were measured as a function of temperature (Figure 2). The data show that at high mechanical stresses, plastic deformation takes place in these polymers far below their glass-transition temperatures. For example, the film elongation at break for polymer 4 at 300 °C, 80 °C below T_g, is 60%, and the tensile strength at this temperature has decreased by a factor of about 3. The results indicate that when these polymers are to be used as load bearing materials their use temperatures lie significantly below their respective T_g or T_m, a phenomena which is not always appreciated in the application of these polymers for use as structural materials.

Under mild tensile stresses as required for dynamic mechanical testing (Figure 3 and Figure 10, ref 5) the mechanical performance of films is as expected relatively constant up to the glass transition temperature. Above T_g mechanical losses become pronounced as effected in a drop in Young's modulus from 2–5 × 10^{10} to less than 10^7 dyn/cm^2. This behavior is typical for noncrystalline, linear high polymers. Mechanical losses of low amptitude are observed in polyquinolines between 100 and 150 °C (Figure 3 and Figure 10, ref 5). While the nature of these losses is presently not understood, we have observed these peaks also in polyimides, polyquinoxalines, polyphenylene ethers, and poly-*as*-triazines, and they are apparently common to most aromatic polymers.

In Table II are listed dynamic mechanical data for four different polyquinolines. It is noted that Young's modulus decreases from 4.8 × 10^{10} dyn/cm^2 for the more rigid polymer **4** to 1.9 × 10^{10} dyn/cm^2 for polymer **14** which contains an additional flexibilizing diphenyl ether linkage between the quinoline groups. The effect of annealing films above T_g on Young's modulus was shown for polymer 11 (Table II). A film sample which was annealed at 280 °C for 2 h followed by cooling at a rate of 0.5 °C/min had a Young's modulus of 6.1 × 10^{10} dyn/cm^2 as compared to the value of 2.3 × 10^{10} for the original film sample. Both samples were essentially x-ray amorphous and the threefold increase in modulus was attributed to ordering of the amorphous material.

Acknowledgment. This research was supported in part by the U.S. Army Research Office, Durham, N.C., and the National Science Foundation.

References and Notes

(1) Y. Imai, E. F. Johnson, T. Katto, M. Kurihara, and J. K. Stille, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2233 (1974).
(2) J. F. Wolfe and J. K. Stille, *Macromolecules*, **9**, 489 (1976).
(3) S. O. Norris and J. K. Stille, *Macromolecules*, **9**, 496 (1976).
(4) Rheovibron Mod. DDV-II Instruction Manual 14, August 1969, Tape Measuring Instrument Co., Ltd.
(5) W. Wrasidlo and J. K. Stille, *Macromolecules*, **9**, 505 (1976).
(6) W. Wrasidlo, *J. Polym. Sci., Part A-2*, 1603 (1971).
(7) R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).
(8) M. C. Shen and A. Eisenberg, *Prog. Solid State Chem.*, **3**, 407 (1966).
(9) J. Heijboer, *Plastica*, **19**, 489 (1966).

The Cross-Linking of Thermally Stable Aromatic Polymers by Aryl Cyanate Cyclotrimerization

J. K. Stille,* R. G. Nelb, II, and S. O. Norris

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.

Received March 1, 1976

ABSTRACT: Thermally stable aromatic polymers have been cross-linked by employing the cyclotrimerization of aryl cyanates as the curing reaction. Biscyanato prepolymers of a phenylated polyphenylene and a polyphenylquinoline were synthesized by the reaction of cyanogen bromide with the corresponding hydroxyl end-capped oligomers. Thermal treatment of these prepolymers afforded a three-dimensional network structure with cyanurate ring structures at the cross-linking site. The cured polymers showed an increase of T_g over that of the corresponding biscyanato prepolymers. These values of T_g did not exceed those of the parent polymers because of the copolymer effect induced by the presence of the cyanurate structures. These materials were insoluble and showed thermal stabilities characteristic of the parent polymer systems, although initial weight losses of 4–8% above 400 °C were shown to be caused by the loss of cyanuric acid from the cross-linking sites. Hydrolytic stabilities of these materials were very good in acidic or basic aqueous media, but complete degradation of the cross-linking structures occurred in a strongly basic, swelling solvent medium.

The processability of thermally stable aromatic polymers is often quite limited because of the high values of T_g usually exhibited by these polymers.[1] The incorporation of flexible structures in the polymer chain makes processing more amenable by lowering the T_g. However, this modification also lowers the use temperature well below the thermal capability of the polymer as defined by the degradation temperature.

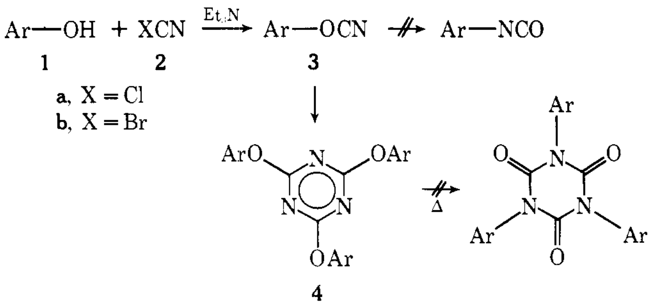
The softening point of a polymer (T_g) can be raised or eliminated by the formation of a network structure. However, there is no general method for introducing cross-links in the relatively inert, totally aromatic or heterocyclic polymer during or after fabrication. Ideally, a cross-linking reaction which is suitable for thermally stable polymers must produce a thermally stable link which is hydrolytically stable, and compatible with the polymer system. Also, it should proceed quantitatively, produce no volatiles, and occur under thermal or catalytic conditions, but not in storage. A reaction which approaches these requirements is the cyclotrimerization of aryl cyanates.

Although cyanates have been synthesized by several different methods,[2] the most convenient route[3] involves treating a phenol **1** and a cyanogen halide **2** with the stoichiometric amount of triethylamine to afford a quantitative yield of the aryl cyanate **3** (Scheme I). Although alkyl cyanates readily undergo rearrangement to the corresponding alkyl isocyanates, **3** is stable[2] and is isolable by distillation or crystallization.

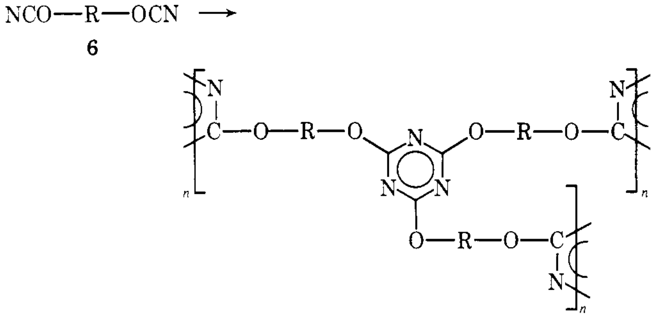
Quantitative yields of trisaryl-*s*-triazine (aryl cyanurate) (**4**) have been obtained from the cyclotrimerization of **3**.[2–4] The reaction is promoted by heat, protonic acids, Lewis acids, and bases,[2,5,6] and can be carried out in a number of solvents or neat.[6] The trimerization of cyanates is highly selective when compared with other cyclotrimerization reactions in which chain polymerization and dimerization compete as side reactions.[6] The phenyl cyanurate **4** (Ar = Ph) has been reported[7,8] to be relatively chemically inert.

