AD-A083 129 COLORADO STATE UNIV FORT COLLINS DEPT OF CHEMISTRY F/G 11/9
HEAT STABLE POLYMERS: POLYQUINOLINES AND OTHER AROMATIC POLYMER--ETC(U)
JAN 80 J K STILLE DAAG29-77-G-0177
UNCLASSIFIED ARO-15303.12-C NL

1 OF 1
AD
A083129

END
DATE
FILMED
5-80
DTIC

DAAG29-77G-0177

ARO 15303.12-C

LEVEL II

12

ADA083129

HEAT STABLE POLYMERS: POLYQUINOLINES AND OTHER AROMATIC POLYMERS

Final Report

J. K. Stille

DTIC
ELECTE
APR 15 1980
S D
C

January 1977-December 1979

U.S. Army Research Office
DAAG29-77G-0177

Department of Chemistry
Colorado State University

80 4 15 003

(18) ARO (19) 15303.12-C

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: DAAG29-77-G-0177
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER: (9)
4. TITLE (and Subtitle): (6) HEAT STABLE POLYMERS: POLYQUINOLINES AND OTHER AROMATIC POLYMERS.
5. ~~TYPE OF REPORT & PERIOD COVERED~~: Final Report. Janu[illegible]1977 [illegible] Dec[illegible]79
6. ~~PERFORMING ORG. REPORT NUMBER~~:
7. AUTHOR(s): (10) J. K. Stille
8. CONTRACT OR GRANT NUMBER(s): (15) DAAG29-77-G-0177
9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Department of Chemistry
Colorado State University
Fort Collins, CO 80523
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: (12) 5
11. CONTROLLING OFFICE NAME AND ADDRESS:
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709
12. REPORT DATE: (11) 1 Janu[illegible]80
13. ~~NUMBER OF PAGES~~: 29
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: NA
16. DISTRIBUTION STATEMENT (of this Report):

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

NA

18. SUPPLEMENTARY NOTES:

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polyquinoline
Crosslinking
Biphenylene
Anisotropic Polymer Solutions
Heat-Stable Polymers
Rigid Chain Polymers
High Performance Polymers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Polyquinolines can be synthesized by an acid catalyzed polymerization reaction that allows a variety of structural modifications, resulting in a range of chain stiffness that can be altered from a relatively flexible amorphous polymer with a moderately low glass transition temperature (250°C) to a rod-like molecule with a high degree of crystallinity and a high crystalline transition temperature (>550°C). Fibers can be spun and films cast from solution. The rigid rod polyquinolines form anisotropic solutions

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

404992

JOB

and, as a result, produce crystalline fibers with a high degree of orientation and a high modulus.

A series of polyquinolines containing biphenylene units in the main chain were prepared in order to effect crosslinking reactions of these materials. Crosslinking took place thermally, above the Tg of the polymer, to give insoluble polymers with higher Tg's and higher moduli both above and below Tg. Transition metals catalyze the crosslinking reactions, allowing lower curing temperatures. Polyaramides, polybenzimidazoles and polyquinoxalines could be similarly crosslinked by incorporating biphenylene into these polymers.

Table of Contents

Table of Figures

Table of Tables

INTRODUCTION

Linear rigid chain macromolecules generally exhibit greater mechanical strength and higher phase transition temperatures than the more flexible chain polymers. Such materials, for example, are fabricated into composites or laminates for use in helmets, helicopter blades, vehicle cabs, rockets, and recoiless rifles where high strength is gained from a high modulus fiber in a matrix, both of which are polyaromatics.[1] High modulus fibers also find use in body armor and high temperature electrical insulation.

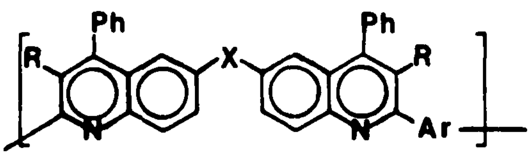
Most of the polymers with highly rigid recurring units in the chain, however, are either crystalline, or have high melting (softening) temperatures and are insoluble in suitable solvents as a result of ring (particularly aromatic ring), spiro, or ladder structures in the main chain. One of the major unsolved problems is in the fabrication of such materials having high use temperatures.

A polymer with a high use temperature is defined by two variables of thermal performance: 1) A threshold temperature at which the polymer loses its mechanical strength under an external applied load of specific magnitude. 2) A threshold temperature corresponding to the occurance of chemical changes in the structure of the polymer accompanied by corresponding changes in properties. The first variable requires a material with a high glass transition temperature, a high crystalline temperature combined with a relatively high degree of crystallinity, or a three dimensional network structure. In order to achieve melt processability, the synthesis of an uncross-linked material with relatively low transition temperatures is necessary. Subsequently these transition temperatures can be raised by some chemical means after processing to give a more rigid chain or a three-dimensional network structure. An alternate approach to this problem is to process the polymer in the amorphous state in which a moderately high glass transition temperature (e.g. 250°C) is obtained, and then develop crystallinity during processing or subsequent annealing to raise the use temperature (e.g. Tm = 450-550°C) to the limit of thermal performance as defined by the second variable.

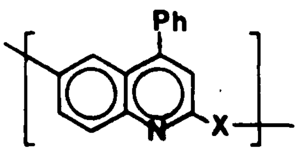
POLYQUINOLINES

Background.

Thermally stable polymers containing quinoline units in the chain can be synthesized by a polymerization reaction that allows a variety of structural modifications, resulting in a range of chain stiffness that can be altered from a relatively flexible polymer with a low glass transition temperature to a rod-like molecule with a high glass transition temperature.[2-7] Most of the materials have high crystalline transition temperatures, but a low degree of crystallinity. For example, polyquinolines **1** (X=O, Ar=4,4'-$C_6H_4OC_6H_4$) containing some flexibility, exhibit lower transition temperatures (Tg=265-350, Tm=450-480) and lower crystallinity (<20%) than the rigid polyquinoline **2** (X=nil, p-C_6H_4; Tg=380-415, Tm=552-580). The largely amorphous polyquinolines, of which **1** is representative, are characterized by high moduli below the glass transition temperature ($E'=6x10^{10}$ dynes/cm^2, **1**, R=H, X=O, Ar=4,4'-$C_6H_4OC_6H_4$), and good solubility in common organic solvents. In addition, all polyquinolines show excellent thermal stability as determined by thermal gravimetric analysis and isothermal ageing.

