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Poly(phenylquinoxalines) Containing Ethynyl Groups

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ABSTRACT: A series of poly(phenylquinoxalines) containing 0, 5, 10, 30, and 100 mol% pendant ethynyl groups were prepared in high molecular weight forms from the reaction of 3,3′,4,4′-tetraaminobiphenyl with aromatic bis(α-diketones) and/or ethynyl-substituted aromatic bis(α-diketones). The novel ethynyl-containing bis(α-diketone) monomers were prepared from the reaction of bromo-substituted bis(α-diketones) with (trimethylsilyl)acetylene, using dichlorobis(triphenylphosphine)palladium as catalyst followed by cleavage of the trimethylsilyl group with a weak base. The polymers were characterized by a variety of thermal methods. The thermally induced reaction of the ethynyl groups cross-linked the polymers, which resulted in an increase in their apparent glass transition temperatures, rendered the polymers insoluble, and lowered their thermooxidative stability. Prior to polymer work, three model compounds were prepared and characterized.

Introduction

High-temperature resins for structural applications (e.g., adhesives and composites) are needed which can be fabricated without the evolution of volatiles and which retain mechanical performance under harsh conditions. In an attempt to develop improved high-temperature structural resins, researchers have used the ethynyl group to end cap a variety of oligomers such as the phenylene,[1] imide,[2] ether–ketone–sulfone,[3] phenylquinoxaline,[4,5] and phenyl-*as*-triazine.[6] The thermally induced reaction of the ethynyl end groups on the oligomers resulted in chain extension. It was initially proposed that this occurred by trimerization of the ethynyl groups to form benzene rings. However, model compound work showed the formation of a complex product consisting of a minor portion (~20%) comprised of dimers, trimers, and tetramer and a major fraction made up of oligomers with molecular weights up to 2100.[7] Linear ether–ketone–sulfone polymers containing pendant ethynyl groups have also been reported.[3,8] A precursor linear polymer containing pendant acetyl groups was first formed. The acetyl groups were converted to ethynyl groups via the Vilsmeyer reaction (phosphorus oxychloride and *N,N*-dimethylformamide) and subsequent cleavage of the intermediate β-chlorocinnamaldehyde with potassium hydroxide.

Poly(phenylquinoxalines) (PPQ) are high-temperature thermoplastic structural resins which exhibit good dimensional stability at temperatures less than their glass transition or heat distortion temperatures.[9] In an attempt to improve the high-temperature dimensional stability of PPQ and also the solvent resistance, a series of linear PPQ containing pendant ethynyl groups were prepared and subsequently thermally cross-linked as reported herein. This work was performed to determine what effect the ethynyl groups had on processability and after the thermally induced reaction, on polymer properties.

Experimental Section

4-(4-Bromophenoxy)benzil (I). A solution of phenylacetyl chloride (30.8 g, 0.2 mol) and 4-bromodiphenyl ether (60.0 g, 0.2 mol) in carbon disulfide (50 mL) was added dropwise during 1 h to a stirred slurry of anhydrous aluminum chloride (30.0 g, 0.23 mol) in carbon disulfide (150 mL) at ~15 °C. The brown reaction mixture was stirred overnight at ambient temperature and subsequently poured into a stirred mixture of ice and hydrochloric acid. Methylene chloride (100 mL) was added to aid in the workup. The organic phase was washed thoroughly with water, dried over calcium sulfate, treated with charcoal, and concentrated to dryness to yield a slightly tacky tan solid (88 g). The solid was washed in a blender with hexanes (300 mL) to yield a light tan solid (56 g), mp 105–114 °C. Recrystallization from a mixture of ethanol (700 mL) and toluene (150 mL) provided a white crystalline solid (40.5 g, 55% yield), mp 116–118 °C. The intermediate ketone (27.5 g, 0.075 mol) and selenium dioxide (8.3 g, 0.075 mol) were refluxed overnight in glacial acetic acid (150 mL). The black reaction mixture was filtered and the cooled filtrate poured into cold water to precipitate a yellow solid. Recrystallization from ethanol (200 mL) provided 4-(4-bromophenoxy)benzil as yellow crystals (22.4 g, 78% yield): mp 85–86 °C; mass spectroscopy (MS), no M^+, major fragment *m/e* 275, 277 ($^+COC_6H_4OC_6H_4Br$).

4-[4-[(Trimethylsilyl)ethynyl]phenoxy]benzil (II). 4-(4-Bromophenoxy)benzil (3.81 g, 0.1 mol), (trimethylsilyl)acetylene (1.96 g, 0.02 mol), and dichlorobis(triphenylphosphine)palladium (0.30 g) in triethylamine (20 mL) were placed under a nitrogen atmosphere in a sealed flask and heated at 66–68 °C for 4 h. The cooled brown reaction mixture was poured into cold dilute hydrochloric acid to yield a brown oil, which was extracted with methylene chloride. The methylene chloride solution was washed with dilute aqueous hydrochloric acid and water, dried over magnesium sulfate, and concentrated on a rotary evaporator to yield a brown gum (4.0 g). The gum was extracted with boiling cyclohexane (100 mL) (a small amount remained insoluble) and the solution treated with charcoal, filtered, and concentrated to yield 4-[4-[(trimethylsilyl)ethynyl]phenoxy]benzil as an orange gum (3.4 g, 85% yield): MS, no M^+, major fragment *m/e* 293 $[^+COC_6H_4OC_6H_4C{\equiv}CSi(CH_3)_3]$.