The cyanate cyclotrimerization reaction has been employed as a polymer forming reaction.[9] The gradual heating of bulk biscyanates **6** to 250 °C with a zinc chloride catalyst afforded

Scheme I

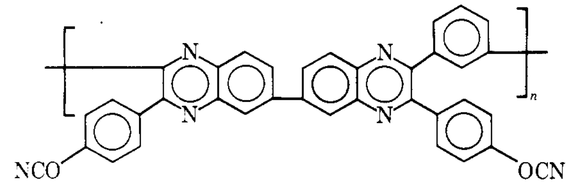


high molecular weight, insoluble and infusible, network polymeric materials **7**. These polymers showed no weight losses up to 400 °C where rapid and complete decomposition began.[10]



7

Cyanate cyclotrimerization at 400 °C also has been used to cross-link the polyquinoxaline **8** which was prepared from the corresponding hydroxyl substituted polymer by treatment with cyanogen chloride (**2a**) and triethylamine.[11] In the cured polymer, no Tg could be detected and it was insoluble in *m*-cresol and concentrated sulfuric acid.



8

Fiberglass laminates prepared using the biscyanate derived from bisphenol-A show high thermostability including good mechanical properties and excellent electrical resistance at elevated temperatures, and excellent chemical resistance.[12]

Results and Discussion

The applicability of cross-linking by aryl cyanate of cyclotrimerization to a wide variety of thermally stable polymers was demonstrated in this study by the synthesis and subsequent cross-linking of phenylated polyphenylene and polyphenylquinoline prepolymers. The only restriction placed upon the type of polymer system which may be utilized is the ease with which hydroxyl groups, which are converted to the cyanate moiety, can be incorporated into the appropriate prepolymer. Phenylated polyphenylenes[13–15] and polyphenylquinolines[16,17] are both very thermally stable and the methods of their syntheses facilitate the incorporation of the necessary hydroxyl functions.

Phenylene Prepolymers. The addition of a monofunctional acetylene, *m*-hydroxyethynylbenzene[18] (**9**), to the polymerization reaction of *p*-diethynylbenzene (**10**) and the oxybistetracyclone **11** served to limit the average molecular weight of the polymer by terminating the growing chains with an aryl hydroxyl group (Scheme II).

A bishydroxyphenylene trimer **12a** was prepared in quantitative yield by the reaction of **11** with 2 equiv of **9** using the polymerization conditions for this polymer system: toluene solution 200 °C, 24 h. The stoichiometry of the reactants allowed the formation of only one product, isolated as a mixture of three isomers due to meta-para catenation in the rings generated by the Diels-Alder reaction.[15] The elemental analysis (Table I) was consistent with the structure **12a** (n = 0). The infrared spectrum contained a band at 3610 cm^{-1} attributed to unassociated hydroxyl groups in addition to the absorptions characteristic of the parent polyphenylene.

The biscyanato prepolymer **13a** was prepared in quantitative yield by the reaction of **12a** with a 25% excess of cyanogen bromide (**2b**) in acetone solution. The infrared spectrum contained no band due to hydroxyl groups and a strong absorption appeared at 2280 cm^{-1} due to the terminal cyanate groups. The elemental analysis was consistent for the biscyanato prepolymer **13a**.

A similar procedure, using a 5:6:2 mol ratio of **10**:**11**:**9**, afforded a second bishydroxy prepolymer **12b**, $\bar{M}_n$ = 4000 (Table I). A weak free hydroxyl absorption was present in the infrared spectrum at 3610 cm^{-1}. The reaction of **12b** with excess cyanogen bromide (**2b**) in chloroform solution resulted in the biscyanato phenylene prepolymer **13b** which contained a cyanate absorption at 2270 cm^{-1} in the infrared spectrum.

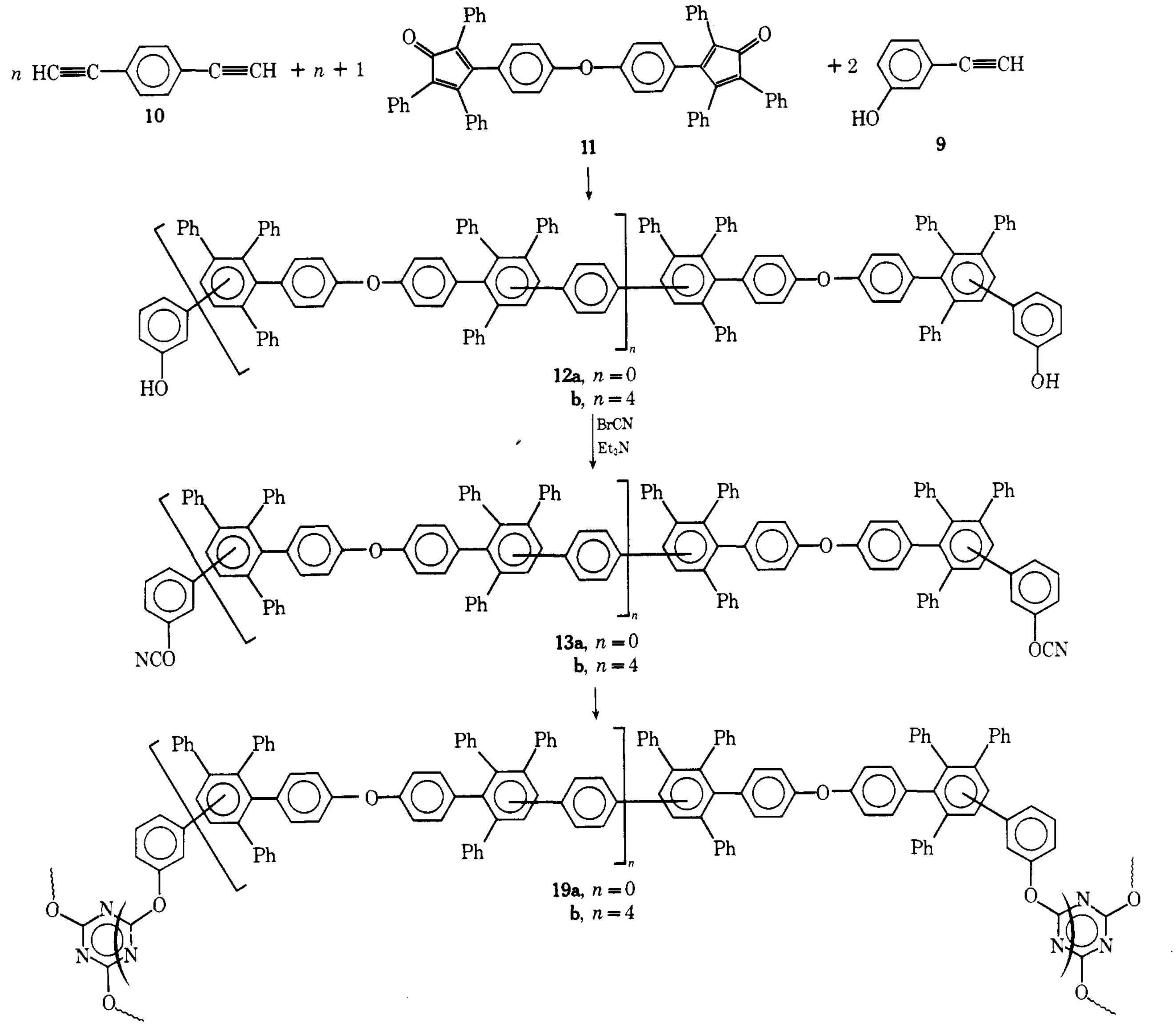
Phenylquinoline Prepolymers. The synthesis of polyphenylquinolines[17] by the condensation of 4,4′-diacetyldiphenyl ether (**14**) with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**15**) is readily adapted to the synthesis of hydroxyl end capped prepolymers by the addition of *p*-hydroxyacetophenone (**16**) to the polymerization reaction. A bishydroxy prepolymer (**17a**) with a relatively short chain length was prepared from a 1:2:2 mol ratio of **14**:**15**:**16** which was converted to the biscyanato phenylquinoline prepolymer **18a** by treatment with excess **2b** in chloroform solution (Scheme III). Although the statistical molecular weight of **18a** should be 1249, the method of isolation of the bishydroxy prepolymer apparently preferentially isolated only the higher molecular weight species of the cyanate derivative **18a** having an $\bar{M}_n$ of 2900 (n = 4) (Table I). The elemental analysis of this material was consistent with a molecular weight higher than statistically expected. The presence of the cyanate moiety was confirmed by the 2240, 2265, and 2285 cm^{-1} absorptions in the infrared spectrum, and the resonance at 108.5 ppm for the cyanate carbon in the ^{13}C NMR spectrum (Table II).

