Poly(phenylquinoxalines) Containing Phenylethynyl Groups

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ABSTRACT: High molecular weight poly(phenylquinoxalines) (PPQs) containing various amounts of pendant phenylethynyl groups were prepared from the reaction of 3,3',4,4'-tetraaminobiphenyl with aromatic bis(phenylethynyl-substituted α-diketones). The latter compounds were prepared from the reaction of aromatic bis(bromo-substituted α-diketones) with phenylacetylene, using dichlorobis(triphenylphosphine)palladium as catalyst. The thermally induced reaction of the phenylethynyl groups cross-linked the polymers, which resulted in higher apparent glass transition temperatures, insolubility, poorer processability, and lower long-term thermooxidative stability than corresponding linear PPQs. Model compounds were also prepared and characterized.

Introduction

Poly(phenylquinoxalines) (PPQs) are high-temperature thermoplastics which exhibit good dimensional stability at temperatures lower than their glass transition (T_g) or heat distortion temperatures.[1] Since their initial disclosure in 1967,[2] several routes have been investigated in an attempt to increase their dimensional stability at elevated temperature without compromising their thermooxidative stability. Cyanato and cyano groups were placed as pendant groups on the polymer chain and thermally reacted to provide cross-linking.[3] The use of a tris(phenyl α-diketone) monomer to provide cross-linking was reported in 1975.[4] Extremely rigid PPQs with high T_g's were prepared by using aromatic fused-ring tetraamines.[5] Poly(phenylquinoxalines) containing a cross-linkable methyl group in the para position of the pendant phenyl group have also been investigated.[6]

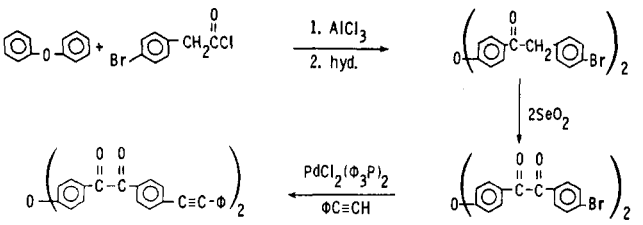
In an attempt to increase the T_g's of PPQs, the 2,2'-bis(phenylethynyl)biphenyl moiety was incorporated within the polymer chain backbone and subsequently thermally reacted to reportedly form rigid 9-phenyldibenz[a,c]anthracene units.[7] This concept has also been extended to imide polymers[8] and ether–ketone–sulfone polymers.[9] Polyimides containing a single pendant phenylethynyl group per mer unit were also recently reported.[10] Linear PPQs containing various amounts of ethynyl groups in the para position of the pendant phenyl groups were recently prepared and subsequently thermally cross-linked.[11] The ethynyl-containing PPQs are attractive for certain functional applications (e.g., films and coatings) but for structural applications (e.g., adhesives and laminates), fabrication by conventional methods is difficult due to the thermal reactivity of the ethynyl group (cross-links). The phenylethynyl group should be less thermally reactive than the ethynyl group. Therefore, a series of phenylethynyl-containing PPQs were prepared and characterized as reported herein in an attempt to improve the processability, obtain high-temperature dimensional stability, and retain good thermooxidative stability.

Experimental Section

Phenylethynyl-Substituted α-Diketones. The three phenylethynyl-substituted α-diketones in Table I were prepared by a modification of the procedure employed for the synthesis of ethynyl-substituted α-diketones.[11] Bromo-substituted α-diketones were reacted with phenylacetylene, using dichlorobis(triphenylphosphine)palladium as catalyst to provide phenylethynyl-substituted α-diketones. The preparation of the bromo-substituted α-diketones is described elsewhere.[11] A representative procedure for the preparation of 4,4'-oxybis[4''-(phenylethynyl)benzil] as shown in Scheme I is given below. Details on the synthesis of the phenylethynyl α-diketones are summarized in Table I.

A flask containing an orange solution of 4,4'-oxybis(4''-bromobenzil) (35.4 g, 0.06 mol), phenylacetylene (15.0 g, 0.15 mol),

Scheme I



and dichlorobis(triphenylphosphine)palladium (0.40 g) in pyridine (300 mL) and triethylamine (75 mL) was flushed with nitrogen, sealed, heated, and stirred at ~97 °C for 4 h. The resultant dark orange solution was poured into methanol (1.4 L) and cooled in a refrigerator overnight to provide a yellow solid (33.3 g, 87% crude yield), mp 118–121 °C. Recrystallization from acetone (1.2 L) afforded yellow needles (23 g, 69% recovery) which sintered slightly at 165 °C and melted at 181–182.5 °C. Characterization of the phenylethynyl-substituted α-diketones is provided in Table II.