4-(4-Ethynylphenoxy)benzil (III). 4-[4-[(Trimethylsilyl)ethynyl]phenoxy]benzil (2.6 g, 0.0065 mol) was dissolved in a mixture of methanol (100 mL) and methylene chloride (10 mL). Potassium carbonate (~0.5 g) was added, and the reaction mixture darkened upon stirring for 1 h at ~40 °C. The reaction mixture was poured into cold aqueous dilute hydrochloric acid to yield a brown oil, which was extracted with methylene chloride. The organic phase was washed with water, dried over magnesium sulfate, and concentrated to yield an orange gum (2.6 g). The gum was boiled in cyclohexane (100 mL) (some insolubles) and the resultant solution treated with charcoal, filtered, and concentrated to yield 4-(4-ethynylphenoxy)benzil as a yellow gum (1.6 g, 57% yield): MS, M^+ *m/e* 326, major fragment *m/e* 221 $[^+COC_6H_4OC_6H_4C{\equiv}CH]$.

4,4′-Oxybis(4″-bromobenzil) (IV). 4,4′-Oxybis(4″-bromobenzil) was prepared according to a known procedure.[10] The acid chloride of (4-bromophenyl)acetic acid was reacted with diphenyl ether in *sym*-tetrachloroethane in the presence of anhydrous aluminum chloride. The resultant intermediate diketone (mp 185–187 °C) was subsequently oxidized with selenium dioxide in refluxing glacial acetic acid. After recrystallization from benzene, 4,4′-oxybis(4″-bromobenzil) was obtained as a yellow crystalline solid, mp 193–194 °C (lit.[10] mp 192–193 °C).

4,4′-Oxybis[4″-[(trimethylsilyl)ethynyl]benzil] (V). 4,4′-Oxybis(4″-bromobenzil) (11.8 g, 0.02 mol), dichlorobis(triphenylphosphine)palladium (0.3 g), cuprous iodide (0.1 g), (trimethylsilyl)acetylene (8.3 g, 0.085 mol), triethylamine (25 mL), and pyridine (100 mL) were stirred in a sealed flask under nitrogen at 80 °C for 3 h. The orange-brown reaction mixture (containing needles) was poured into cold dilute aqueous hydrochloric acid to precipitate an orange gum. The gum was washed with water and dissolved in benzene (150 mL), and the resultant solution was treated with charcoal, filtered, and concentrated to yield an orange gummy residue (12.5 g). The residue was boiled in cyclohexane (300 mL) and the resultant solution treated with charcoal, filtered, and concentrated to a volume of ~100 mL. A pale yellow solid (7.3 g, 58% yield), mp 122–124 °C, formed upon cooling, which was recrystallized from cyclohexane (~100 mL) to yield 4,4′-oxybis[4″-[(trimethylsilyl)ethynyl]benzil] as a yellow crystalline solid (5.1 g): mp 124–125 °C; MS, no M^+, major fragment *m/e* 201 $[^+COC_6H_4C{\equiv}CSi(CH_3)_3]$.

4,4′-Oxybis(4″-ethynylbenzil) (VI). 4,4′-Oxybis[4″-[(trimethylsilyl)ethynyl]benzil] (4.4 g, 0.007 mol) was dissolved in hot methanol (500 mL) and the solution cooled to 35 °C. Powdered potassium carbonate (2.0 g) was added to the yellow solution and a golden crystalline solid precipitated upon stirring for a few minutes. After stirring for 1 h at 30–35 °C, the reaction mixture was cooled and filtered to provide a yellow crystalline solid (2.8 g, 82% yield), mp 162–164 °C. The solid was washed with water and dissolved in a hot mixture of methanol (350 mL) and benzene (100 mL), and the resultant solution was treated with charcoal and filtered. The yellow filtrate was partially concentrated and cooled to provide 4,4′-oxybis(4″-ethynylbenzil) as a bright yellow crystalline solid (2.1 g): mp 164–165 °C (placed in a preheated oil bath at 160 °C); MS, no M^+, major fragments at *m/e* 196, 129 $(^+COC_6H_4C{\equiv}CH)$, and 101 $(^+C_6H_4C{\equiv}CH)$.

1,3-Bis[[4-(4-bromophenoxy)phenyl]glyoxylyl]benzene (VII). A solution of the diacid chloride of 1,3-phenylenediacetic acid (46.2 g, 0.2 mol) and 4-bromodiphenyl ether (104 g, 0.41 mol) in carbon disulfide (250 mL) was added dropwise during 4 h to a stirred slurry of anhydrous aluminum chloride (56 g, 0.42 mol) in carbon disulfide (200 mL) at ~10 °C. After complete addition, the dark red reaction mixture was stirred at ambient temperature for 3 h and poured into ice and hydrochloric acid. Methylene chloride (300 mL) was added to facilitate the separation and the organic phase was washed thoroughly with water, dried over calcium sulfate, concentrated to a volume of ~200 mL, and poured slowly into stirred cyclohexane (600 mL). A white solid (96.5 g) precipitated which melted at 128–138.5 °C. Recrystallization from a 1:1 mixture (800 mL) of benzene and methanol provided the intermediate diketone as a white solid (70.7 g, 54% yield): mp 139–141 °C; MS, M^+ *m/e* 656, major fragment *m/e* 275, 277 $(^+COC_6H_4OC_6H_4Br)$. A solution of the intermediate diketone (47.5 g, 0.07 mol) and selenium dioxide (16.0 g, 0.14 mol) in glacial acetic acid (600 mL) was refluxed overnight. The hot black reaction mixture was filtered and the resultant yellow filtrate was cooled to yield a yellow crystalline solid (42.6 g), mp 119–121 °C (resolidified and remelted at 144–146 °C). The yellow crystalline solid was recrystallized from a mixture of ethanol (500 mL) and benzene (250 mL) (charcoal treated) and the resultant yellow solution cooled slowly to provide 1,3-bis[[4-(4-bromophenoxy)phenyl]glyoxylyl]benzene as yellow crystals (37.7 g, 79% yield): mp 146–147 °C; MS, no M^+, major fragment *m/e* 275, 277 $(^+COC_6H_4OC_6H_4Br)$. When the ethanol/benzene recrystallization solution was cooled fast, a kinetically favored crystalline form was obtained which melted at 120–122 °C, resolidified, and remelted at 145.5–147 °C.