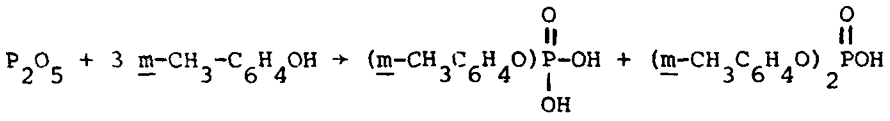


1 R=H , C_6H_5



2

The polymerization reaction of an aromatic bis-*o*-aminoketone with an aromatic bisketomethylene monomer has been shown to give high molecular weight polyquinoline by acid catalysis. The reaction is first order in aminoketone concentration and first order in ketomethylene concentration. Optimum polymerization rates and molecular weights were obtained in mixtures of *m*-cresol and the reaction product of *m*-cresol and phosphorus pentoxide. The reaction product was shown[8,9] by ^{31}P nmr to consist of an equimolar mixture of mono-(**3**) and di-*m*-cresol (**4**) esters of phosphoric acid, as the stoichiometry suggests.



$$P_2O_5 + 3\ \underline{m}\text{-}CH_3\text{-}C_6H_4OH \rightarrow (\underline{m}\text{-}CH_3C_6H_4O)\underset{\overset{|}{OH}}{\overset{\overset{O}{\|}}{P}}\text{-}OH + (\underline{m}\text{-}CH_3C_6H_4O)_2\overset{\overset{O}{\|}}{P}OH$$

3 **4**

Both esters, **3** and **4** were independently synthesized, and although mixtures of ester **3** and *m*-cresol were marginally effective as a polymerization medium, ester **4** with *m*-cresol effected the polymerization at about the same rate as the *m*-cresol phosphorous pentoxide reaction mixture. One added advantage of the independently synthesized (and purified) diester **4** is that much higher molecular weights could be obtained. The upper degree of polymerization attainable in the phosphorus pentoxide *m*-cresol reaction mixture appears to be about 320, possibly as a result of some side reaction with one or more of the monomer functional groups. Acid catalyzed cyclotrimerization has been suggested[4] as a reaction which would not only consume ketomethylene groups, but also would lead to branching. Polymerization in a mixture of *m*-cresol and **4** , however, gives a DP>550 in 24 h.

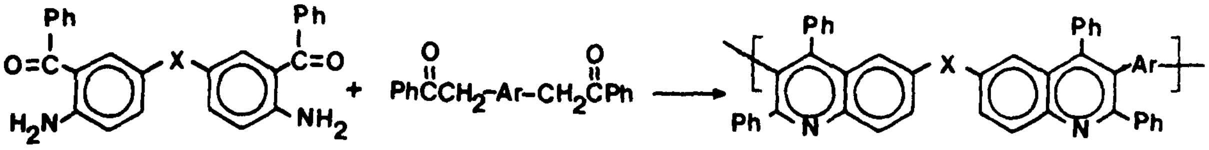
In most cases, the processability of thermally stable polymers is limited by insolubility and high phase transition temperatures. A soluble polyaromatic is often amorphous and has a relatively low glass transition temperature. If the Tg or Tm of thermally stable amorphous or crystalline polyaromatics are low such that they can be processed by melt techniques, then their use temperature is low, limited by Tg or Tm.

Polyquinolines of the general structure 1 (x=O) are largely amorphous and have glass transition temperatures of 350°C or lower. Thus, although they are soluble in common organic solvents, and can be readily fabricated from solution, their use temperature is limited to 350°C or lower. The use temperature cannot be raised to the crystalline transition temperatures since annealing does not develop sufficient crystallinity.

Polyquinolines 2 (x=nil, p-C_6H_4) are sufficiently crystalline and have high enough crystalline transition temperatures, 480°C and 580°C, respectively, but are soluble only in strong acids such as sulfuric acid. The storage moduli of each one is also sufficiently high, ($E' \approx 4 \times 10^{10}$ dyn/cm^2 even above their glass transition temperatures ($E' \approx 2.5 \times 10^{10}$ dyn/cm^2 such that good mechanical properties are retained up to Tm.

Polymers Containing 3,6-Quinoline Units[10]

In an effort to prepare polyquinolines which would have good solubilities and show the ability to crystallize by annealing above the Tg, polymers containing 3,6-quinoline units in the main chain were synthesized. These polymers can be prepared by the condensation of bis-o-amino ketones with bis-phenacyl monomers in place of the bis-phenylacetyl monomers. Thus, the synthesis of a number of new bis-phenacyl monomers was accomplished.



5

These polymers (**5**) showed improved solubilities over the analagous polyquinolines with the 2,2'-catenation, being readily soluble in chloroform or sym-tetrachloroethane (TCE). Tough, transparent films of **5a-c** could be cast from 10-15% by wt. solutions of the polymers in chloroform, TCE or m-cresol. When preparation of a 10-15% by wt. solution of **5c** in chloroform was attempted, the polymer initially went into solution, but then slowly precipitated. The solvent was allowed to evaporate slowly and the resultant thick opaque film was analyzed for crystallinity. From x-ray analysis, the film was estimated to be approximately 50 percent crystalline, exhibiting very light diffuse halos due to amorphous regions at 9.0 and 4.9 Å and numerous sharp diffraction lines due to crystalline regions the most intense of which were at 11.4, 8.7, 5.0, 4.5 and 4.0 Å. Thus, polymer **5c** could be crystallized to a moderately high degree from a chloroform solution.

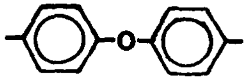
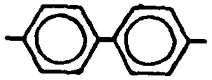
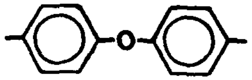
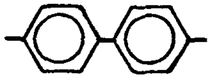
Polymers **5d,f** exhibited good solubilities in m-cresol, whereas, **5e** exhibited only limited solubility in concentrated sulfuric acid. Films of **5d,f** could be cast from 10% wt. solutions of the polymers in m-cresol. A film of **5e** could not be obtained due to the polymer's poor solubility.

Pressed powder and film samples of polyquinolines (**5**) were analyzed by differential scanning calorimetry (DSC) and by dynamic thermomechanical analysis to obtain information on thermal transitions that occur in the polymers (Table 1). The glass transition temperatures (Tg) ranged from 255 to 390°C, with polymers **5d-f** having Tg's 50-65°C higher than the more flexible polymers **5a-c**.

Polymers **5d-e** exhibited crystalline transition temperatures (Tm) ranging from 475-530°C, whereas, polymers **5a-c** did not exhibit crystalline transitions. This difference in crystallinity of the polymers apparently is due,

TABLE 1

Properties of 3,6-Polyquinolines

Polymer	X	Ar	Solubility[a]	[n] (solvent) dl/g	DSC	E"max	Tc(°C)	Tm(°C)	Thermal Stability Air Break	Thermal Stability Nitrogen Break	Thermal Stability Nitrogen % wt. loss at 800°C
5a	O		$CHCl_3$	1.2($CHCl_3$)	255	250	-	-	530	575	30
5b	O		$CHCl_3$	0.7($CHCl_3$)	312	310	-	-	535	570	28
5c	O		TCE[b]	3.6(m-cresol)	325	335	-	-	530	550	28
5d	nil		m-cresol	0.8(m-cresol)	305	310	415	475	575	580	30
5e	nil		H_2SO_4	0.5(H_2SO_4)	370	-	437	550	570	575	25
5f	nil		m-cresol	2.4(m-cresol)	390	420	-	530	570	585	25

a. Solubility defined as the ability to dissolve 10% by wt. of polymer

b. sym-tetrachloroethane

at least to some extent, to the variation in the rigidity of the polymer chains, since rigid polymers generally exhibit a higher degree of crystallinity than flexible polymers. The difference in the amount of crystallinity is apparently small though, since both types of polymers **5a-c** and **5d-f** are essentially x-ray amorphous (<20% crystalline).

In addition to high crystalline transition temperatures, polymers **5d,e** showed crystallization temperatures (Tc) of 415 and 437°C. When polymers **5c** and **5e** were annealed at their respective Tc's for one hour and then slowly cooled and the DSC scan was run again, the magnitude of the Tg had decreased and the exotherm corresponding to the Tc was no longer observed. The continued presence of the Tg indicates that the polymers still have amorphous regions which did not crystallize on annealing.