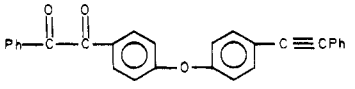
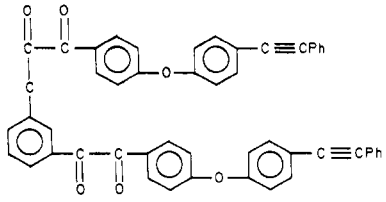
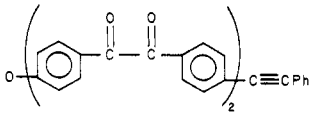
Other Reactants and Monomers. 4,4'-Oxydibenzil,[12] mp 105–106 °C (lit.[13] mp 106.4–107.4 °C), 1,3-bis(phenylglyoxylyl)benzene[14], mp 98–99 °C (lit.[15] mp 98–99.5 °C), and 1,3-bis[4-(phenoxyphenyl)glyoxylyl]benzene,[3] mp 131–132 °C (lit.[16] mp 131.5–132.5 °C) were prepared according to known procedures. 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.[17] mp 179–180 °C) were obtained in 70% recovery. The polymerization solvent, *m*-cresol, was redistilled prior to use.

Model Compounds. Three model compounds were prepared according to the reactions in Scheme II in near-quantitative crude yield by the following general procedure. Stoichiometric quantities of the phenylethynyl α-diketone and 1,2-diaminobenzene were refluxed in benzene for 1 h. After removal of the benzene, the residual solid was recrystallized. Characterization is given in Table III.

Polymer. Polymer synthesis as represented in Scheme III 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 a reddish orange color, 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 200 °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. Characterization is given in Tables IV and V.

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. 9006000902). 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. The

Table I
Synthesis of Phenylethynyl-Substituted α-Diketones

compound	reaction scale, mol	workup medium	crude product form	crude product yield, %	crude product mp, °C	recrystallized product solvent	recrystallized product form	recrystallized product recovery, %	recrystallized product mp, °C
 I	0.01	dil aq HCl	orange gum	120[a]		cyclohexane	yellow solid	45	82-83
 II	0.02	methanol	yellow solid	72	129-134	benzene	yellow crystals	29	186.5-187.5
 III	0.06	methanol	yellow solid	87	118-121	acetone	yellow needles	69	181-182.5

[a] Contains a byproduct from the reaction of phenylacetylene with itself.

Table II
Characterization of Phenylethynyl α-Diketones

compound no.	mass spectroscopic data M⁺	mass spectroscopic data m/e, major fragment	formula	elemental anal.,[a] % C	elemental anal.,[a] % H
I	m/e 402	297, $^{+}COC_6H_4OC_6H_4C{\equiv}CC_6H_5$	$C_{28}H_{18}O_3$	83.51 (83.56)	4.56 (4.51)
II	ND[b]	297, $^{+}COC_6H_4OC_6H_4C{\equiv}CC_6H_5$	$C_{50}H_{30}O_6$	81.85 (82.63)	4.58 (4.16)
III	ND	205, $^{+}COC_6H_4C{\equiv}CC_6H_5$ 196, unknown 177, $^{+}C_6H_4C{\equiv}CC_6H_5$	$C_{44}H_{26}O_5$	83.37 (83.26	4.35 (4.13)

[a] Theoretical values in parentheses. [b] ND = not detected.

Table III
Characterization of Model Compounds

compound no.[a]	recrystallization solvent	form	mp, °C	M⁺ m/e	formula	elemental anal.,[b] % C	H	N
IV	1:1 n-hexane/cyclohexane	off-white solid	152-153	474	$C_{34}H_{22}N_2O$	85.83 (86.03)	4.76 (4.67)	5.88 (5.90)
V	1:2 ethanol/toluene	pale yellow solid	261-262	779	$C_{56}H_{34}N_4O$	86.37 (86.35)	4.55 (4.40)	7.15 (7.19)
VI	1:1 ethanol/benzene	off-white solid	164-166	881	$C_{64}H_{48}N_4O_2$	84.47 (84.52)	5.31 (5.49)	6.37 (6.36)

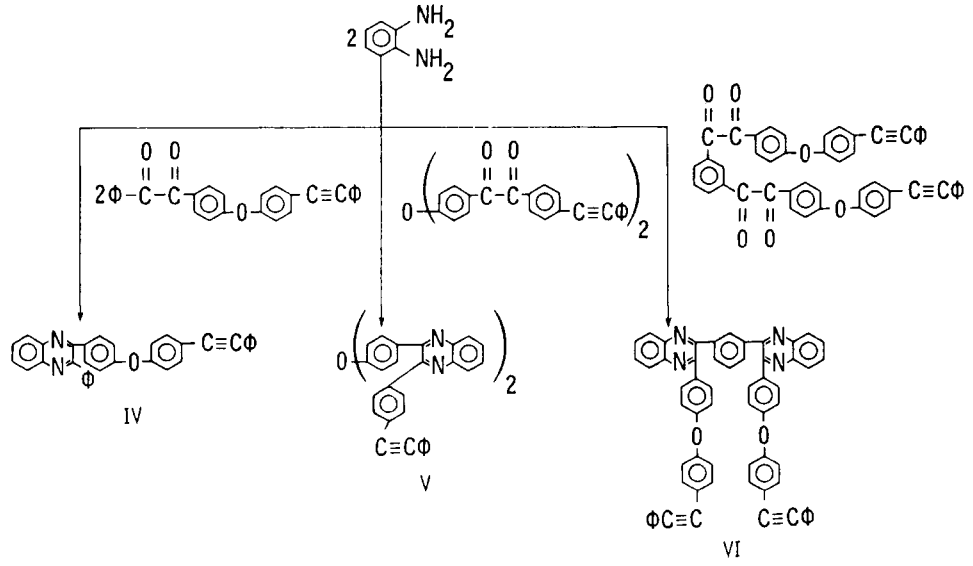
[a] See Scheme II. [b] Theoretical values in parentheses.