1,3-Bis[[4-[4-[(Trimethylsilyl)ethynyl]phenoxy]phenyl]glyoxylyl]benzene (VIII). 1,3-Bis[[4-(4-bromophenoxy)phenyl]glyoxylyl]benzene (13.7 g, 0.02 mol), dichlorobis(triphenylphosphine)palladium (0.5 g), (trimethylsilyl)acetylene (8.3 g, 0.85 mol), triethylamine (20 mL), and pyridine (60 mL) were placed in a sealed flask under a nitrogen atmosphere and stirred at 72–78 °C for 4 h. The orange solution darkened to a brown reaction mixture (containing needles), which was poured into cold dilute aqueous hydrochloric acid. A gum precipitated, which slowly solidified to a brown solid. Recrystallization from ethanol (800 mL) after charcoal treatment provided a granular yellow solid (11.0 g) which softened at 105 °C, wet at 106 °C, and cleared at 113 °C. The yellow solid was recrystallized again from ethanol (600 mL) to provide 1,3-bis[[4-[4-[(trimethylsilyl)ethynyl]phenoxy]phenyl]glyoxylyl]benzene as a fine granular yellow solid (9.1 g, 63% yield): mp 109.5–111 °C; MS, no M^+, major fragment *m/e* 293 $[^+COC_6H_4OC_6H_4C{\equiv}CSi(CH_3)_3]$, 73 $[^+Si(CH_3)_3]$.

1,3-Bis[[4-(4-ethynylphenoxy)phenyl]glyoxylyl]benzene (IX). 1,3-Bis[[4-[4-[(trimethylsilyl)ethynyl]phenoxy]phenyl]glyoxylyl]benzene (5.0 g, 0.007 mol) was dissolved in hot methanol (600 mL) and powdered potassium carbonate (1.0 g) was added. The reaction mixture was heated at reflux for 0.5 h and then cooled. A yellow solid (3.0 g), mp 119.5–121 °C, separated and was recrystallized from a 1:1 mixture (150 mL) of benzene and ethanol (charcoal treated). The yellow solution was partially concentrated and cooled to yield 1,3-bis[[4-(4-ethynylphenoxy)phenyl]glyoxylyl]benzene as a yellow solid (2.5 g, 63% yield): mp 121–123 °C; MS, no M^+, major fragment *m/e* 221 $(^+COC_6H_4OC_6H_4C{\equiv}CH)$.

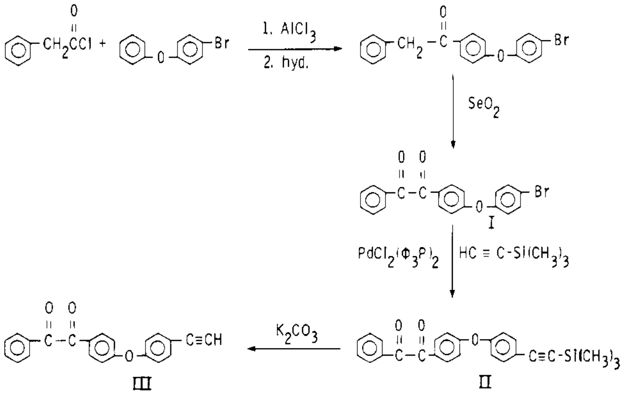
Other Reactants and Monomers. 4,4′-Oxydibenzil[11] [mp 105–106 °C (lit.[12] mp 106.4–107.4 °C)], 1,3-bis(phenylglyoxylyl)benzene[10] [mp 98–99 °C (lit.[13] mp 98–99.5 °C)], and 1,3-bis[(4-phenoxyphenyl)glyoxylyl]benzene[10] [mp 131–132 °C (lit.[14] mp 131.5–132.5 °C)] were prepared according to known procedures. 3,3′,4,4′-Tetraaminobiphenyl was recrystallized from water (20 g/L) containing a pinch of sodium dithionite under nitrogen. Near-white crystals [mp 176–177.5 °C (lit.[15] mp 179–180 °C)] were obtained in 70% recovery. Other reactants [(trimethylsilyl)acetylene, (4-bromophenyl)acetic acid, 1,3-phenylenediacetic acid, etc.] were obtained commercially. The polymerization solvent, *m*-cresol, was redistilled prior to use.

2-[4-(4-Ethynylphenoxy)phenyl]-3-phenylquinoxaline (X). This model compound was prepared from the reaction of 4-(4-ethynylphenoxy)benzil and 1,2-diaminobenzene as described elsewhere.[16] A pale yellow solid, mp 134–135 (lit.[16] mp 132–134 °C), was obtained. MS, M^+ *m/e* 398.

2,2′-(4,4′-Oxydiphenylene)bis[3-(4-ethynylphenyl)quinoxaline] (XI). 4,4′-Oxybis(4″-ethynylbenzil) (0.964 g, 0.002 mol) and 1,2-diaminobenzene (0.432 g, 0.004 mol) in benzene (25 mL) were stirred at ambient temperature for 0.5 h and at reflux for 0.5 h. The benzene solution was concentrated to a volume of ~15 mL and poured into methanol (50 mL) to yield a yellow solid (1.2 g, 77% yield), mp 263–265 °C dec (placed in a preheated oil bath at 260 °C). Recrystallization from a 1:1 mixture (60 mL) of toluene and ethanol (charcoal treated) provided 2,2′-(4,4′-oxydiphenylene)bis[3-(4-ethynylphenyl)quinoxaline] as a pale yellow solid (0.9 g): mp 264 °C dec (placed in a preheated oil bath at 260 °C); MS, M^+ *m/e* 627, major fragment *m/e* 91.