The reaction of **14**, **15**, and **16** in a 10:11:2 mol ratio, followed by cyanation with **2b** in chloroform, resulted in the biscyanato phenylquinoline prepolymer **18b**, $\bar{M}_n$ = 6800 (n = 10–11) (Table I) containing the characteristic cyanate absorptions in the infrared spectrum. The elemental analysis was consistant with a chain length of n = 10–11. The molecular weight of **18b** was sufficiently large to allow clear, tough films to be cast from chloroform solution.

Thermal Analysis of the Prepolymers. Thermal analyses of the biscyanato prepolymers **13** and **18** by differential scanning calorimetry (DSC) were performed in order to determine the temperature at which the cyanate end groups underwent thermally initiated cyclotrimerization to form the cyanurate cross-linking unit. The results of this study are summarized in Table III, and a representative DSC scan of **13a** is shown in Figure 1.

The molecular weight differences between **13a** and **13b** and **18a** and **18b** gave rise to the differences in the T_g observed for the prepolymers before cyclotrimerization since T_g depends upon $\bar{M}_n$, at least in the lower molecular weight range.[19] The difference in the temperature at which the exothermic peak occurred was also dependent upon the molecular weights of

Scheme II



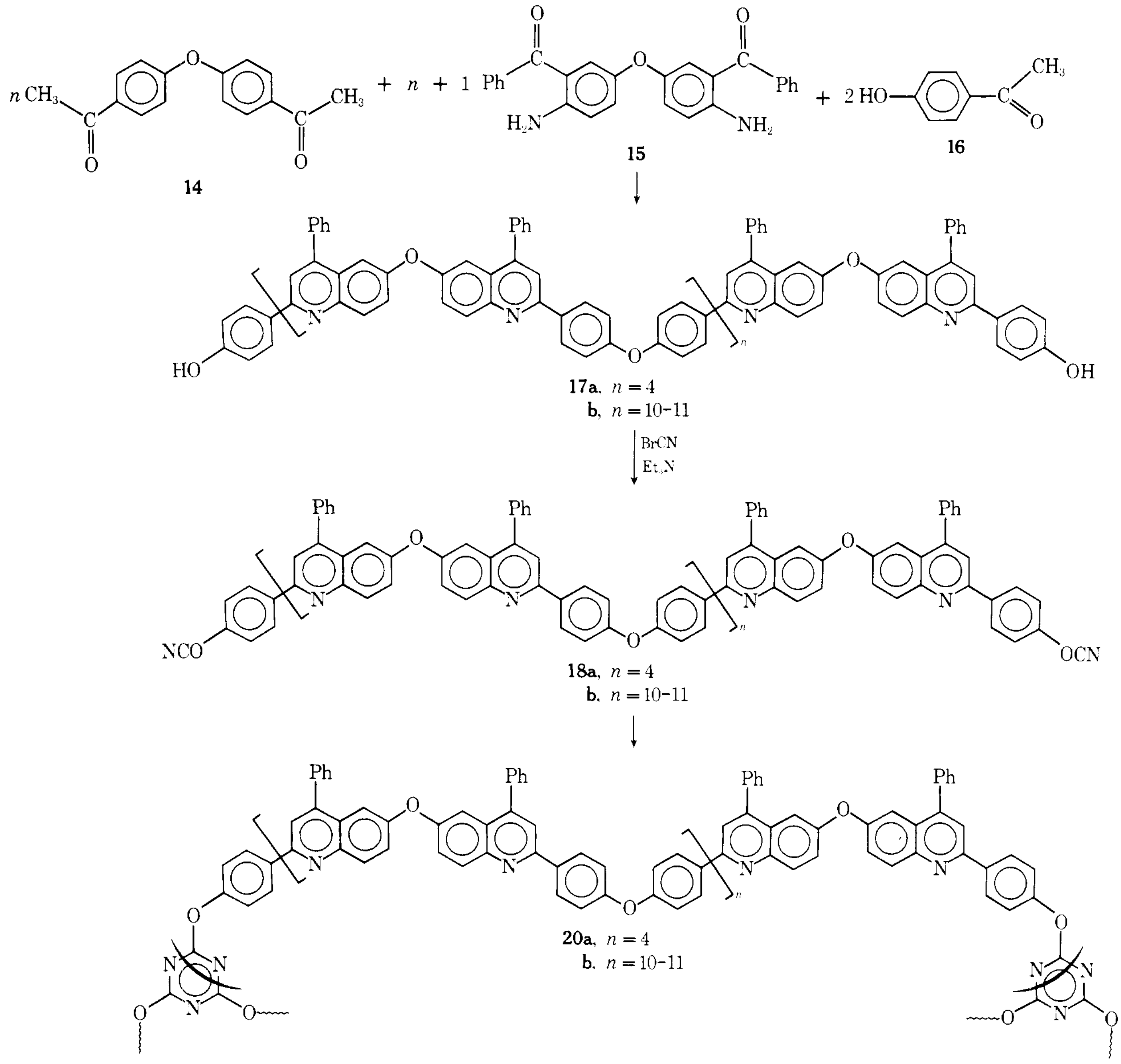
the two classes of prepolymer in that the cyclotrimerization of the smaller prepolymer occurred ~100 °C lower than the higher molecular weight prepolymer. This effect is related to the differences in the polymer chain mobility at various temperatures, as indicated by the value of T_g, since three cyanate end groups must come together for the reaction to occur. The temperature at which the exothermic peak reached a maximum was somewhat lower for the phenylquinolines **18**