Dynamic thermomechanical analysis showed that polymer **5d** exhibited only a small loss of modulus at its Tg, indicative of the presence of a considerable amount of crystallinity in the polymer. When **5c** was annealed at 440°C, within 15 min., the storage modulus had increased 2.6×10^{8} to 1.1×10^{10} dynes/cm^{2}, as a result of an increase in crystallinity to approximately 30 percent.

As expected, the polyquinolines synthesized in this work showed outstanding thermal stability both in inert atmospheres as well as in air (Table 1). Thermogravimetric analysis (TGA) of the polymers showed breaks in air at 530-570°C, with breaks in nitrogen at 550-585°C and only 25-30% weight loss at 800°C under nitrogen.

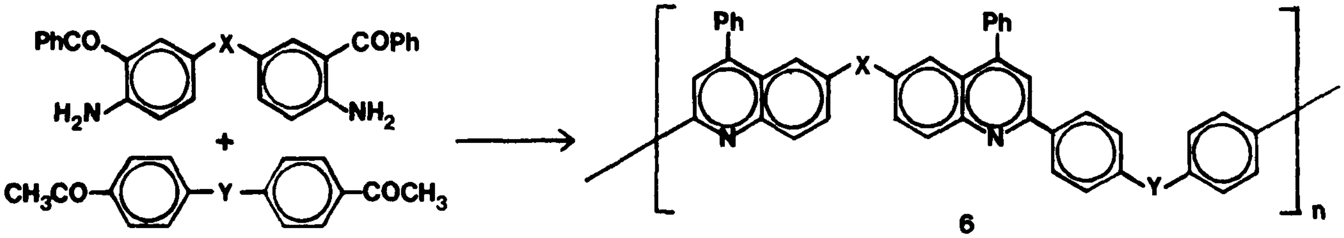
Cardo Polyquinolines.

Polymers that contain pendant spiro loops attached to the polymer backbone, "cardo" polymers, give the chain enhanced rigidity.[11] The loops are perpendicular to the chain direction, and depending on the structural symmetry, can produce either an ordered structure or a chain which approximates an atactic arrangement as a result of the randomness characteristic of step-reaction polymerizations.

Polymers containing the cardo structure generally possess greater rigidity, enhanced thermal stability, and excellent solubility. Most of these polymers are amorphous, primarily as a result of the bulky pendant ring and the "atactic" structure resulting from dissymmetric rings. However, polycarbonates such as the symmetrical one can be prepared in crystalline and amorphous forms. Certain cardo polymers can be crystallized with solvent or by annealing.

High heat distortion temperatures and high oxidative thermal stability also are observed. Polymers from cardo monomers having the largest value of reduced volume of the cycle to molecular weight -- for example fluorene, $K_i/M=1.58$ -- exhibit the highest heat distortion temperatures. Polymers containing cardo monomers derived from anthraquinone, however, have the best thermal stability but slightly lower heat distortion temperatures ($K_i/M=1.56$).

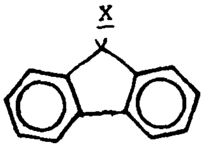
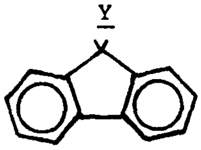
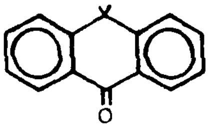
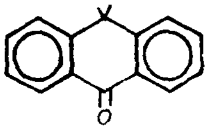
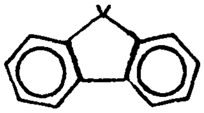
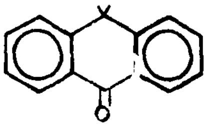
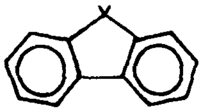
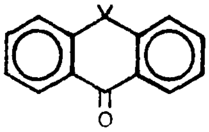
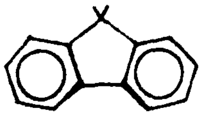
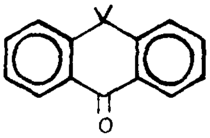
Polyquinolines containing spiro fluorene and anthraquinone units have been synthesized from the appropriate spiro-containing bismethyleneketone and bisaminoketone monomers.[12] The greater rigidity of the cardo polymers over the non-cardo analogs (X,Y=O) is responsible for the higher glass transition temperatures (Table 2) yet these polymers remain soluble in common organic solvents. Glass transition temperatures were 120-140°C higher when both X and Y were cardo units, as compared to X=Y=O and only



6

TABLE 2

Properties of Polyquinolines (6) Containing Cardo Units

	Polyquinoline 6		[n]	Tg(°C)	Td(°C)	E'(25°C) (dyn/cm^2) x 10^{10}
	X	Y				
a.			0.58^a	390	580	2.1
b.	"		0.70^b	385	530	2.2
c.			1.30^b	405	540	-
d.	"		0.53^b	390	520	1.5
e.	nil		2.5^a	420	570	1.3
f.	O	"	1.70^a	310	570	2
g.	nil			417	560	1.9
h.	O		0.87^b	340	580	1.8
i.		nil	1.95^c	380	580	1.8
j.		O	0.56^c	315	575	2.5
k.		nil	0.69^a	350	530	2.2
		O	0.97	320	535	-

a. CHCl$_3$ b. CHCl$_2$-CHCl$_2$ c. m-cresol

45-90°C higher when only one of the oxygen units, X or Y, was replaced by a cardo group. Thus, the use temperature of polyquinolines (**6**) containing dicardo structures can be increased to the 400°C range. All the cardo polymers exhibited good thermal stability (Td>500°C).

Rigid Rod Polyquinolines.

The series of stiff-chain polyquinolines that have been synthesized are crystalline and insoluble in common organic solvents (Table 3). The degree of crystallinity depends on the thermal history of the sample, but crystallinities of 60-80% can be achieved. The polymers are characterized by high crystalline transition temperatures (>500°C) and high glass transition temperatures (>330°C).

Although the polymers are insoluble in common organic solvents, they are soluble in strong acids (H_2SO_4, CF_3CO_2H, CF_3SO_3H) and most importantly, the polymers remain soluble in the polymerization dope at the end of the polymerization. As a result, films can be cast and fibers wet spun from the polymerization medium. Solutions of rigid rod polymer **7b** forms anisotropic solutions in the polymerization solvent (dicresylphosphate m-cresol 1:5) at about the 10 wt. percent level.

Thus, fibers spun from anisotropic solutions show orientation of the polymer chains along the direction of the fiber axis (x-ray). High dynamic storage moduli are observed for films of the polymer. The modulus is maintained even above Tg (**7a**), whereas a polyquinoline such as **1** (X=O, R=H, Ar=p,p'-$C_6H_4OC_6H_4$) amorphous loses its strength at Tg (Fig 1).

