diylbis(oxy-4,1-phenylene)]bis[3-phenyl-1-triazene] (3i). The general procedure was followed except 7.50 g (20.4 mmol) of 4,4′-bis(4-aminophenoxy)biphenyl was employed. The intermediate bis(diazonium) salt was treated with 5.80 g (44.8 mmol) of aniline. Recrystallization of the crude product from a mixture of dichloromethane/acetone (1:5, v/v) afforded 6.80 g (61%) of **3i**, mp 155–7 °C. IR (KBr): 3265, 1500, 1246, 1100 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 7.0–7.8 (m, ArH). Anal. Calcd for $C_{36}H_{28}N_6O_2$: C, 74.98; H, 4.89; N, 14.57. Found: C, 75.31; H, 5.08; N, 13.32

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