Table IV
Characterization of Polymers of Structure VII (Scheme III)

X	η_{inh},[a] dL/g	DSC data,[b] °C init T_g	DSC data,[b] °C exothermic peak	DSC data,[b] °C final T_g[c]	TBA data,[d] °C heatup peaks	TBA data,[d] °C cooldown peak	TMA,[e] °C T_g
H	1.54	291	none	293	-35, 289	295	306
H (95%) C≡CPh (5%)	1.39	302	450	330	-30, 291	340	341
H (90%) C≡CPh (10%)	1.33	306	448	333	-28, 291	345	345
H (70%) C≡CPh (30%)	1.42	309	434	ND[f]	-20, 292, 407	440	392
C≡CPh[g]	1.05	325	430	ND	-25, 305, 355	ND	400

[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 475 °C in nitrogen. [d] Heating rate of 3 °C/min, nitrogen atmosphere, maximum damping peak reported, braid heated to 450 °C. [e] Heating rate of 5 °C/min, film heated at 350 °C in nitrogen for 0.5 h and rerun. [f] ND = not detected. [g] Anal. Calcd for $(C_{56}H_{32}N_4O)_n$: C, 86.58; H, 4.15; N, 7.21. Found: C, 85.48, H, 4.25; N, 7.12.

Scheme II



Scheme III

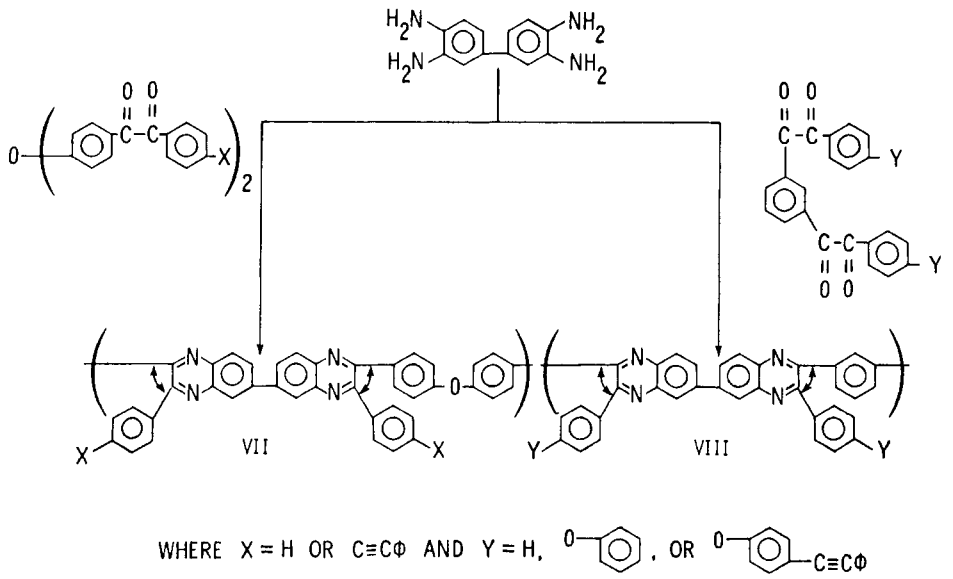


Table V
Characterization of Polymers of Structure VIII (Scheme III)

Y	η_{inh},[a] dL/g	DSC,[a] °C: init T_g	DSC,[a] °C: exothermic peak	DSC,[a] °C: final T_g[a]	TBA data,[a] °C: heatup peaks	TBA data,[a] °C: cooldown peak
H	0.61	313	none	315	−32, 312	319
OC_6H_5	0.83	246	none	249	−38, 246	253
H (95%) $OC_6H_4C{\equiv}CPh$ (5%)	0.68	311	448	338	−33, 296	355
H (90%) $OC_6H_4C{\equiv}CPh$ (10%)	0.71	309	445	340	−32, 298	358
H (70%) $OC_6H_4C{\equiv}CPh$ (30%)	0.64	285	429	ND[a]	−30, 388	430
$OC_6H_4C{\equiv}CPh$[b]	0.43	231	377	ND	−23, 232, 351	ND

[a] See Table III for description. [b] Anal. Calcd for $(C_{62}H_{36}N_4O_2)_n$: C, 85.69; H, 4.18; N, 6.45. Found: C, 84.33; H, 4.25; N, 6.78.

apparent glass transition temperature (T_g) was taken at the inflection point of the ΔT vs. temperature curve. Torsional braid analyses (TBA) were conducted at a heating rate of 3 °C/min in a nitrogen atmosphere over the temperature range −100 to +475 °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 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.