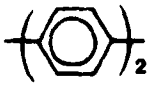
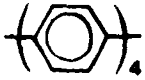
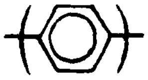
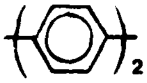
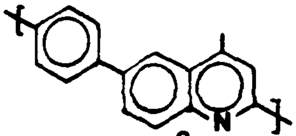
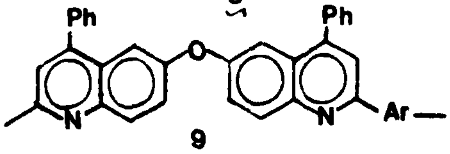
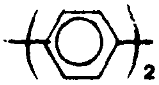
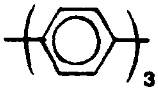
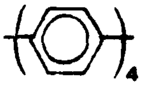
CROSSLINKING REACTIONS

Biphenylene Crosslinking

Biphenylene (**10**) undergoes thermolysis at ∿400°C and, depending on the

TABLE 3

Rigid Rod Polyquinolines

Polymer 7						E' (dynes/cm^2 x10^{10})	
R	Ar	[η] (dl/g)	Tg	Tm	Td(N$_2$)	25°	Above Tg
a H		7.0[a]	365	b	595	4.2	1.9
b		14.5[a]	330	500	577	3.9	1.8
c		22.0[a]	360	504	600	2.6	0.42
d		i	360	b	600	c	c
e Ph		17.0[a]	355	b	540	2.5	0.19
f		22	365	b	595	1.7	0.18
	 8	11.6	380	580	610	4.2	0.36
	 9						
a		1.1[d]	300	455			
b		3.1[e]		480			
c		3.5[a]	280	f	540	0.37	g
d		i	305	f	560	c	c

a. CF_3SO_3H solvent.

b. Tm>Td

c. Unable to obtain films

d. $CHCl_3$

e. m-cresol

f. No Tm observed

g. 9.7 x 10^7

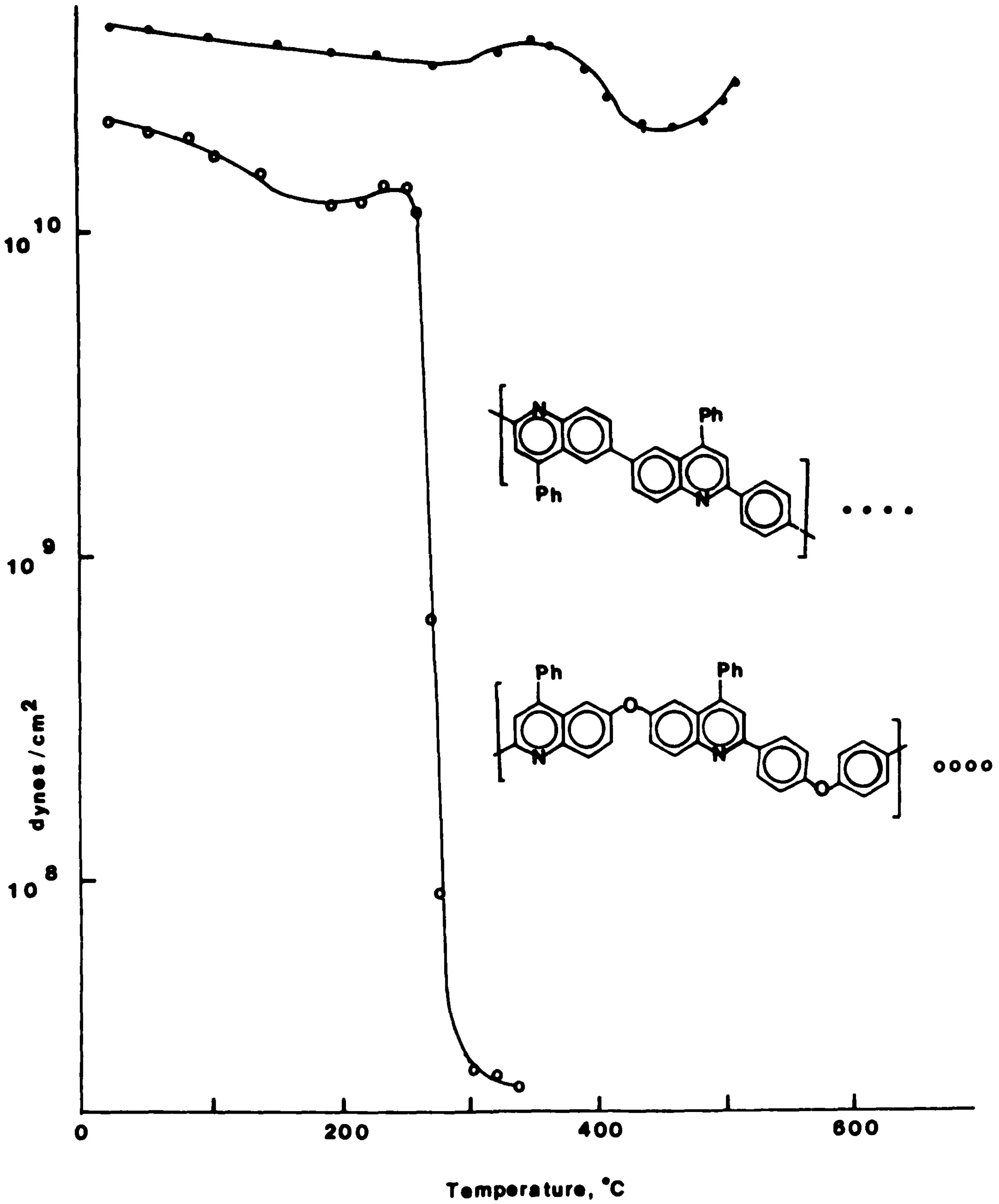
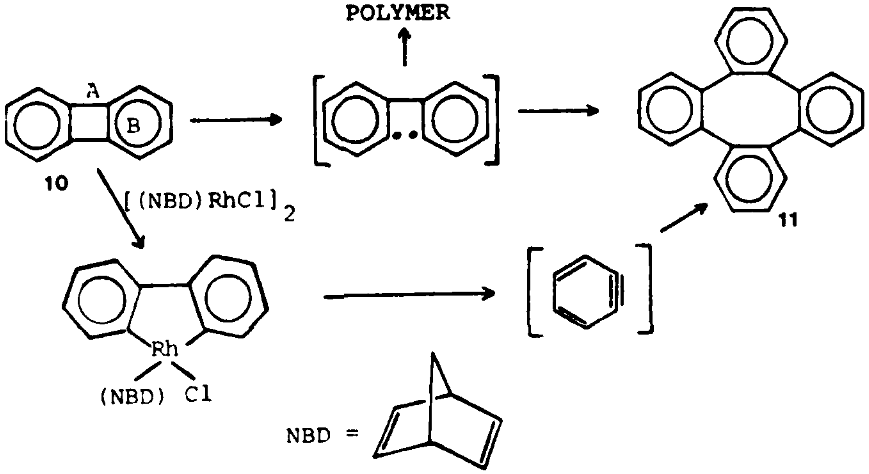