2,2′-(1,3-Phenylene)bis[3-[4-(4-ethynylphenoxy)phenyl]quinoxaline] (XII). 1,3-Bis[[4-(4-ethynylphenoxy)phenyl]glyoxylyl]benzene (0.2873 g, 0.5 mmol) and 1,2-diaminobenzene (0.1081 g, 1.0 mmol) were stirred in benzene (15 mL) at ambient

Scheme I



temperature for 0.5 h and at reflux for 0.5 h. The yellow solution was cooled to yield a tan solid (0.3 g, 83% yield), mp 208–211 °C. The solid was dissolved in benzene (10 mL), and cyclohexane was added (50 mL) in an attempt to effect a recrystallization. No solid separated upon cooling. The yellow solution was concentrated to a volume of ~15 mL to afford 2,2′-(1,3-phenylene)bis[3-[4-(4-ethynylphenoxy)phenyl]quinoxaline] as a light tan solid (0.25 g): mp 209–211 °C dec; MS, M$^+$ m/e 719.

Polymer. Polymer synthesis was performed by using stoichiometric quantities of monomers on a 2.0-mmol scale in *m*-cresol at a concentration (w/v) of 10%. The bis(1,2-diketone) monomer(s) was stirred in the appropriate volume of *m*-cresol and powdered 3,3′4,4′-tetraaminobiphenyl was added. The reaction mixture turned reddish orange, which eventually faded to provide an amber-colored viscous solution after stirring at ambient temperature for 4–6 h and at ~90 °C for 1 h. A portion of the viscous solution was doctored onto plate glass and stage dried to a final temperature of 110 °C in vacuo for 4–6 h. The resultant transparent yellow film was fingernail creaseable. The remaining *m*-cresol solution was poured into methanol in a blender to precipitate a yellow solid, which was thoroughly washed in boiling methanol and dried at 90 °C in air.

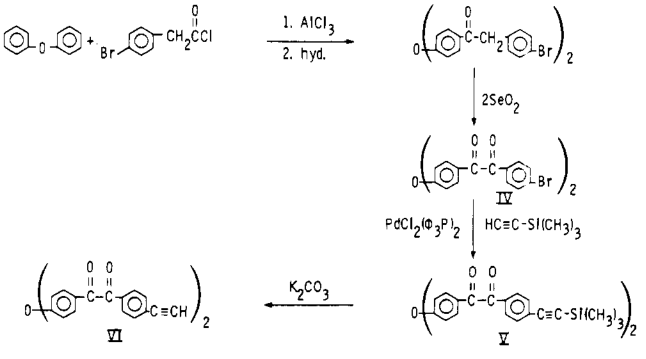
Thermal Characterization. Differential scanning calorimetric (DSC) curves were obtained with a Du Pont Model 990 thermal analyzer in combination with a standard DSC cell (Du Pont catalog no. 9006000-902). The samples were hermetically sealed in Du Pont-supplied aluminum cups. Each sample was run in a nitrogen atmosphere at a heating rate of 20 °C/min. Torsional braid analyses (TBA) were conducted at a heating rate of 3 °C/min in a nitrogen atmosphere over the temperature range -100 to +400 °C. Heatup and cooldown curves were obtained on the same samples. Thermal mechanical analyses (TMA) were obtained on films, using a Du Pont Model 990 thermal analyzer in combination with a Du Pont 940 thermomechanical analyzer at a heating rate of 5 °C/min in static air. Thermogravimetric analyses (TGA) were performed with a Perkin-Elmer program temperature controller Model UU-1 in combination with a heater controller and an autobalance Model AR-2 at a heating rate of 2.5 °C/min in nitrogen and flowing air.

Results and Discussion

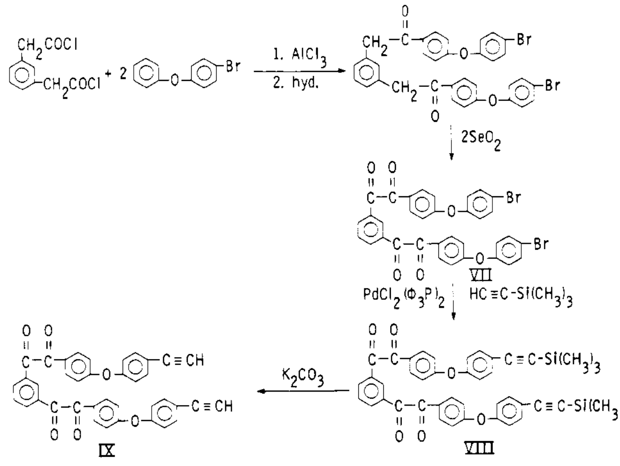
Synthesis. Monomers. Several methods are available to prepare arylacetylenes, such as the displacement of an aryl iodide with cuprous acetylide, conversion of an aromatic acetyl group via the Vilsmeyer reaction and subsequent caustic cleavage of the chlorocinnamaldehyde, and dehydrohalogenation of appropriate aromatic dihaloethanes. An improved synthesis of arylacetylenes was reported[17] in 1979 which involved the reaction of an aryl bromide with 2-methyl-3-butyn-2-ol, using a dichlorobis(triphenylphosphine)palladium/cuprous iodide catalyst followed by cleavage of the intermediate with sodium hydroxide. However, this route was unattractive to prepare the desired ethynyl-containing α-diketones since α-diketones undergo cleavage and rearrangement in the presence of a strong base. A variation of this route employed the use of (trimethylsilyl)acetylene instead of 2-methyl-3-butyn-2-ol.[18] The trimethylsilyl group can be cleaved from the intermediate with a weak base (potassium carbonate). As shown in Schemes I–III, this route was used to prepare the desired α-diketone compounds. Characterization of the various reactants and monomers is presented in Table I. Since the primary objective of this synthesis was to acquire adequate monomer of high purity for polymer preparation, no work was performed to optimize reaction conditions to improve yields. It is suspected that the yields can be improved significantly, as indicated by work of others on related compounds.[17,18]