Table I
Prepolymers

	n	Mol wt,[a] $\overline{M}_n$ (Calcd)[b]	Elemental Anal. (Calcd)[b] %C	%H	%N
			Phenylene		
12a	0	 (963.12)	89.92 (89.73)	5.73 (5.23)	
12b	4	4000 (4375.16)	91.98 (92.24)	5.20 (5.21)	
13a	0	 (1013.14)	87.52 (87.72)	4.82 (4.78)	2.70 (2.76)
13b	4	 (4425.18)	91.98 (91.73)	5.26 (5.10)	0.38 (0.63)
			Phenylquinoline		
18a	4	2900 (3021.48)	83.52 (84.27)	4.37 (4.34)	5.87 (5.56)
18b	10–11	6800 (6565.62–7156.31)	84.96 (84.88 and 84.93)	4.46 (4.39 and 4.39)	5.00 (5.10 and 5.09)

[a] Vapor pressure osmometry. [b] Calculated using: $C_{72}H_{50}O_3$ + $(C_{66}H_{44}O)_n$ for **12**. $C_{74}H_{48}O_3N_2$ + $(C_{66}H_{44}O)_n$ for **13**. $C_{44}H_{26}N_4O_3$ + $(C_{42}H_{26}N_2O_2)_n$ for **18**.

Scheme III



than for the phenylenes **13** of similar molecular weight. This may be due to a small catalytic effect caused by the basic phenylquinoline units. The higher density of cyanate end groups which underwent cyclotrimerization resulted in a larger peak area observed for the exothermic transitions of **13a** and **18a** relative to **13b** and **18b**.

Repeating the DSC scans of these now cured samples under identical conditions showed no exothermic transitions but T_g of the cross-linked material had increased relative to the T_g of the prepolymers (vide infra).

Cross-Linking Conditions. Samples of the prepolymers were cross-linked by the thermal cyclotrimerization of the terminal cyanate groups to form three-dimensional, cyanurate-linked network structures (Schemes II and III). Generally the prepolymers were heated to a temperature well above the onset temperature of the exothermic transitions, but not necessarily as high as the transition maxima (Table III). Lower temperatures and longer reaction times (e.g., 6 h at 200 °C for **13a**) resulted in incomplete reaction as indicated by an exothermic transition in the DSC thermogram of the resulting material.

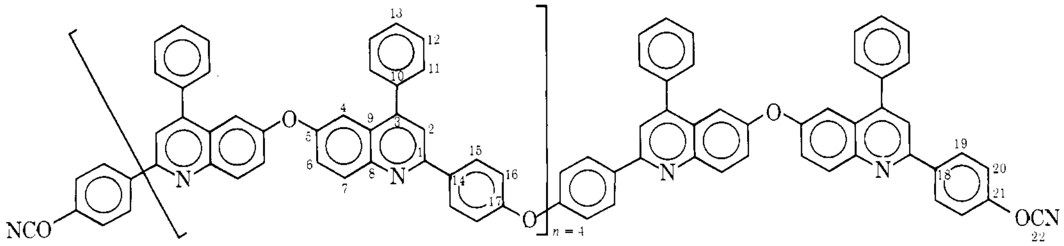
Both of the phenylene prepolymers **13a** and **13b** were able to flow during the initial heating and formed hard, tough amber "buttons" of the polymers **19a** and **19b** respectively at the bottom of the ampules. Polymer **19a** was more brittle due to the higher cross-link density in this sample. Voids in the prepolymer powder prior to the reaction resulted in a honeycomb structure in the interior of the button since no pressure was applied during the processing step.

Neither of the two phenylquinoline prepolymers **20** showed any tendency to flow during the initial heating period. In contrast to the polyphenylenes, the parent polyphenylquinoline[17,20] has some crystalline character (T_m 448 °C) and a T_g of 266 °C. Viscous flow of a similar polyphenylquinoline[16] occurs at 430 °C only under high pressure.

A film of the biscyanato phenylquinoline prepolymer **18b** cast from chloroform solution was also cross-linked by thermal treatment under similar conditions to afford a transparent, tough amber film. The cyanate absorptions at 2240, 2260, and 2280 cm^{-1} disappeared in the infrared spectrum (Figure 2), and the film was insoluble in chloroform.

Characterization of the Cured Polymers. The increase in the value of T_g with the degree of cross-linking can be used to measure the relative extent of the cross-linking reaction. The curing conditions employed resulted in the maximum T_g's recorded for the cured materials indicating that the maximum degree of cross-linking detectable by the increase in the T_g had been obtained under the curing conditions.

Table II
Carbon-13 Spectra of Biscyanato Phenylquinoline Prepolymer 18a



C No.	Chemical shift[a,b]	C No.	Chemical shift[a,b]	C No.	Chemical shift[a,b]	C No.	Chemical shift[a,b]
1	155.1	7	132.1	13	128.7	19	153.4[e]
2	122.9	8	145.8	14	134.7	20	115.5
3	148.3	9	126.4	15	127.7[d]	21	153.4
4	112.4	10	138.0	16	126.7[d]	22	108.5
5	154.5	11	129.3[c]	17	158.1		
6	119.2	12	129.3[c]	18	154.3[e]		

[a] Chloroform solution, TMS internal standard. [b] Chemical shift values assigned by comparison with assignments for parent polymer (S. O. Norris and J. K. Stille, *Macromolecules*, in press) and phenylcyanate (R. Radeglia, W. Storek, G. Engelhardt, F. Ritschl, E. Lippmaa, T. Pehk, M. Mägi, and D. Martin, *Org. Magn. Reson.*, 5, 419 (1973)). [c] Overlapping peaks. [d] Assignments may be reversed. [e] Assignments may be reversed.