Figure 1
Thermomechanical Properties of Polyquinolines

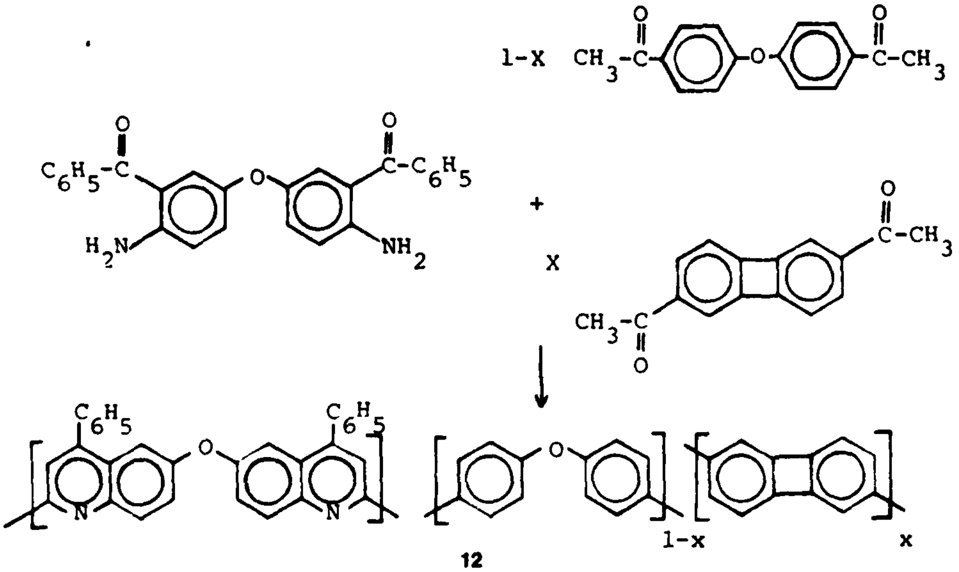
reaction conditions, yields tetrabenzocyclooctatetraene (11), polymer, or biphenyl -- resulting from radical abstraction of hydrogen from solvent.[13-15] Although the structure of the polymer was not determined, it likely contains poly-(o-phenylene) segments. These reports suggest a diradical as the reactive intermediate in pyrolysis. Thus, any structure formed as a result of the thermolysis of a biphenylene unit in a thermally stable polymer would be expected to maintain the high temperature structural integrity of the polymer.



SCF-MO calculations suggest[16] that biphenylene is anti-aromatic and should be somewhat chemically unstable, undergoing reactions in the anti-aromatic cyclobutadiene ring. Both calculations[17] and structure determination[18] show longer bond lengths between the benzo units (A) than within the benzo units (B). Calculated heats of formation for biphenylene are higher by 27.5 kcal/mol than those observed from heats of combustion;[15] this difference has been attributed[16] to strain energy.

Rhodium catalysts are known to open strained cyclic hydrocarbons by an oxidative addition mechanism.[19] Thermolysis of biphenylene containing a catalytic amount of the rhodium catalyst at 200°C produced dibenzocyclooctatetraene in a 44% yield (recrystallized) and polymer. Thus, the products of the catalyzed reaction are the same as those obtained from the uncatalyzed thermolysis. By analogy to the cubane reaction,[19] however, it might be expected the benzyne is the reactive intermediate. This temperature is approximately 200°C lower than that required for the uncatalyzed reaction.

The incorporation of varying portions of biphenylene in place of diphenylether into a polyquinoline was accomplished by balancing the appropriate amounts of 2,6-diacetylbiphenylene in place of 4,4'-diacetyldiphenylether under standard polymerization conditions.[20-22]



12

		Tg
a.	x = 1.0	297
b.	x = 0.5	270
c.	x = 0.25	258
d.	x = 0.05	240
e.	x = 0.025	232
f.	x = 0	266

The glass transition temperature of the parent polyquinoline containing all biphenylene units was lowered by increasing the content of diphenylether units: copolymer **12c** has a lower Tg than the homopolymer **12f**. A reaction exotherm attributed to the opening of the biphenylene ring was observed above 300°C. The time required for curing depended on the curing temperature (340-380°C), as well as the biphenylene content of the polymer. The onset of the exotherm for crosslinking increased with an increasing biphenylene amount and paralleled the increase in Tg. (Fig 2).

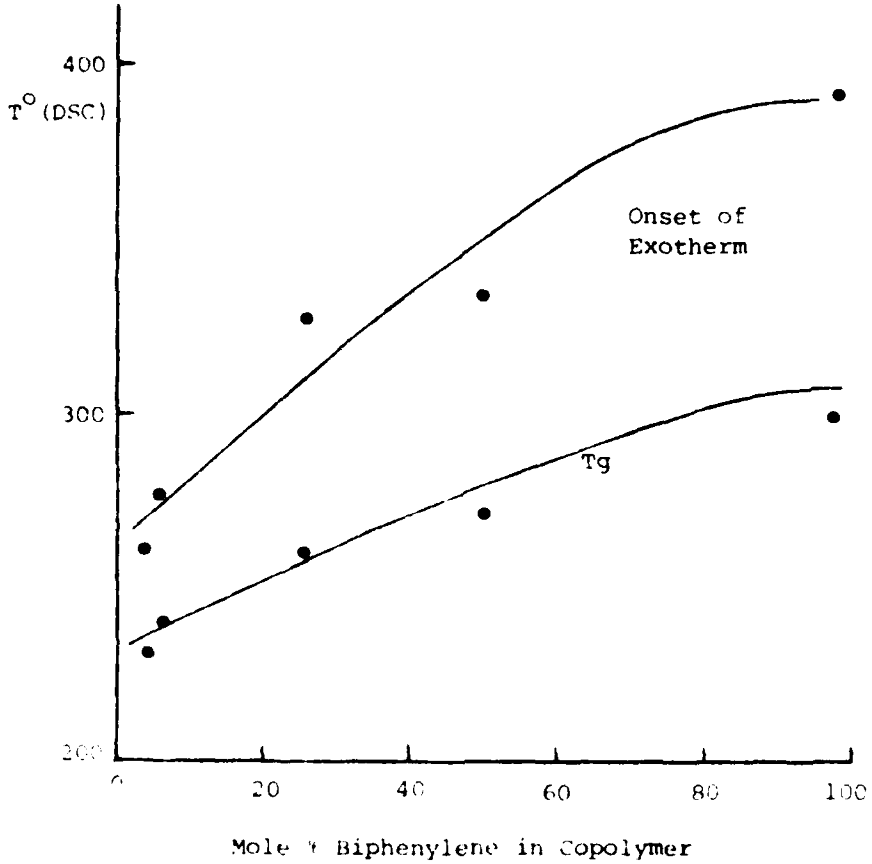


Fig. 2. Dependence of Exotherm Onset on Biphenylene Content

Since biphenylene underwent a rhodium catalyzed ring-opening at much lower temperatures to afford the same products as obtained from the uncatalyzed reaction, curing was carried out on polymer samples containing catalytic amounts of norbornadiene-chlororhodium(I) dimer. Generally, lower temperatures and shorter reaction times were used to effect the same crosslinking reaction. The thermal mechanical analysis of polymers **12c** and **12d** showed that curing at 380°C for 1 hour was sufficient to erase the glass transition temperature. In polymer **12e**, a very high transition temperature is observed after curing at 380°C for 1 hour. At 380°C, the effect of curing time on the glass transition temperature of this polymer (**12e**) containing only 2.5% biphenylene units, is to increase Tg. Rhodium catalysis does this more effectively (Fig. 3). At a curing time of 3 min, the difference in the rhodium cures and the catalyzed curing is most pronounced with polymer **12c** containing 25% biphenylene. Generally, curing was accompanied by insolubility in all solvents, an increase in Tg and finally disappearance of Tg.