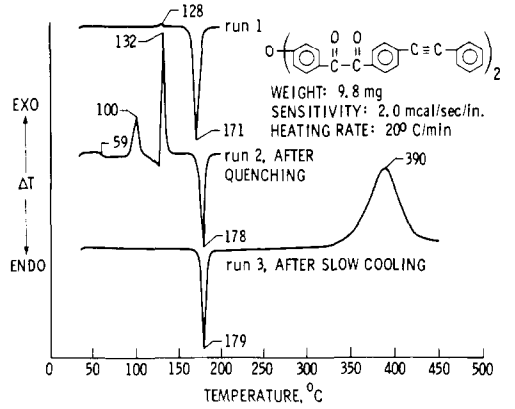


Figure 1. Differential scanning calorimetric curves of 4,4′-oxybis[4″-(phenylethynyl)benzil].

Results and Discussion

Synthesis. Phenylethynyl α-Diketones. The phenylethynyl-substituted α-diketones in Table I were prepared from the reaction of a bromo-substituted α-diketone with phenylacetylene, using dichlorobis(triphenylphosphine)palladium as catalyst. The synthesis is a variation of a route recently employed to prepare aromatic ethynyl-substituted α-diketones, such as 4,4′-oxybis(4″-ethynylbenzil).[11] No work was performed to optimize reaction parameters to improve yields since the primary purpose was to acquire adequate phenylethynyl α-diketone of high purity for model compound and polymer synthesis. Compound III was obtained in higher crude yield than compounds I and II, as indicated by high-pressure liquid chromatography (HPLC). This suggests that an activated bromo group as in 4,4′-oxybis(4″-bromobenzil) (para position to a carbonyl group) is more easily displaced by phenylacetylene using a palladium catalyst than a bromo group such as in 1,3-bis[[4-(4-bromophenoxy)phenyl]glyoxylyl]benzene (para position to an ether oxygen).

The bis(phenylethynyl α-diketones) can exist as a glass or in more than one crystalline form. The differential scanning calorimetric (DSC) curves of compound III, which was recrystallized from a benzene/cyclohexane mixture, are shown in Figure 1. Run 1 showed a weak reorganization exotherm peaking at 128 °C and a strong endotherm peaking at 171 °C due to melting. The sample was heated to 200 °C in nitrogen, quenched, and rerun. Quenching destroyed the crystalline character and provided a glass. As seen in run 2, a second-order transition occurred with an inflection point of 59 °C. The material then underwent two reorganizations, as evidenced by the exothermic peaks at 100 and 132 °C, followed by an endothermic melting peak at 178 °C. The sample was cooled slowly (~2 °C/min) and rerun. Run 3 exhibited an endothermic melting peak at 179 °C and a broad strong exotherm peaking at 390 °C due to reaction of the phenylethynyl groups. Compound II exhibited similar behavior in the DSC, with a sharp melting endotherm peaking at 186 °C. After heating to 200 °C in nitrogen and quenching, the glassy sample showed a weak second-order transition at 55 °C, a strong exothermic peak at 120 °C with a milder one at 143 °C, and a melting endothermic peak at 184 °C. The sample, after slow cooling, showed a weak exothermic peak at 144 °C and two endothermic peaks at 180 and 185 °C.

Model Compounds. The three model compounds in Table III were prepared in high yields according to the reactions in Scheme II. Since nucleophiles such as aromatic primary amines are known to add across the triple bond of acetylenic ketones, the possiblity of the amine reacting with the phenylethynyl group in the para position to a ketone such as in compound III was of concern. However, there was no evidence by HPLC that this reaction occurred.

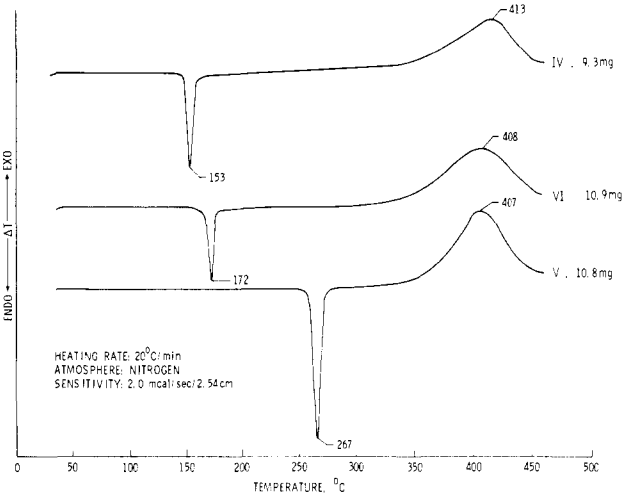


Figure 2. Differential scanning calorimetric curves of model compounds.