Table III
Thermal Transitions of the Biscyanato Prepolymers and the Cross-Linked Polymers

Prepolymer	T_g,[a,b] °C	Range of exotherm,[a] °C (max)	Curing conditions		Cured polymer	T_g,[a,b] °C	Elemental Anal. (Calcd)[c]		
			Temp, °C	Time, min			%C	%H	%N
13a	136	180–370 (300–310)	150 to 300	90	**19a**	216	87.05 (87.72)	4.87 (4.78)	2.94 (2.76)
13b	272	325–450 (400–410)	350	120	**19b**	305	91.74 (91.73)	5.05 (5.10)	0.40 (0.78)
			350	120	**19c**[d]	294			
18a	183	215–360 (270–275)	150 to 300 then 300	60 30	**20a**	260	83.24 (83.55)	4.19 (4.27)	5.80 (6.09)
18b	240	300–435 (390–400)	200 to 350 then 350	40 80	**20b**	265	84.79 (84.88)	4.24 (4.39)	5.03 (5.12)

[a] Measured by DSC, heating rate 20 °C/min, nitrogen atmosphere. [b] Parent polyphenylene T_g = 327 °C. Parent polyphenylquinoline T_g = 266 °C. [c] Calculated using molecular formulas in Table I, footnote *b*. [d] Cured in the presence of 1.8 wt % *p*-toluenesulfonic acid.

A sample of the biscyanato phenylene prepolymer **13b** which was polymerized in the presence of 1.8 weight percent of *p*-toluenesulfonic acid as a catalyst showed no increase in the T_g of the resulting polymeric material **19c** indicating that no significant increase in the degree of cross-linking resulted from the presence of an acid catalyst under these conditions.

Values of T_g higher than observed for the parent polymer systems were not realized because of the copolymerization effect[21] induced by the cyanurate ring structures. In the absence of the copolymer effect, the T_g's of the cross-linked phenylene polymers **19** should occur at temperatures above 327 °C, the T_g measured for the parent polymer. Since **19a** has a higher cross-link density than **19b**, the T_g of **19a** should be higher than **19b**. An analogous situation should exist for the phenylquinoline polymers **20a** and **20b** whose parent polymer[17,20] has a T_g of 266 °C. These trends, however, were not observed experimentally. The values of T_g for the phenylene polymers **19** were both lower than 327 °C and their order was reversed from that predicted solely on the basis of polymer chain immobilization during cross-linking. The experimental results are consistent with a reduction of the T_g by the copolymer effect which should be greater in **19a** than in **19b** because of the differences in the cross-link density. The observed values of T_g for the phenylquinoline polymers **20a** and **20b** can be accounted for by a similar explanation although the magnitude of the effect was much smaller. Apparently the cyanurate cross-linking structures were less compatible with the phenylene segments than with the phenylquinoline segments, perhaps because of the heterocyclic structure of the latter.

Thermogravimetric analyses in both air and nitrogen atmospheres were conducted on all four polymer samples (Table IV). The effect of the cyanurate cross-link structures was to reduce the thermal stability by causing the initial weight loss to occur at 400 °C. This change was especially evident in the highly cross-linked samples, such as **19a** (Figure 3), where an initial weight loss of 4–8% was observed in both air and nitrogen. However, after this initial loss, the materials behaved much as the parent polymers.[13,17]

The long-term thermal stabilities of the polymer samples, measured at 300 °C over a 100-h period (Table IV), were quite good with only the highly cross-linked phenylene polymer **19a** having a significant weight loss of 6% under these conditions. Except for **19a** which turned from amber to black, there was little color change in the samples used in these analyses.

In order to determine the identity of the volatile products responsible for the initial weight losses observed in the TGA's, the highly cross-linked phenylene polymer **19a** was pyrolyzed in vacuo at 400–425 °C, and the resulting pyrolyzate was

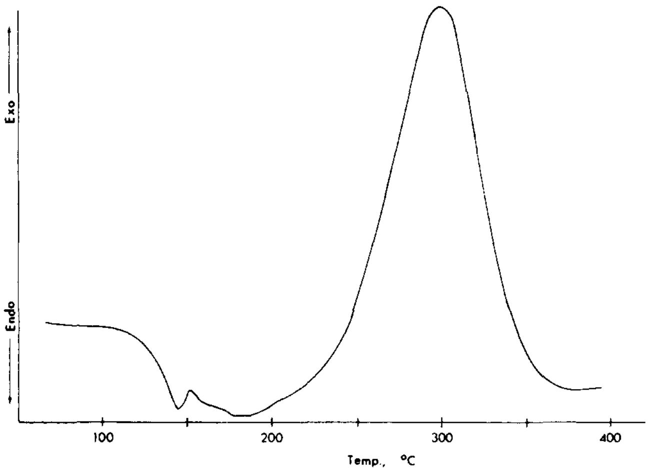


Figure 1. DSC thermogram of the biscyanato phenylene prepolymer **13a** (nitrogen, heating rate = 20 °C/min).

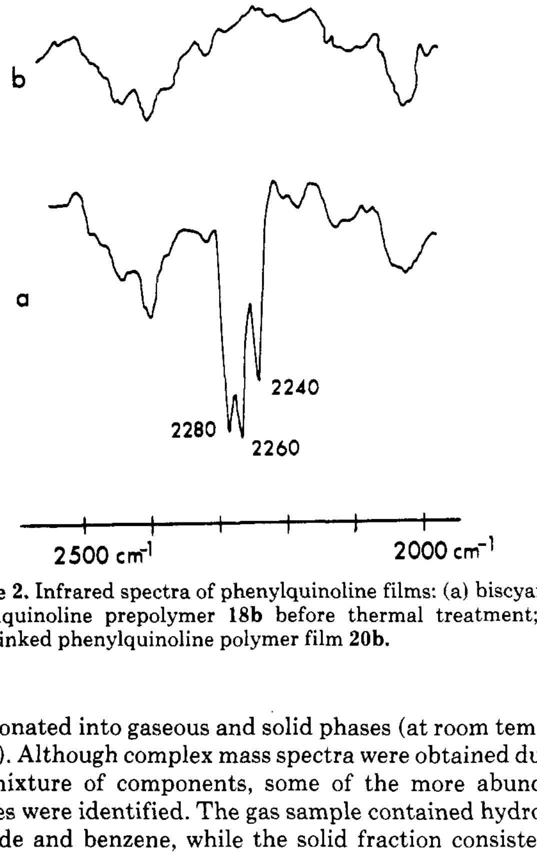
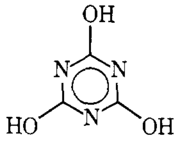


Figure 2. Infrared spectra of phenylquinoline films: (a) biscyanato phenylquinoline prepolymer **18b** before thermal treatment; (b) cross-linked phenylquinoline polymer film **20b**.

fractionated into gaseous and solid phases (at room temperature). Although complex mass spectra were obtained due to the mixture of components, some of the more abundant species were identified. The gas sample contained hydrogen cyanide and benzene, while the solid fraction consisted of mainly cyanuric acid (**21**), resulting from the complete ester cleavage of the triarylcyanurate cross-linking structures. At the pyrolysis temperatures, **21** would degrade to cyanic acid (HO—C≡N) which would again cyclize upon cooling. Hydrogen cyanide also resulted from the degradation of the cross-linking structures. The loss of some pendent phenyls[13] accounted for the presence of benzene in the gas sample. Triphenylcyanurate (**4**, Ar = Ph) was also pyrolyzed under similar conditions. Mass spectrometric analysis of the gaseous portion revealed only fragmentation products of triphenyl cyanurate. No fragmentation pattern characteristic of phenol was observed and no hydrogen cyanide was present. The occurrence of carbon oxides, which have been reported[10] to be the major volatile pyrolysis products of **4**, could not be established by the technique used.