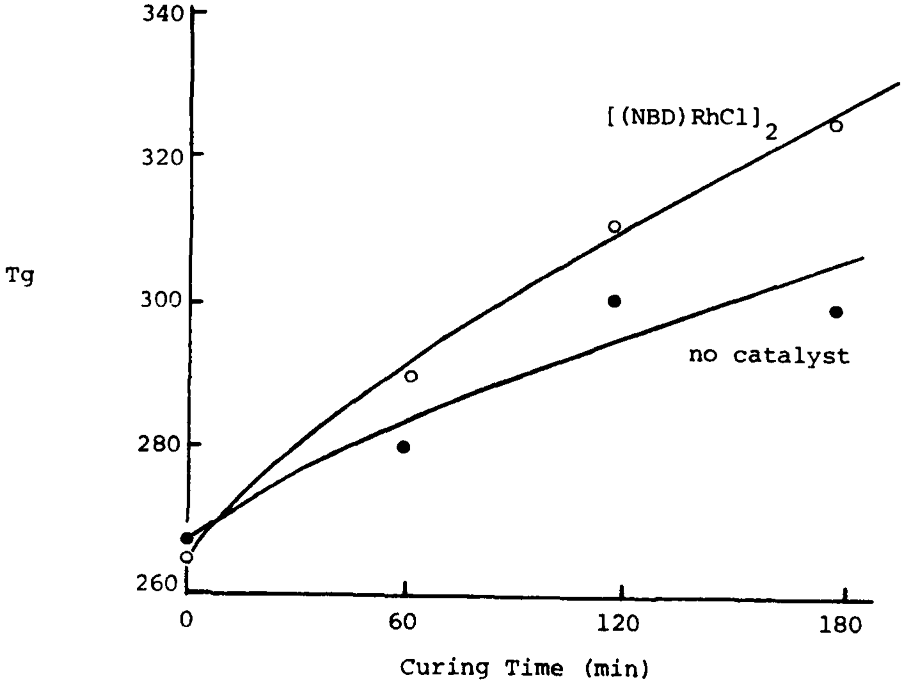


Fig. 3. Copolymer **12e** Curing

The dynamic mechanical properties of uncured and cured films of polyquinolines **12a-f** were obtained from room temperature up to 380°C. Under the mild tensile stresses required, the mechanical performance of films is relatively constant up to the glass transition temperature.

The dynamic moduli of the cured polymers at low temperature (25-250°C) are, as expected, higher than those of the uncured polymers. The glass transition temperatures after curing are 30-60°C higher than the uncured samples, as measured by the moduli. More importantly, the moduli of the cured polymers above Tg are much higher than those of the homopolymer, **12f**, and are a function of the percent biphenylene in the copolymer (Fig 4). Even a low biphenylene incorporation (2.5%, **12e**) is sufficient to raise the value from 2.4×10^7 to 3.8×10^8 dyn/cm^2 (Fig 5).

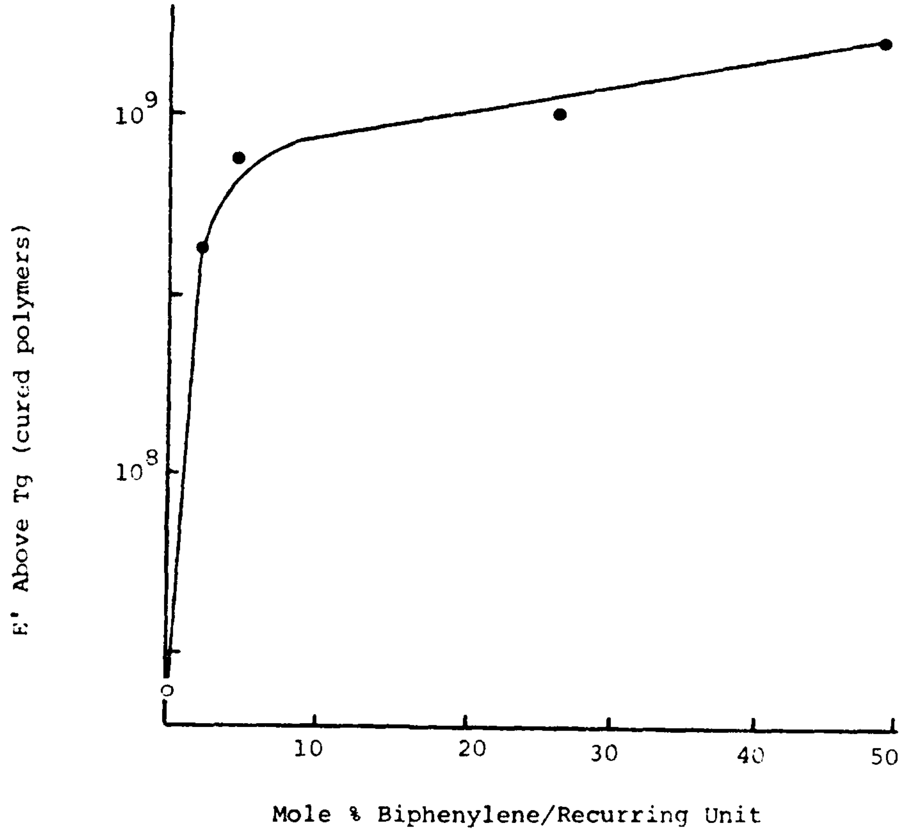


Fig. 4. E' of **12e** (cured) Above Tg

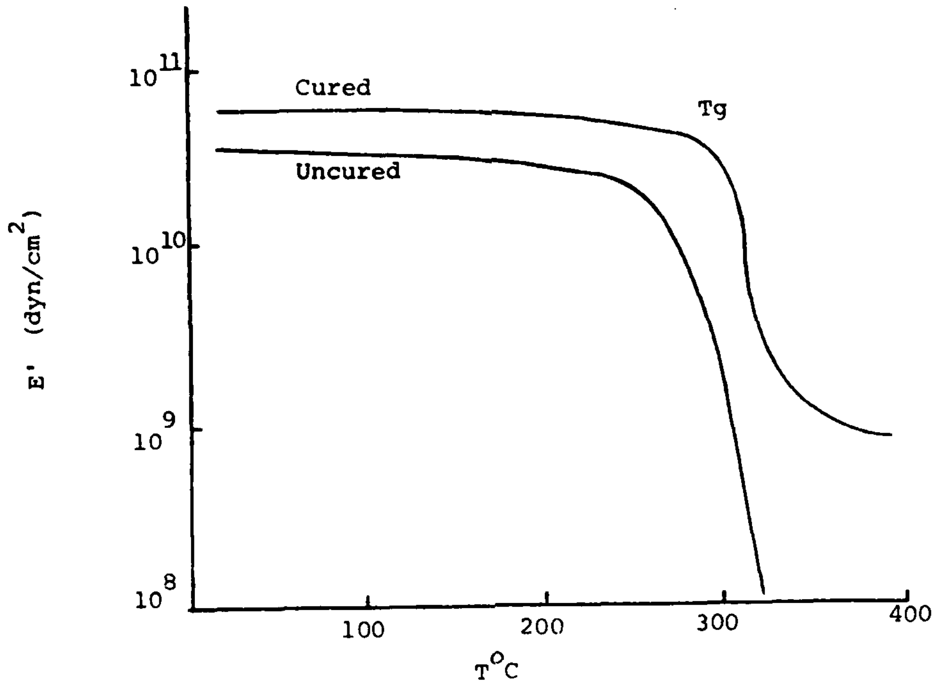


Fig. 5. E' of Copolymer **12e** vs Temperature

Finally, it is instructive to compare the dynamic storage moduli (E') above Tg for polymer **12e** cured with and without catalyst as a function of curing time (Fig 6). As expected, the catalytic effect is reflected by the generation of higher moduli for the low curing times.