The DSC curves of the ethynyl-substituted α-diketones are shown in Figure 1. Compounds III and IX exhibited

Scheme II



Scheme III



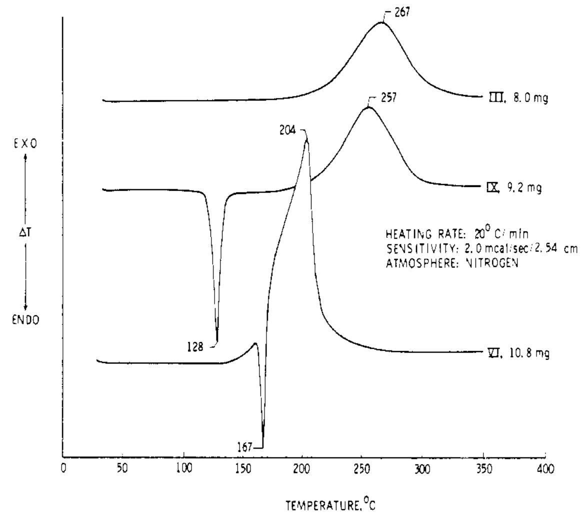


Figure 1. Differential scanning calorimetry curves of ethynyl-substituted α-diketones.

Table I
Characterization of Reactants and Monomers

compound no.	form	mp, °C	formula	elemental anal.,[a] % C	H	Br
I	yellow crystals	85-86	$C_{20}H_{13}BrO_3$			
II	orange gum		$C_{25}H_{22}O_3Si$	75.00 (75.34)	5.88 (5.57)	
III	yellow gum		$C_{22}H_{14}O_3$	80.66 (80.97)	4.39 (4.32)	
IV	yellow crystals	193-194 (lit.[11] mp 192-193)				
V	yellow crystals	124.5-125.5	$C_{38}H_{34}O_5Si_2$	72.91 (72.81)	5.61 (5.47)	
VI	yellow crystals	164-165	$C_{32}H_{18}O_5$	79.56 (79.66)	3.79 (3.76)	
VII	yellow crystals	145-146	$C_{34}H_{20}Br_2O_6$	64.22 (64.34)	3.31 (3.18)	 (25.18)
VIII	yellow solid	109.5-111	$C_{44}H_{38}O_6Si_2$	73.02 (73.50)	5.16 (5.33)	
IX	yellow solid	121-123	$C_{38}H_{22}O_6$	79.56 (79.43)	3.79 (3.86)	

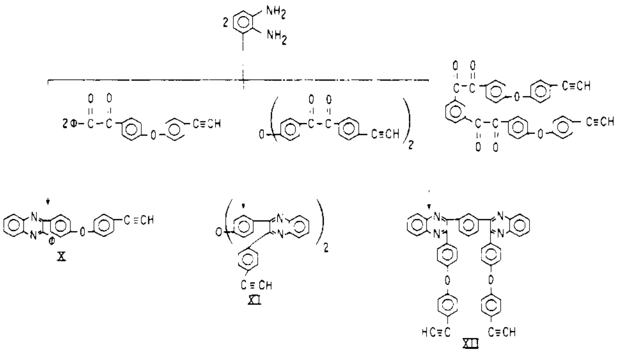
[a] Theoretical values in parentheses.

Table II
Characterization of Model Compounds

compound no.	form	mp, °C	formula	elemental anal.,[a] % C	H	N
X	yellow crystals	133-134 (lit.[16] mp 132-134)	$C_{28}H_{18}N_2O$			
XI	pale yellow solid	264[b]	$C_{44}H_{26}N_4O$	84.45 (84.32)	4.26 (4.18)	8.78 (8.94)
XII	light tan solid	204-206	$C_{50}H_{30}N_4O_2$	83.04 (83.55)	4.11 (4.21)	7.48 (7.80)

[a] Theoretical values in parentheses. [b] Introduced into a preheated oil bath at 260 °C.

Scheme IV



exotherms of similar shape due to the reaction of the ethynyl groups whereas compound VI displayed a more intense, sharper exotherm which peaked at a lower temperature. It is postulated that the ethynyl groups on compound VI undergo more of an intramolecular reaction whereas compounds III and IX undergo intermolecular reactions. The exact nature of the product formed is unknown although previous work with ethynyl-containing imide model compounds has provided insight regarding the composition. This will be discussed later.

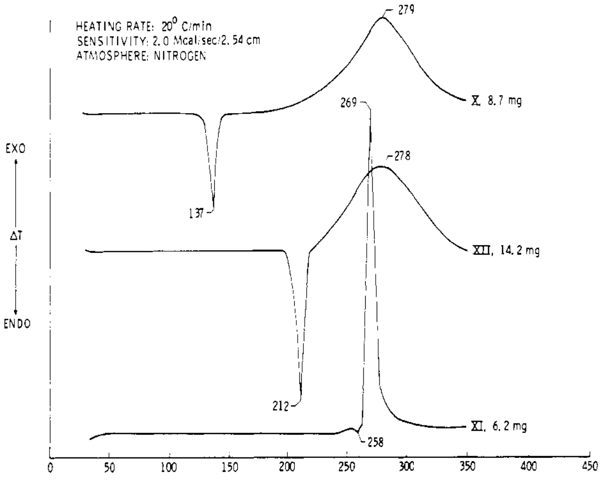


Figure 2. Differential scanning calorimetry curves of model compounds.