Model compound work was performed primarily to determine if the desired model compounds were formed in quantitative yield to constitute a polymer-forming reaction and to gain insight into the thermal bahavior of the polymers. However, the thermally induced reaction of the model compounds served only as a guide since the polymers were expected to behave differently due to factors such as decreased molecular mobility and phenylethynyl density. The DSC curves for the three model compounds in Figure 2 display a sharp endothermic peak due to melting followed by a broad exotherm peaking at ~410 °C due to reaction of the phenylethynyl group. The product from the thermally induced reaction of the phenylethynyl group is unknown but is thought to consist of a complex mixture of components. The product from the simplest model compound, IV, was not completely soluble in any of the solvents tried, which discouraged characterization. Previous work has shown the product from the thermally induced reaction of an ethynyl imide model compound at 255 °C in nitrogen to be a complex mixture, consisting of a minor fraction (~20%) composed of two dimers, three trimers, and a tetramer and a major fraction (~80%) of higher molecular weight oligomers (as high as 2100).[18]

Polymers. The two basic polymers shown in Scheme III, one containing a diphenyl ether moiety in the backbone with pendant phenyl groups while the other has 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 because information is available on their physical, thermomechanical, and structural properties.[3,19] As indicated in Tables IV and V, polymers containing various amounts of phenylethynyl groups were prepared by varying the mole percent of the appropriate bis(α-diketone) monomers. The distribution of the phenylethynyl groups is considered to be random, although block segments could be present in certain polymers. The aromatic bis(phenylethynyl-substituted α-diketone) monomers are less soluble in *m*-cresol than the aromatic bis(α-diketones). As a result, the polymerization may proceed initially through reaction of the bis(α-diketone) monomer with the tetraamine followed by the reaction of residual tetraamine and 1,2-diamino end-capped oligomer with the phenylethynyl α-diketone monomer.

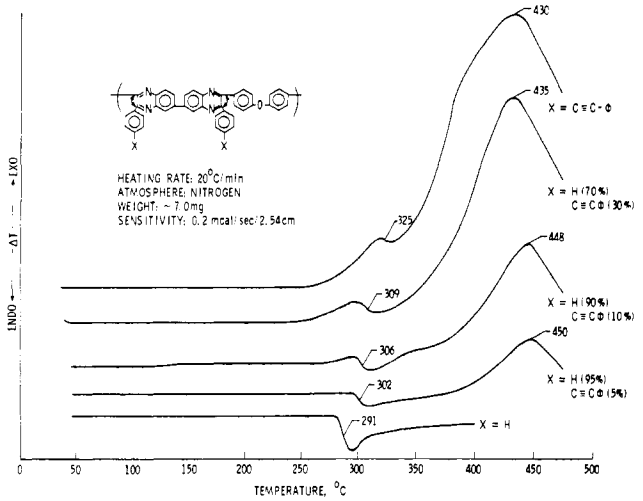


Figure 3. Differential scanning calorimetric curves of polymers.

Thermal Characterization of Polymers. Differential Scanning Calorimetry (DSC). Pertinent DSC data are presented in Tables IV and V. As shown in Figure 3 and Table IV, the polymer of structure VII, which is void of phenylethynyl groups, has a T_g of 291 °C. The T_g of the polymer is increased as phenylethynyl groups are placed on the pendant phenyl groups. As the mole percent of phenylethynyl groups in the polymers is increased, the T_g and intensity of the exotherm are increased while the exothermic peak temperature is decreased. The exotherm is due to the reaction of the phenylethynyl groups, as evidenced by infrared spectroscopic work before and after the thermal exposure (disappearance of the C≡C stretch at 2220 cm^{-1}).

Samples of each phenylethynyl-substituted PPQ were cured in the DSC cell by heating to 475 °C under nitrogen. Each sample retained its original yellow color. The samples were cooled and rerun. As shown in Tables IV and V, the T_g's of the 475 °C cured polymers increased as the mole percent of phenylethynyl groups increased, presumably due to cross-linking. The T_g of the 475 °C cured polymers containing 30 and 100 mol% phenylethynyl groups could not be detected.

In general, the cured phenylethynyl-substituted polymers of structure VIII exhibited T_g's higher than those of structure VII. As the mole percent of phenylethynyl groups was increased in the polymers of structure VIII, a more drastic decrease in the exothermic peak temperature was observed. This is apparently due to greater mobility of the 4-(phenylethynyl)phenoxy group in polymers of structure VIII relative to the more rigid phenylethynyl group in polymers of structure VII. As shown in Table V, introduction of the bulky but flexible phenoxy group into the para position of the pendant phenyl group on the polymer resulted in a significant lowering of the T_g.