21

Two important factors in the evaluation of these cross-linked polymeric materials which may place limitations upon the used environment are the amount of the soluble fraction and the stability of the cyanate cross-link structure toward acidic and basic media.

The percent soluble fraction (Table V) was determined by extracting the phenylene polymers **19** with benzene and the phenylquinoline polymers **20** with chloroform for 24 h in a Soxhlet extractor. The percents of the soluble fraction as a result of degradation were also determined in the same manner following the treatment of each sample with 1 N aqueous sulfuric acid and 1 N aqueous potassium hydroxide for 100 h at room temperature.

Little swelling was observed for the highly cross-linked polymers **19a** and **20a**, and the percents sol were quite low because of the high probability of reaction during the cross-linking process. The polymer samples with a lower cross-link density, **19b** and **20b**, swelled several times their original size and a substantial weight fraction of the material was soluble.

No catastrophic degradation by hydrolysis of the esterlike cyanurate linkage (which would tend to increase the percent sol as branch points were broken) was observed after prolonged contact with acid or base in a nonswelling solvent.

Treatment of the phenylene polymer **19b** with a strong base in a swelling medium led to the complete solubilization of the polymer after only 48 h at room temperature. Thus, when **19b** in benzene was stirred for 48 h with 5 N aqueous potassium hydroxide and 25 wt % of tetrabutylammonium hydroxide, the polymer became completely soluble in the benzene layer. Precipitation into ethanol afforded an off-white material with an infrared spectrum characteristic of the phenylene chain segments and a hydroxyl absorption at 3680 cm^{-1}, indicative of hydrolysis to the hydroxy prepolymer.

Table IV
Thermogravimetric Analyses of Polymers of 19 and 20

	Air		Nitrogen			
Polymer	Initial break, °C (% wt loss[a])	Major break, °C	Initial break, °C (% wt loss[a])	Major break, °C	% wt loss at 800 °C	Isothermal aging,[b] % wt loss
19a	400 (8)	527	400 (7)	550	25	6
19b		535		545	29	1
20a	380 (5)	510	400 (4)	530	25	1
20b		510		540	33	1

[a] Percent weight loss at the temperature of the major break. [b] Isothermal aging, 100 h at 300 °C in an atmosphere of circulating air.

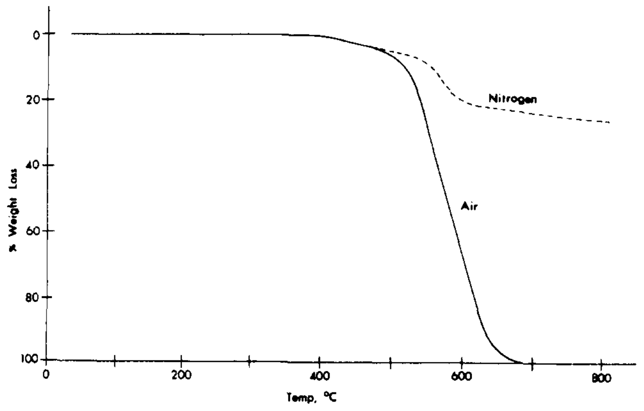


Figure 3. Thermogravimetric analysis of the phenylene polymer **19a.**

Table V
Percent Sol in the Cured Polymers 19 and 20

	Percent sol[a]	Percent sol[b] after 100 h in 1 N H_2SO_4 (aq) (Δ%[c])	Percent sol[b] after 100 h in 1 N KOH (aq) (Δ%[c])
		Phenylene[d]	
19a	3	6 (+3)	7 (+4)
19b	38	40 (+2)	42 (+4)
		Phenylquinoline[e]	
20a	9	8 (−1)	8 (−1)
20b	27	24 (−3)	25 (−2)

[a] Determined by Soxhlet extraction for 24 h. [b] Determined by Soxhlet extraction for 24 h after contact with acidic or basic media. [c] Difference in absolute percentage sol from control sample. [d] Extracted with benzene. [e] Extracted with chloroform.

No noticeable swelling occurred when the cross-linked phenylquinoline film of **20b** was placed in chloroform for 48 h at room temperature.

Experimental Section

A Hewlett-Packard Mecrolab Vapor Pressure Osmometer Model 301A was used to determine the number average molecular weights $\bar{M}_n$ of the prepolymers at 37 °C using a benzil standard in benzene, tetrahydrofuran, or chloroform solution.

Thermal transitions were measured using a Differential Scanning Calorimetry cell attachment for a DuPont 900 Differential Thermal Analyzer under a nitrogen atmosphere at a heating rate of 20 °C/min. The 950 Thermogravimetric Analyzer attachment was used isothermally in circulating air or at a heating rate of 5 °C/min under circulating air or nitrogen atmospheres.

Bishydroxy Phenylene Prepolymer (n = 0) (12a). In a 100 ml glass ampule was placed 3.64 g (4.65 mmol) of the oxybistetracyclone[22] **11** (mp 271–272 °C, lit.[15] 270 °C), 1.10 g (9.32 mmol) of freshly distilled *m*-hydroxyethynylbenzene[18] (**9**) [bp 57–63 °C (2–3 mm) [lit.[18] bp 105–120 °C (16 mm)]: ^{1}H NMR δ 3.08 (s, 1 H), 6.32 (broad s, 1 H), and 6.6–7.2 ppm (m, 4 H); ir (neat) 3100–3600 (OH), 3300 (≡C—H), and 2120 cm^{-1} (C≡C).], and 40 ml of toluene. After three freeze–thaw cycles, the ampule was sealed *in vacuo*. The ampule was placed in a temperature-regulated, 600-ml Paar reactor containing 100 ml of toluene to equalize the pressure in the ampule. After 20 h at 190 °C, the reaction mixture was cooled to room temperature and precipitated into 800 ml of Skelly B to afford 4.43 g (4.60 mmol, 98.9%) of **12a** as an amorphous white powder: ir (CCl_4) 3610 cm^{-1} (OH). The elemental analysis is listed in Table I.

Biscyanato Phenylene Prepolymer (n = 0) (13a). To a solution of 1.345 g (1.397 mmol) of **12a** and 0.369 g (3.48 mmol) of cyanogen bromide (**2b**) in 20 ml of acetone at 0 °C under a nitrogen atmosphere was added dropwise a solution of 0.314 g (3.10 mmol) of triethylamine in 10 ml of acetone. After 1 h, the reaction mixture was filtered and precipitated into water to afford 1.311 g (1.294 mmol, 92.63%) of **13a** as an amorphous white powder: ir (CCl_4) 2280 cm^{-1} (OC≡N). The elemental analysis is listed in Table I and an exothermic reaction with a maximum at 300–310 °C was observed by DSC (Table III) (Figure 1).