Model Compounds. Three model compounds were prepared in high yields according to Scheme IV. Their characterization is presented in Table II. The model compound work was performed to gain insight into the anticipated behavior of the polymers. However, model compound work serves only as a guide since polymers can behave grossly different due to factors such as differences in molecular mobility and ethynyl density. As shown in the DSC curves in Figure 2, compounds X and XII exhibited similarly shaped curves with a sharp endothermic peak due to melting followed by a broad exotherm peaking at ~278 °C due to reaction of the ethynyl group. Compound XI displayed a grossly different DSC curve. A weak endothermic peak is present at 258 °C, which is followed immediately by an intense sharp exotherm peaking at 269 °C. The general shape of the exotherm suggests that the ethynyl groups are reacting to provide a product that is more homogeneous (simpler) than that obtained from compound X or XII. It has been shown that the product from the thermally induced reaction of an acetylene-containing imide [*N*-(3-ethynylphenyl)phthalimide] consisted of a minor fraction (~20%) composed of two dimers, three trimers, and a tetramer and major fraction composed of oligomers with molecular weight as high as 2100.[7] The

Table III
Characterization of Polymers of Structure XIII

X	η_{inh},[a] dL/g	DSC data,[b] °C initial T_g	DSC data exothermic peak	DSC data final T_g[c]	TBA data,[d] °C heatup peaks	TBA data cooldown peak	TMA,[e] °C T_g
H	1.54	291	none	292	−35, 289	295	306
H (95%) C≡CH (5%)	1.61	ND[f]	324	321	−22, 342	330	337
H (90%) C≡CH (10%)	1.72	ND	313	333	−20, 336	344	348
H (70%) C≡CH (30%)	1.93	ND	285	ND	−22, 330	ND	378
C≡CH[g]	1.23	ND	247	ND	−24, 249	ND	ND

[a] Inherent viscosity; 0.5% solution in *m*-cresol at 25 °C. [b] Heating rate of 20 °C/min, nitrogen atmosphere, T_g taken at the inflection point. [c] After heating to 375 °C in nitrogen. [d] Heating rate of 3 °C/min, nitrogen atmosphere, maximum damping peak reported, braid heated to 400 °C. [e] Heating rate of 5 °C/min. [f] ND = not detected. [g] Elemental Anal. Calcd for $(C_{44}H_{24}N_4O)_n$: C, 84.59; H, 3.87; N, 8.96. Found: C, 84.58; H, 3.94; N, 8.76.

Table IV
Characterization of Polymers of Structure XIV

Y	η_{inh},[a] dL/g	DSC data,[b] °C initial T_g	DSC data exothermic peak	DSC data final T_g[c]	TBA data,[d] °C heatup peaks	TBA data cooldown peak
H	0.61	313	none	314	−32, 312	319
OC_6H_5	0.83	246	none	248	−38, 246	253
H (95%) $OC_6H_4C{\equiv}CH$ (5%)	0.93	ND[f]	340	323	−36, 321	332
H (90%) $OC_6H_4C{\equiv}CH$ (10%)	0.82	ND	330	334	−38, 333	338
H (70%) $OC_6H_4C{\equiv}CH$ (30%)	1.13	ND	313	ND	−34, 278	362
$OC_6H_4C{\equiv}CH$	0.47	ND	257	ND	−30, 261	ND

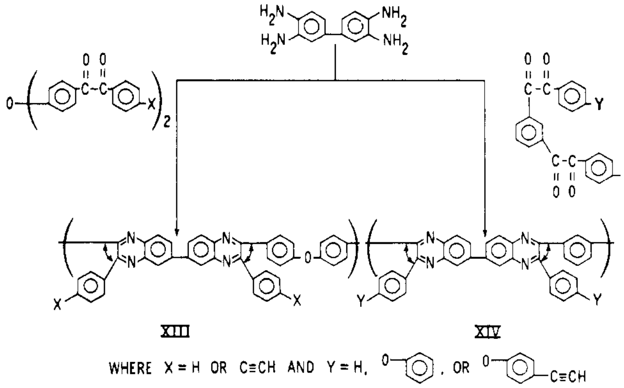
[a-f] See Table III footnotes.

thermal reaction of compounds X and XII probably provides a similar complex product. The product from the thermal reaction of compound XI is proposed to be predominantly a macrocyclic compound resulting from the intramolecular reaction of the ethynyl groups to form moieties such as vinylacetylene (enyne, C≡CCH=CH) and others. The infrared spectrum of the product was complex and showed no C≡C—H stretch in the 3300-cm^{-1} region and a very weak band at 2170 cm^{-1} due to the C≡C absorption. The product was insoluble in all of the organic solvents (*N,N*-dimethylacetamide, *sym*-tetrachloroethane, *m*-cresol, diethyl ether, alcohol) tried, which precluded further characterization.

Polymers. The two basic polymers shown in Scheme V, one containing a diphenyl ether moiety in the backbone with pendant phenyl groups and the other containing a 1,3-phenylene unit in the chain with pendant 4-phenoxyphenyl groups, were selected for study since monomers were available to make the unsubstituted polymers for comparison and also since information is available on their physical, thermomechanical, and structural properties.[10,19,20] As indicated in Tables III and IV, polymers containing various amounts of ethynyl groups were prepared by varying the mole percent of the appropriate bis(α-diketone) monomers. The distribution of the ethynyl groups is considered to be random although block segments could be present in certain polymers. For example, monomer VI was not readily soluble in *m*-cresol, whereas the 4,4′-oxydibenzil was. The polymerization probably proceeded initially through the predominant reaction of 4,4′-oxydibenzil with the tetramine followed by reaction of the residual tetramine and 1,2-diamino end-capped oligomer with the ethynyl-substituted bis(α-diketone).