Torsional Braid Analysis (TBA). The polymers were also characterized by TBA, with the T_g taken as the temperature of the damping peak during the heatup and cooldown cycle. Pertinent TBA data are given in Tables IV and V. A representative TBA curve is presented in Figure 4. A low-temperature damping peak (~28 °C) is present, apparently due to motion of the pendant phenyl and (phenylethynyl)phenyl groups on the quinoxaline ring. As the braid was heated, a damping peak occurred at 291 °C, which coincided with a rapid change in rigidity. The braid was heated in nitrogen to 475 °C and a cooldown curve obtained which displayed a damping peak at 340 °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. Braids of several polymers were heated in the TBA instrument to 200 °C to remove residual solvent and moisture and rerun. The low-temperature damping peak was present in these dried samples, which indicated that it is probably due to motion of some portion of the polymer and not moisture or residual solvent. As shown in Tables IV and V, the temperature of the cooldown damping peak (T_g) for the cured phenylethynyl-substituted polymers increased as the mole percent of the phenylethynyl groups in the polymers increased. The T_g's of the cured phenylethynyl-substituted polymers of structure VIII were higher than those of structure VII, apparently due to more efficient cross-linking (more mobility of the phenylethynyl groups).

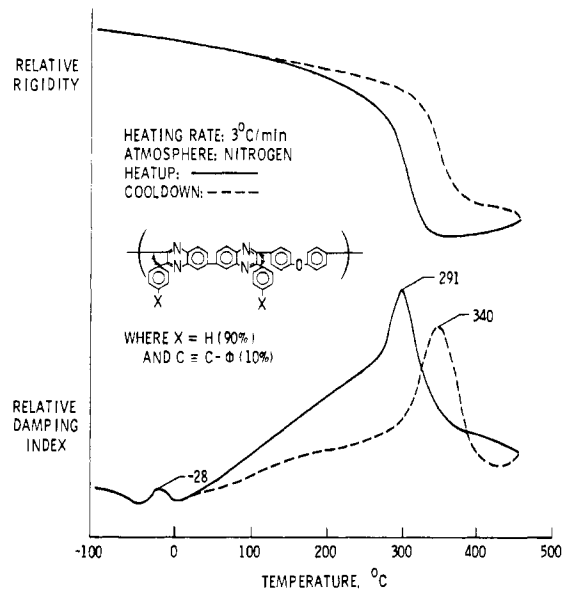


Figure 4. Torsional braid analysis of phenylethynyl-substituted poly(phenylquinoxaline).

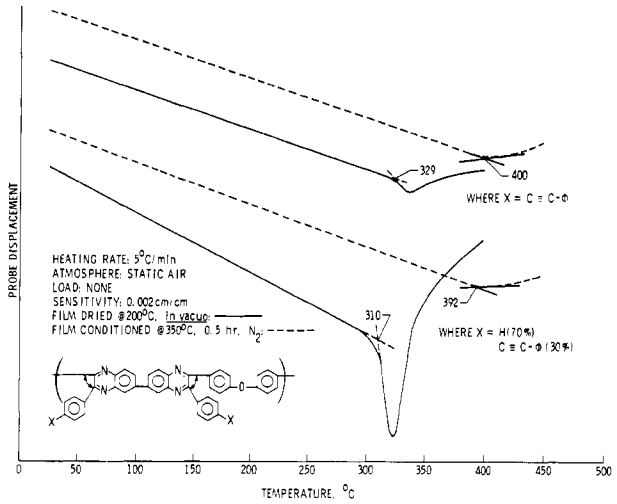


Figure 5. Thermal mechanical analysis of polymers (elongation of films).

Thermal Mechanical Analysis (TMA). Films of the polymers in Table IV were subjected to TMA (film elongation). Solution-cast films which were dried in vacuo at 200 °C exhibited elongation in the general temperature range where the apparent initial T_g by DSC was found. Specimens of these films were conditioned in the TMA apparatus to induce cross-linking by heating at 350 °C for 0.5 h under a nitrogen blanket. The temperatures reported in Table IV are for the films after the 350 °C conditioning.

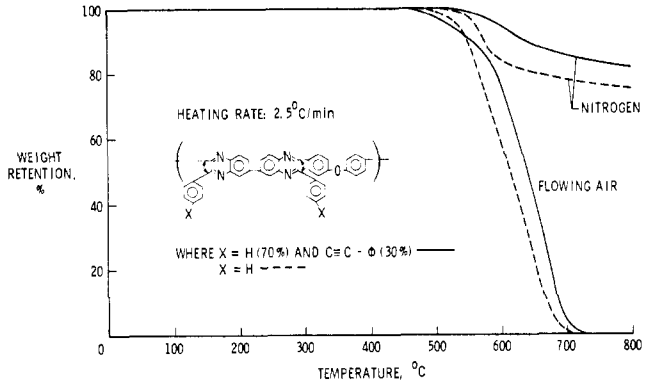


Figure 6. Thermogravimetric analysis of polymers.