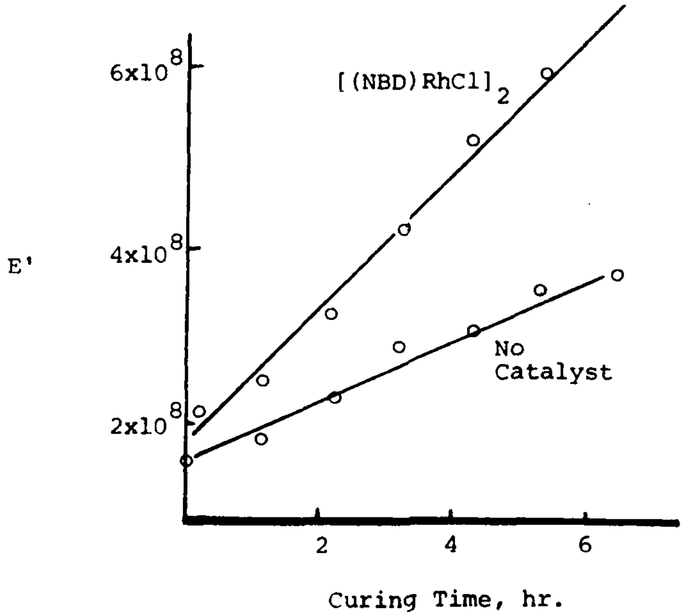
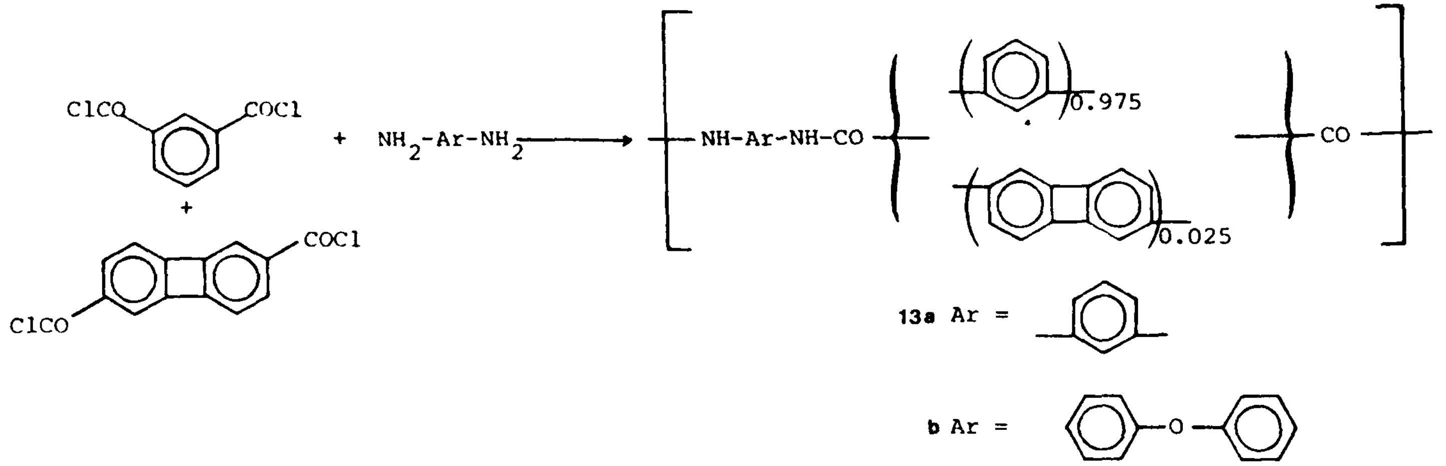


Fig. 6. E' Above Tg vs Curing Time, Copolymer **12e**

The thermal gravimetric analysis of cured polymer samples and of the parent polymer (**12f**) that does not contain the biphenylene units showed breaks at the same temperatures, and under nitrogen, suffered the same weight loss up to 800°C. This provides some evidence that in the curing reaction, stable crosslinks are indeed formed.

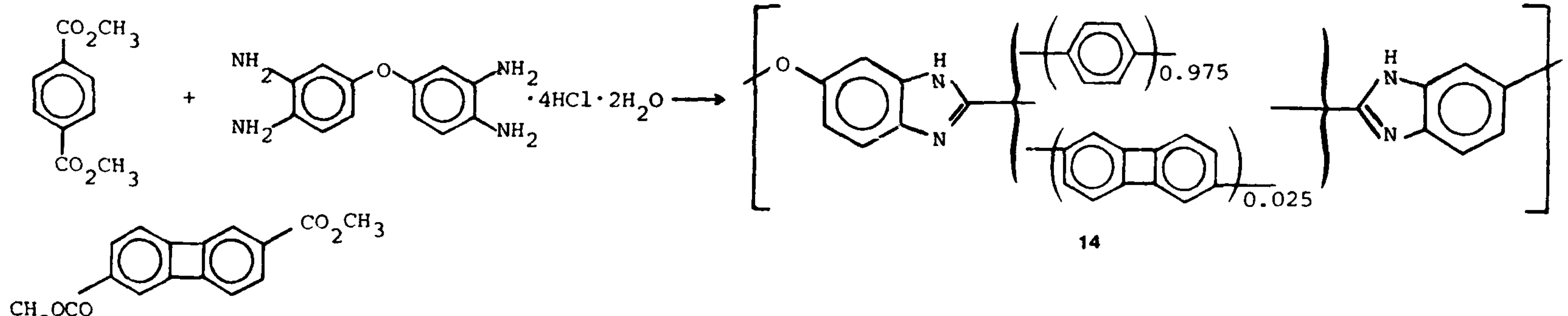
This method of crosslinking polyquinolines is applicable to crosslinking a wide variety of thermally stable polymers, including polyamides, polybenzimidazoles, and polyquinoxalines.[23] Aromatic polyamides (**13**) have been synthesized by substituting biphenylene-2,6-dicarboxylic acid chloride (2.5 mole percent) for isophthaloyl chloride in polymerization with two different amines, m-phenylenediamine and 4,4'-diaminodiphenylether in N'-methylpyrrolidone with propylene oxide as an acid acceptor.[24,25] A polyaromatic benzimidazole (**14**) was synthesized by substituting dimethyl biphenylene-2,6-dicarboxylate (2.5%) for dimethyl terephthalate in polymerization with 3,3'-4,4'-tetraminodiphenylether tetrahydrochloride in polyphosphoric acid at 200°C. Polyquinoxalines (**15**) were synthesized by substituting 2,6-diglyoxalylbiphenylene (2.5%) for two dibenzils in polymerization with 3,3'-4,4'-tetraaminodiphenylether in a 1:1 mixture of m-cresol-xylene at ambient temperature.

The DSC and TMA cells were used to cure samples of polymer film. After curing, the Tg of the samples were recorded as well as their thermal behavior up to 400°C. In all cases the magnitude of the deflection at Tg in the cured samples was sharply reduced compared to those recorded during the heating period up to the curing temperature. The samples were completely insoluble after curing 3 h at 380°C; however, the DSC trace still exhibited an intense exothermic peak after curing.