Thermal Characterization of Polymers. Differential Scanning Calorimetry. The polymers were char-

Scheme V



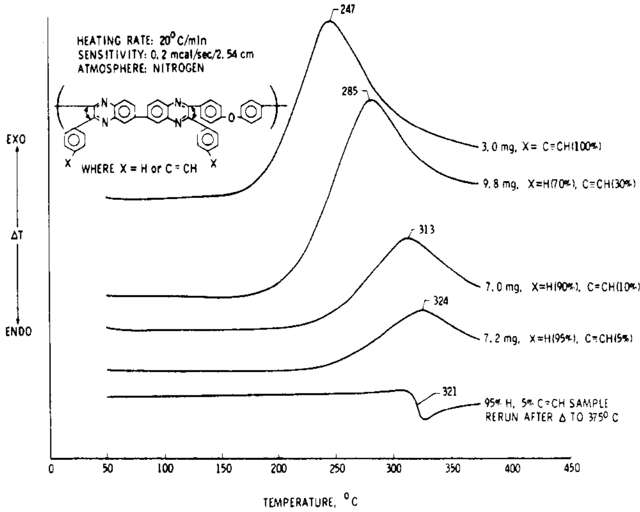


Figure 3. Differential scanning calorimetry curves of polymers.

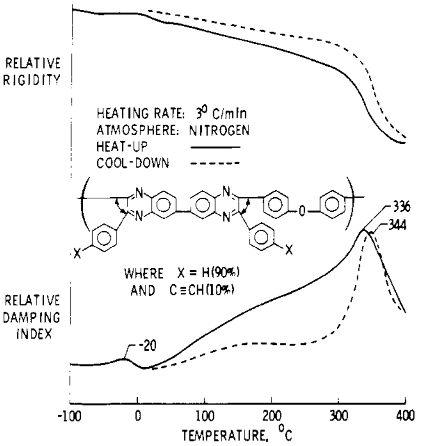


Figure 4. Torsional braid analysis of ethynyl-substituted poly(phenylquinoxaline).

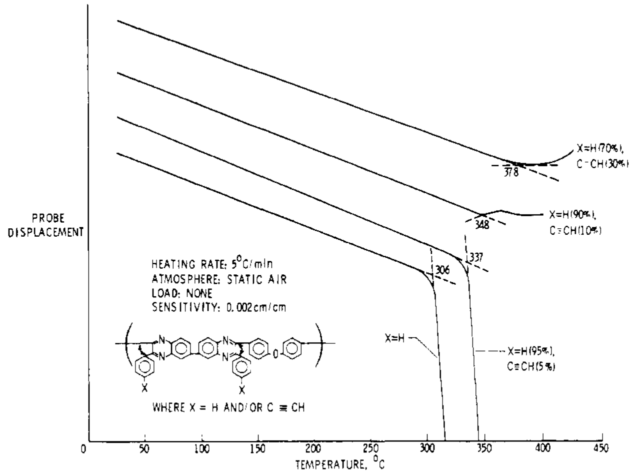


Figure 5. Thermal mechanical analysis of polymers (elongation of films).

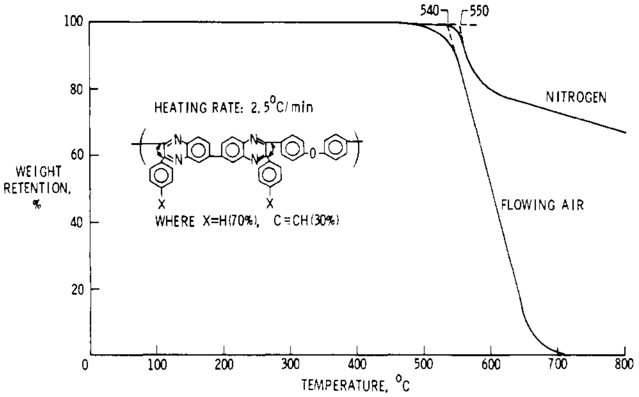


Figure 6. Thermogravimetric analysis of ethynyl-substituted poly(phenylquinoxaline).

acterized by DSC at a heating rate of 20 °C/min in a nitrogen atmosphere. The apparent glass transition temperature (T_g) was taken at the inflection point of the ΔT vs. temperature curve, as shown in the representative curve in Figure 3. As indicated in Tables III and IV, no initial T_g could be detected for the ethynyl-containing polymers because it was masked by the broad exothermic reaction of the ethynyl groups. After heating a sample to 375 °C in nitrogen, cooling, and rerunning the same sample, those polymers containing 5 and 10 mol % ethynyl groups exhibited a T_g (see Tables III and IV). The T_g of polymers containing 30 and 100 mol % ethynyl groups could not be detected after heating to 375 °C, apparently due to the high cross-link density.

As the mole percent of ethynyl groups in the polymer increased, the temperature of the exothermic peak decreased and the intensity of the exotherm increased. The exotherm is presumably due to the reaction of an ethynyl group with another, in contrast to other reactions such as the addition of the ethynyl group across an aromatic ring. High ethynyl density permitted the reaction to occur at a lower temperature (less time required for the ethynyl groups to collide), which resulted in an intense exotherm. As the ethynyl density decreased, more time was required for collision and obviously fewer groups reacted, resulting in less heat generated. The possibility of some intramolecular reaction of the ethynyl groups in polymers of structure XIII, especially the polymer containing 100 mol % ethynyl groups, must be considered. Intramolecular reaction of the ethynyl groups was proposed for compounds VI and XI. In the DSC curves in Figure 3, the polymer containing 100 mol % ethynyl groups (sample size of 3.0 mg) displayed an intense exotherm peaking at 247 °C, whereas the polymer containing 30 mol % ethynyl groups (sample size of 9.8 mg) exhibited a broad exotherm peaking at 285 °C. The polymers containing 5 and 10 mol% ethynyl groups exhibited peak exotherms at higher temperatures.

The T_g's of polymers containing no ethynyl groups were included in Tables III and IV for comparison and exhibited essentially no increase after heating to 375 °C in nitrogen. Those polymers containing ethynyl groups which were exposed to 375 °C exhibited T_g's higher than the corresponding unsubstituted polymers. This is presumably due to thermally induced cross-linking. Further evidence to support cross-linking will be discussed later.