Bishydroxy Phenylene Prepolymer (n = 4) (12b). A solution containing 0.2527 g (2.139 mmol) of *m*-hydroxyethynylbenzene[18] (**9**), 4.0243 g (6.4171 mmol) of the oxybistetracyclone[22] **11**, and 0.6747 g (5.348 mmol) of *p*-diethynylbenzene[23] (**10**) in 50 ml of toluene was degassed by three freeze–thaw cycles and sealed in a 100-ml glass ampule. The ampule was placed in a temperature-regulated, 600-ml Paar reactor containing 100 ml of toluene to equalize the pressure in the ampule. After 24 h at 200 °C, the solution was precipitated into Skelly B to afford 5.432 g (97.14%) of **12b** as an amorphous white powder: ir (CCl_4) 3610 cm^{-1} (OH). The elemental analysis is listed in Table I and an $\bar{M}_n$ of 4000 (Table I) was determined by vapor pressure osmometry (VPO) in benzene.

Biscyanato Phenylene Prepolymer (n = 4) (13b). To a stirred solution of 5.63 g of **12b** and 0.394 g (3.72 mmol) of cyanogen bromide (**2b**) in 40 ml of chloroform at 0 °C under nitrogen was slowly added 0.372 g (3.68 mmol) of triethylamine in 5 ml of chloroform. After 1 h, the reaction mixture was filtered and precipitated into 95% ethanol to afford 5.46 g of **13b** as an amorphous white powder: ir (CCl_4) 2270 cm^{-1} (OC≡N). The elemental analysis is listed in Table I and the DSC thermogram indicated an exothermic maximum at 400–410 °C (Table III).

Bishydroxy Phenylquinoline Prepolymer (n = 4) (17a). A solution of 4.0846 g (10.000 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether[17] (**15**), 1.2714 g (5.000 mmol) of 4,4′-diacetyldiphenyl ether[17] (**14**), and 1.3615 g (10.000 mmol) of *p*-hydroxyacetophenone (**16**) (Aldrich) in the polymerization solvent prepared from 14 g of phosphorus pentoxide and 60 ml of distilled *m*-cresol was heated for 20 h at 125 °C under a nitrogen atmosphere. The reaction mixture was precipitated into 10% triethylamine in 95% ethanol to afford 3.0 g (50%) of the bishydroxy prepolymer **17a** which was reprecipitated from chloroform solution into Skelly B: ir ($CHCl_3$) 3600 cm^{-1} (OH).

Biscyanato Phenylquinoline Prepolymer (n = 4) (18a). To a solution of 2.45 g of **17a** and 0.656 g (6.19 mmol) of cyanogen bromide (**2b**) in 40 ml of chloroform at 0 °C under nitrogen was slowly added 0.609 g (6.03 mmol) of triethylamine in 5 ml of chloroform. After stirring for 1 h, the reaction mixture was precipitated into methanol to afford 2.41 g of **18a** as an amorphous white powder: ir ($CHCl_3$) 2240, 2265, and 2285 cm^{-1} (OC≡N). The ^{13}C NMR spectral data are listed in Table II, and the elemental analysis is listed in Table I. A $\bar{M}_n$ of 2900 (Table I) was determined in tetrahydrofuran by VPO and the DSC thermogram contained an exothermic maximum at 270–275 °C (Table III).

Bishydroxy Phenylquinoline Prepolymer (n = 10–11) (17b). A solution of 8.9861 g (22.000 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether[17] (**15**) and 5.0858 g (20.000 mmol) of 4,4′-diacetyldiphenyl ether[17] (**14**) in the polymerization solvent prepared from 34 g of phosphorus pentoxide and 100 ml of distilled *m*-cresol was heated at 125 °C for 6 h. A solution of 0.5446 g (4.000 mmol) of *p*-hydroxyacetophenone (**16**) (Aldrich) in 20 ml of *m*-cresol was then added and the heating was continued for an additional 11 h. The reaction mixture was precipitated into 10% triethylamine in 95% ethanol. The precipitate was collected, continuously extracted with 95% ethanol for 24 h, and reprecipitated in 95% ethanol from a chloroform solution to afford 10.0 g (76.7%) of **17b** as a white, fibrous material: ir ($CHCl_3$) 3600 cm^{-1} (OH).

Biscyanato Phenylquinoline Prepolymer (n = 10–11) (18b). To a solution of 5.07 g of **17b** and 0.438 g (4.13 mmol) of cyanogen bromide (**2b**) in 75 ml of chloroform at 0 °C under nitrogen was slowly added 0.407 g (4.03 mmol) of triethylamine in 10 ml of chloroform. After 1 h, the solution was filtered and precipitated into 95% ethanol to afford 4.97 g of **18b** as a white fibrous material: ir ($CHCl_3$) 2240, 2260, 2280 cm^{-1} (OC≡N) (Figure 2). An $\bar{M}_n$ of 6800 (Table I) was determined by VPO in chloroform solution and the DSC indicated an exothermic reaction maximum at 390–400 °C (Table III). The elemental analysis is listed in Table I.

Thermal Cross-Linking Reactions. The biscyanato prepolymers **13** and **18** were placed in glass ampules and flushed with nitrogen at least three times by evacuating the ampule and refilling with nitrogen. The ampules were sealed under a nitrogen atmosphere and heated in a Wood's metal bath according to the conditions listed in Table III. The ampules were then broken and the polymeric material removed. The elemental analyses are listed in Table III. The T_g's of these samples, obtained by DSC, are listed in Table III, and the TGA's are summarized in Table IV.

A film, cast from a 10 wt % solution of **18b** in chloroform and dried in vacuo at 120 °C for 24 h, was placed in an ampoule under nitrogen and thermally cross-linked as described previously. The ir is shown in Figure 2.

Acid-Catalyzed Cross-Linking Reaction. A solution of 0.318 g of the biscyanato phenylene prepolymer **13b** and 0.0058 g of *p*-toluenesulfonic acid in 4 ml of 20% ether in benzene was placed in a glass ampule, freeze dried, flushed with nitrogen, and sealed. The cross-linking reaction was carried out by heating the ampoule at 350 °C for 2 h. The T_g (Table III) was measured by DSC.

Pyrolysis of the Phenylene Polymer 19a. The phenylene polymer **19a** was pyrolyzed in a glass apparatus consisting of three side arms connected to a horizontal tube. The sample, 900 mg of **19a**, was introduced into the first side arm and the system was evacuated and sealed. The sample tube was then placed in a Wood's metal bath at 200 °C and the temperature was increased to 400 °C over a 20-min period while the second side arm, consisting of a mass spectrometer sample bulb, was cooled to dry ice temperature. After 45 min at 400–425 °C the apparatus was returned to room temperature while the third side arm, a break-seal tube with a fitting for the mass spectrometer gas inlet system, was cooled in liquid nitrogen and was sealed off from the remaining apparatus. The gas and solid samples thus obtained were analyzed by mass spectroscopy.