Representative TMA curves for two polymers are shown in Figure 5. The 200 °C dried film of the polymer containing 30 mol % phenylethynyl groups began to stretch at ~310 °C and as the temperature was increased, cross-linking occurred. After a film of this polymer was conditioned at 350 °C for 0.5 h, cross-linking occurred, which resulted in an increase in the T_g (392 °C). The same trend occurred in films of the polymer containing 100 mol % phenylethynyl groups. The 200 °C dried film exhibited a T_g of 329 °C, which compares favorably with the 326 °C found by DSC. After conditioning of the film at 350 °C, the T_g increased to ~400 °C due to induced cross-linking. All of the films from the phenylethynyl-substituted polymers in Table IV exhibited an increase in the T_g as the mole percent of phenylethynyl groups increased.

Thermogravimetric Analysis (TGA). Several of the polymers in Tables IV and V were cured for 0.5 h at 350 °C in nitrogen and subsequently subjected to TGA, with representative curves shown in Figure 6. In flowing air, the phenylethynyl-containing PPQ exhibited initial weight loss at ~460 °C, with drastic weight loss occurring at ~600 °C. In nitrogen, initial weight loss for the phenylethynyl-containing PPQ occurred at ~520 °C, with a char residue of >80% at 800 °C. All of the phenylethynyl-substituted PPQs exhibited similar curves. The thermal stability by TGA for the phenylethynyl-containing polymers appears to be higher than that of ordinary PPQ (Figure 6). However, higher molecular weight fragments are probably formed from the decomposition of the phenylethynyl-containing PPQ which demand a higher temperature to volatilize, resulting in a higher apparent polymer decomposition temperature. A more meaningful measure of thermal stability is isothermal aging at elevated temperatures.

Isothermal Analysis. Films of three polymers in Table IV which were conditioned at 350 °C for 0.5 h in nitrogen to remove residual solvent and induce cross-linking were aged simultaneously in a circulating air oven at 316 °C (±5 °C). The change in weight, flexibility, and color were recorded as a function of time (Figure 7). In general, the films from the polymers containing phenylethynyl groups were less stable at 316 °C than the PPQ containing no phenylethynyl groups, as evidenced by higher weight loss and faster discoloration. When films of the same three polymers were aged at 232 °C in circulating air for 1000 h, essentialy no difference in weight loss was observed. However, the phenylethynyl-containing polymers became brittle as expected due to cross-linking and exhibited slightly more discoloration. The PPQ film void of phenylethynyl groups was transparent orange and fingernail creaseable after aging for 1000 h at 232 °C.

Solubility of Polymers. Similar to ordinary linear PPQs, the phenylethynyl-containing PPQs were readily

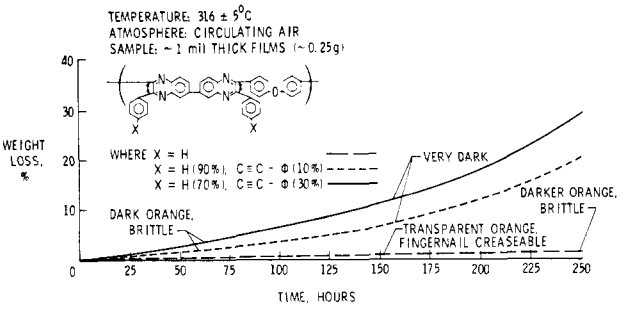


Figure 7. Isothermal aging curves of polymers.

soluble at ambient temperatures in solvents such as *m*-cresol, chloroform, and *sym*-tetrachlorethane 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 phenylethynyl-containing polymers failed to exhibit even partial solubility in chloroform, *sym*-tetrachloroethane, or *m*-cresol whereas films from polymers void of phenylethynyl groups readily dissolved. The films of the polymers containing 5 mol % phenylethynyl groups exhibited slight swelling whereas no detectable swelling was observed in the films containing ≥10 mol % phenylethynyl groups. In addition, films of polymers containing 5, 10, and 30 mol % phenylethynyl groups which were dried for several hours at 300 °C in vacuo were also insoluble in chloroform and *m*-cresol.

Processability. Samples of the polymers in Tables IV and V 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 phenylethynyl groups fused to form transparent orange films. The polymer containing 5 and 10 mol % phenylethynyl groups exhibited good fusion to form transparent orange films with some integrity. Polymers containing 30 mol % phenylethynyl groups exhibited partial fusion whereas the PPQs containing 100 mol % phenylethynyl groups failed to fuse. On the basis of these findings, PPQs containing more than 30 mol % phenylethynyl groups may not be amenable to processing in the conventional manner as laminating resins or adhesives. The phenylethynyl group readily cross-links at elevated temperature to reduce the flow and inhibit the processability of the polymer.

Conclusions

Relatively high molecular weight linear soluble PPQs containing pendant phenylethynyl groups were successfully synthesized. The thermally induced reaction of the phenylethynyl groups provided insoluble cross-linked polymers with high T_g's. Depending upon the phenylethynyl density, the phenylethynyl-containing polymer exhibited good to poor processability by compression molding. The cured phenylethynyl-containing polymers exhibited lower thermooxidative stability than that of a corresponding polymer with no phenylethynyl groups. A new method of introducing a controlled amount of cross-linking into a polymer via pendant phenylethynyl groups was demonstrated. This cross-linking route can be extended to a variety of other polymer systems.