Torsional Braid Analysis. The polymers were also characterized by TBA under 1 Hz at a heating rate of 3 °C/min in nitrogen. The apparent T_g was taken as the temperature of the damping peak during the heatup and cooldown cycle and is given in Tables III and IV. A representative TBA curve is presented in Figure 4. A low-temperature damping peak (~-22 °C) is present, apparently due to motion of the pendant phenyl group on the quinoxaline ring. As the braid is heated, the ethynyl groups react to provide a material with an apparent T_g of 336 °C. The damping peak at 336 °C coincides with a rapid change in the rigidity. The braid was heated in nitrogen to 400 °C and a cooldown curve was obtained which displayed a damping peak at 344 °C. Significant scatter of the data points occurred in the 0 to -100 °C range in the cooldown curve such that the presence of a low-temperature damping peak was inconclusive.

As indicated in Tables III and IV, as the mole percent of the ethynyl group in the polymer increased, the temperature of the major heatup damping peak decreased while the temperature of the cooldown damping peak increased. The only exception to this trend was the polymer in Table IV containing 10 mol % ethynyl groups.

Thermal Mechanical Analysis (TMA). Films of the polymers in Table III were dried at 350 °C in nitrogen for 0.5 h and subjected to TMA (film elongation) at a heating rate of 5 °C/min. The drying conditions induced cross-linking in those polymers containing ethynyl groups. As shown in Figure 5, the films of the polymers containing 0 and 5 mol % ethynyl groups exhibited substantial elongation near their T_g's. Films of the polymers containing 10 and 30 mol % ethynyl groups exhibited no pronounced elongation near their T_g. The temperature indicated is somewhat subjective but the trend is evident. The apparent T_g increased as the amount of ethynyl

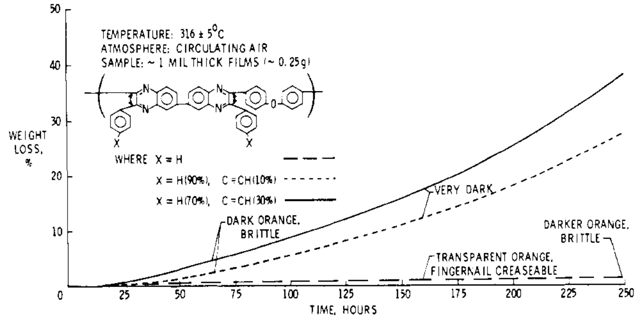


Figure 7. Isothermal aging curves of polymers.

groups (cross-linking) increased in the films.

Thermogravimetric Analysis (TGA). Several of the polymers in Tables III and IV were subjected to TGA at a heating rate of 2.5 °C/min; a representative curve is shown in Figure 6. Regardless of ethynyl content, the polymers exhibited essentially the same TGA curves, with polymer decomposition temperatures in air and in nitrogen of ~540 and ~550 °C, respectively.

Isothermal Analysis (ITA). Films of three of the polymers in Table III which were dried at 316 °C for 4 h to remove residual solvent (~3%) were aged in a circulating air oven at 316 °C (±5 °C) and changes in their weight, flexibility, and color recorded as a function of time (Figure 7). The films from polymers containing ethynyl groups exhibited significantly poorer thermooxidative stability, as evidenced by their higher weight losses and faster discoloration, than that which contained no ethynyl groups.

Solubility of Polymers. Similar to linear poly(phenylquinoxalines), the ethynyl-containing poly(phenylquinoxalines) in Tables III and IV were readily soluble at ambient temperature in solvents such as *m*-cresol, chloroform, and *sym*-tetrachloroethane at concentrations of 20% (w/v) and insoluble in highly polar solvents such as *N*,*N*-dimethylacetamide and dimethyl sulfoxide. After heating at 350 °C for 0.5 h in nitrogen, films from the ethynyl-containing polymers failed to exhibit even partial solubility in chloroform, *sym*-tetrachloroethane, or *m*-cresol, whereas films from polymers void of ethynyl groups readily dissolved. The films of the polymers containing 5 mol % ethynyl groups exhibited slight swelling, whereas no detectable swelling was observed in the films containing 10 mol % or more ethynyl groups. In addition, films of polymers containing 5, 10, and 30 mol % ethynyl groups which were dried for several hours at 150 °C in vacuo were also insoluble in chloroform and *m*-cresol. The ethynyl group can react at moderate temperatures to provide cross-linking.

Processability. Samples of the polymers in Tables III and IV in powder form were sandwiched between aluminum foil, introduced into a preheated press at 371 °C, subjected to ~0.69-MPa (~100 psi) pressure, and held under these conditions for 0.5 h. The polymers containing no ethynyl groups fused to form transparent orange films. The polymers containing 5 and 10 mol % ethynyl groups exhibited partial fusion to form opaque films with some integrity. Polymers containing 30 and 100 mol % ethynyl groups failed to fuse and formed compressed powder disks which easily crumbled upon handling. On the basis of these findings, poly(phenylquinoxalines) containing more than 10 mol % ethynyl groups are not amenable to processing in the conventional manner as laminating resins or adhesives. The ethynyl groups readily react at elevated temperature to reduce the flow and render the polymer unprocessable. However, these materials may show promise as coatings for use in a hostile environment since they can be applied in solution form and subsequently cross-linked.

Conclusions

Relatively high molecular weight linear soluble poly(phenylquinoxalines) containing pendant ethynyl groups were synthesized. Thermally induced reactions of the ethynyl groups provided insoluble cross-linked polymers with high T_g's. Depending upon the ethynyl density, the ethynyl-containing polymer exhibited fair to poor processability by compression molding due to the thermal reaction of the ethynyl groups which inhibited polymer flow. The cured ethynyl-containing polymers exhibited lower thermooxidative stability than that of a corresponding polymer with no ethynyl groups. In general, ethynyl-containing poly(phenylquinoxalines) would not be expected to be useful as laminating resins or adhesives due to processing difficulties but may be useful as solvent and corrosion-resistant high-temperature coatings.

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