Gas sample: *m/e* (rel intensity[24]) benzene 73 (62) and hydrogen cyanide 27 (100). Major unidentified peaks distinguishable from an air sample occurred at: 91 (44), 71 (78), and 56 (31).

Solid sample: *m/e* (rel intensity[24]) cyanuric acid 129 (12), 86 (2), 56 (2), and 43 (100). No other major peaks (>5) distinguishable from an air sample were observed.

Pyrolysis of Triphenylcyanurate (4, Ar = Ph). Triphenyl cyanurate (4, Ar = Ph) was pyrolyzed in a glass apparatus consisting of a break-seal tube fitted with a ground glass fitting compatible with the mass spectrometer gas inlet system. Compound 4 (Ar = Ph) was placed in the tube which was then evacuated and sealed. The sample tube was then placed in a Wood's metal bath at 200 °C and heated to 400–425 °C for 1 h. The tube was allowed to cool before it was fitted to the mass spectrometer. The break-seal was broken and the mass spectral analysis of the volatile products revealed only fragments of phenyl cyanurate: mass spectrum *m/e* (rel intensity[24]) 162 (37) $C_8H_5N_2O_2$, 131 (3) C_8H_5NO, 93 (100) C_6H_5O, and 78 (6) C_6H_6. No peak at *m/e* 65 characteristic of phenol degradation.

Solubility and Hydrolytic Stability Studies. The polymer samples were weighed in coarse fritted glass filters which had been brought to constant weight. The filters were then placed into a Soxhlet extraction apparatus and continuously extracted for 24 hr with benzene or chloroform. The filters were placed in an oven at 100 °C for 12 h, then heated at 130 °C in vacuo for 12-h periods until constant weights were achieved (generally after 24 h). The percents sol were determined from the weights of the residues and the initial weights and are listed in Table V.

The polymer samples were weighed into test tubes that had been dried at 100 °C for several hours, and 5 ml of 1 N aqueous sulfuric acid or 5 ml of 1 N aqueous potassium hydroxide were added. After 100 h at room temperature, the polymer samples were collected in coarse fritted glass filters that were at constant weight. The samples were allowed to soak in water for 1–2 h then washed with 95% ethanol. The percents sol phase were determined as previously described and the results are reported in Table V.

The phenylene polymer **19b**, 0.4036 g, was placed in 10 ml of benzene, and 5 ml of 5 N aqueous potassium hydroxide and 100 mg of tetrabutylammonium hydrogen sulfate were added. After 48 h at room temperature, the benzene phase was homogeneous. The organic phase was separated and precipitated in 95% ethanol to afford an off-white powder which was dried in vacuo at 120 °C: ir ($CHCl_3$) 3680 cm^{-1} (OH) and aromatic features.

Acknowledgment. This research was supported by the U.S. Army Research Office, Durham, N.C.

References and Notes

(1) S. S. Hirsch and F. P. Darmory, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **12(2)**, 9 (1971).

(2) E. Grigat and R. Pütter, *Angew. Chem., Int. Ed. Engl.*, **6**, 206 (1967), and references therein.

(3) E. Grigat and R. Pütter, *Ber.*, **97**, 3012 (1964).

(4) D. Martin, *Ber.*, **97**, 2689 (1964).

(5) V. V. Korshak, *Polym. Sci. USSR (Engl. Transl.)*, 1066 (1974).

(6) E. Grigat and R. Pütter, German Patent 1/183/507 (December 17, 1964); *Chem. Abstr.*, **62**, P14705e (1965).

(7) A. K. Bonetskaya, M. A. Kravchenko, Ts. M. Frenkel', V. A. Pankratov, S. V. Vinogradova, and V. V. Korshak, *Dokl Akad. Nauk SSSR*, **212**, 1353 (1973).

(8) E. M. Smolin and L. Rapoport, "The Chemistry of Heterocyclic Compounds", Vol. 13, Interscience, New York, N.Y., 1959, p 87.

(9) V. V. Korshak, S. V. Vinogradova, V. A. Pancratov, and A. G. Puchin, *Dokl. Akad. Nauk SSSR*, **202**, 347 (1972).

(10) V. V. Korshak, P. N. Gribkova, A. V. Dmitrenko, A. G. Puchin, V. A. Pankratov, and S. V. Vinogradova, *Polym. Sci. USSR, (Engl. Transl.)*, 15 (1974).

(11) P. M. Hergenrother, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15(1)**, 781 (1974).

(12) R. Kubens, H. Schultheis, R. Wolf, and E. Grigat, *Kunststoffe*, **58**, 827 (1968).

(13) H. Mukamal, F. W. Harris, and J. K. Stille, *J. Polym. Sci., Part A-1*, **5**, 2721 (1967).

(14) J. K. Stille and G. K. Noren, *J. Polym. Sci., Part B*, **7**, 525 (1969).

(15) J. K. Stille and G. K. Noren, *Macromolecules*, **5**, 49 (1972).

(16) J. F. Wolfe and J. K. Stille, *Macromolecules*, in press.

(17) S. O. Norris and J. K. Stille, *Macromolecules*, in press.

(18) F. Bohlmann, K. D. Albrecht, and G. Schmidt, *Ber.*, **99**, 2822 (1966).

(19) F. W. Billmeyer, "Textbook of Polymer Science", 2nd ed, Wiley-Interscience, New York, N.Y., 1971.

(20) W. Wrasidlo, S. O. Norris, J. F. Wolfe, T. Katto, and J. K. Stille, *Macromolecules*, in press.

(21) L. E. Nielsen, *J. Macromol. Sci., Rev. Macromol. Chem.*, **c3**, 69 (1969).

(22) M. A. Ogliaruso, L. A. Shadoff, and E. I. Becker, *J. Org. Chem.*, **28**, 2725 (1963).

(23) A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).

(24) The relative intensities are based on peaks other than those present in an air sample.

Synthesis and Ring-Opening Anionic Polymerization of a Paracyclophane Heterocycle

W. R. Hertler,* W. H. Sharkey, and B. C. Anderson

Central Research and Development Department,[1] Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.

Received December 15, 1975

ABSTRACT: 1-Aza-2-keto[2.3]paracyclophane has been synthesized by two routes and has been polymerized with sodium hydride to poly(imino-1,4-phenylene-1,2-ethanediyl-1,4-phenylenemethylenecarbonyl).

Ring-opening anionic polymerization has been widely used to polymerize heterocycles to linear, high molecular weight polymers, often with low polydispersity. Such polymers invariably have aliphatic backbones. We wish to report the preparation of a polyamide containing aromatic rings in the backbone by ring-opening anionic polymerization of 1-aza-2-keto[2.3]paracyclophane (**1**). The lactam **1** was synthesized by Beckmann rearrangement of the oxime of 1-keto[2.2]paracyclophane[2] using sulfuric acid in dioxane. The preferred method of synthesis, however, was by the reaction of 1-keto-[2.2]paracyclophane with hydrazoic acid (Schmidt reaction). The Schmidt reaction can also be carried out on 1,1-di-