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Rodlike Nature of α-Helical Polypeptides in Solution

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ABSTRACT: Light scattering, viscosity, and sedimentation measurements were performed on solutions of poly(ϵ-carbobenzoxy-L-lysyl-γ-benzyl-L-glutamate) in *N,N*-dimethylformamide to obtain the light scattering radius $\langle S^2\rangle_z^{1/2}$, intrinsic viscosity $[\eta]$, and limiting sedimentation coefficient s_0 as functions of molecular weight. The results showed that the α helix of this polypeptide is intact and straight at weight-average molecular weights lower than 200 000 but exhibits flexibility at higher molecular weights. The data for $[\eta]$ and s_0 in the lower molecular weight region combined with similar data for poly(γ-benzyl L-glutamate) in *N,N*-dimethylformamide were analyzed by the hydrodynamic theories of Norisuye et al. and Yoshizaki and Yamakawa for cylindrical molecules, yielding molecular dimensions consistent with the α helices of these polypeptides.

Doty et al.[3] were the first to show from light scattering and viscosity data that poly(γ-benzyl L-glutamate) (PBLG) is α-helical in *N,N*-dimethylformamide (DMF) and $CHCl_3$ and behaves as a rigid rod. Subsequent studies on various synthetic polypeptides,[4-7] however, have revealed that the polypeptide chain in the α-helical conformation exhibits flexibility as it becomes very long. It has also been shown[7,8] that although low molecular weight PBLG and poly(ϵ-carbobenzoxy-L-lysine) (PCBL) are rodlike in DMF at room temperature, PCBL is more flexible than PBLG at high molecular weight. This is ascribed to the difference in helix stability between these polypeptides in helix-supporting solvents.[9,10] Since the helix stability is related to the chemical structure of the polypeptide chain, it is interesting to study sequential polypeptides consisting of γ-benzyl-L-glutamyl and ϵ-carbobenzoxy-L-lysyl residues. In a previous publication[11] we have shown that poly(ϵ-carbobenzoxy-L-lysyl-γ-benzyl-L-glutamate) (poly[Lys(Cbz)-Glu(OBzl)]) assumes an α-helical conformation in DMF, 2,2,2-trifluoroethanol, and other helix-supporting solvents. In this study we made light scattering, viscosity, and sedimentation measurements on dilute solutions of poly[Lys(Cbz)-Glu(OBzl)] in DMF. The light scattering data obtained are compared with similar data for PBLG and PCBL to examine whether or not a poly[Lys(Cbz)-Glu(OBzl)] molecule takes the shape of a rigid rod. The viscosity and sedimentation data for poly[Lys(Cbz)-Glu(OBzl)] together with those for PBLG are analyzed by recent hydrodynamic theories for cylindrical molecules.[12,13]

Experimental Methods

Polypeptide Samples. The poly[Lys(Cbz)-Glu(OBzl)] samples LG-1 through LG-10 were used: LG-1 and LG-4 were those used previously[14] (CF-H-2 and CF-F-2, respectively, in the previous designation) and the rest were the fractions chosen from our stock.[11,14] The PBLG samples used for viscosity measurements were those characterized in our previous study[15] (Table I).

Table I
Viscosity Data for Poly(γ-benzyl L-glutamate)[a]

sample code	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta] \times 10^{-2}$/cm^3 g^{-1} DMF, 25 °C	$[\eta] \times 10^{-2}$/cm^3 g^{-1} DCA,[b] 25 °C
A-1	0.347		0.0378	0.0715
A-2	0.476		0.0374	0.083
A-3	1.06		0.055	0.121
A-4	1.42		0.0745	0.152
A-5	2.21		0.120	0.205
A-6	3.70	3.20	0.238	0.301
A-IV	6.35	5.49	0.526	0.450
E-4	8.08	7.14	0.708	0.547
E-3	15.8	12.8	1.94	0.898
A-X	18.8		2.42	0.98
E-2	23.7		3.62	1.22
A-IX	35.4		6.0	1.60
F-2	47.7		9.20	2.17
E-1	56.7	42.2	12.8	2.48

[a] The data for A-IV through E-1 have been taken from ref 23. [b] DCA = dichloroacetic acid.

Light Scattering. Intensities of light scattered from solutions of poly[Lys(Cbz)-Glu(OBzl)] in DMF at 25 °C were measured by using a FICA 50 photogoniometer[16] with vertically polarized incident light of wavelengths of 436 and 546 nm at scattering angles ranging from 15 to 150°. The photogoniometer was calibrated with benzene at 25 °C as the standard liquid by taking the Rayleigh ratio to be 46.5×10^{-6} cm^{-1} at 436 nm and 16.1×10^{-6} cm^{-1} at 546 nm.[17] The data were extrapolated to infinite dilution and zero scattering angle by Berry's method.[18] Polymer

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