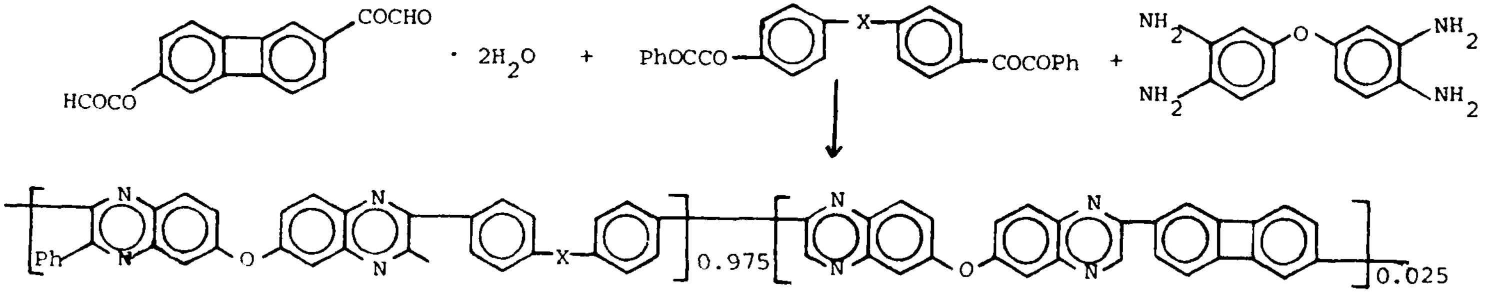


13a Ar =

b Ar =



14



15a ;   X=O

b ;   X=nil

The dynamic mechanical properties of uncured and cured films of polyamides **13** and polyquinoxalines **15** were obtained from room temperature to 450°C.

In the case of polybenzimidazole **14** no Tg was visible by DSC at the highest sensitivity of the instrument. Modulus measurements were not made since good films could not be obtained as a result of the poor solubility of the polymer in the common organic solvents. Thus, the crosslinking could be followed only by its solubility before and after curing. The uncured polybenzimidazole was soluble in concentrated sulfuric acid and partially soluble in DMAC, DMSO and DMF. After curing 3 h at 380°C the polymer sample was completely insoluble in DMSO, DMF and DMAC, but it required 6 h curing to achieve insolubility in concentrated sulfuric acid. The Young's modulus of films are relatively constant up to the glass transition temperature both for polyamides and polyquinoxalines. A major relaxation occurs in the glass transition interval, resulting in a decrease of E' from the order of 10^{10} to 10^{7} - 10^{8} dynes/cm^{2}.

In the case of polyamide **13a** the E' above Tg was found to have a value of 2.8×10^{9} and the polymer could not be cured at temperatures higher than 340°C because broken films resulted. These facts provide some evidence that this polymer maintains a high degree of crystallinity even after the introduction of biphenylene in the chain. Correlations between DSC, TMA and the maximum in the loss modulus (E") were relatively good for all the polymers. The effect of curing on the dynamic storage moduli of polyquinoxaline **15b** is shown in Figure 7. The sharp decrease in the dynamic storage moduli representing the Tg of polyquinoxalines void of biphenylene units is progressively shifted towards higher temperatures by heating the films at 400°C in an inert atmosphere. This effect was attributed to pyrolitic crosslinking. However, introduction of biphenylene in the polymer chain allows the use of lower curing temperatures (350°C vs 400°C) and lower curing times (4 h vs 8 h) to give a material that undergoes a maximum in loss modulus at higher temperatures, and has a higher modulus, especially above the Tg (Fig 7). It is interesting to note also that within the two

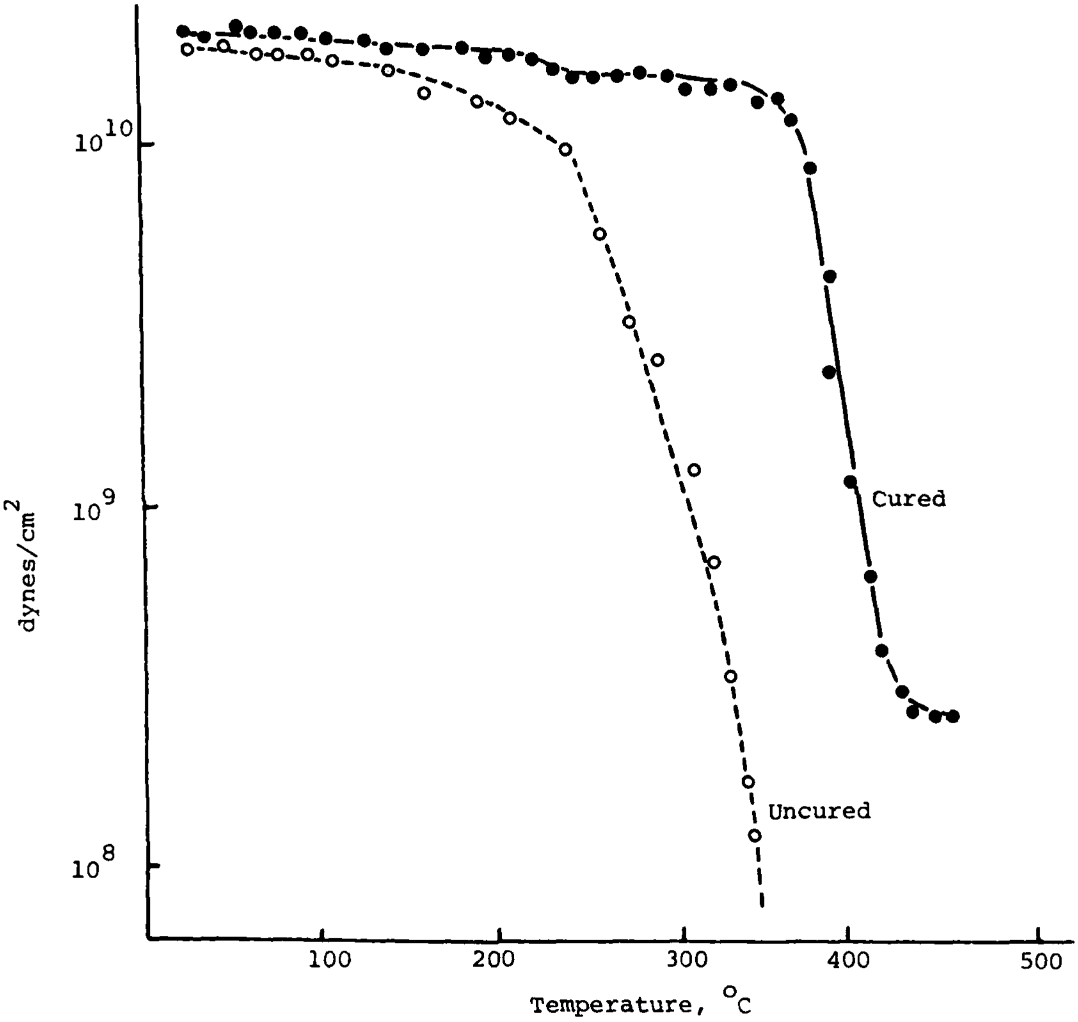


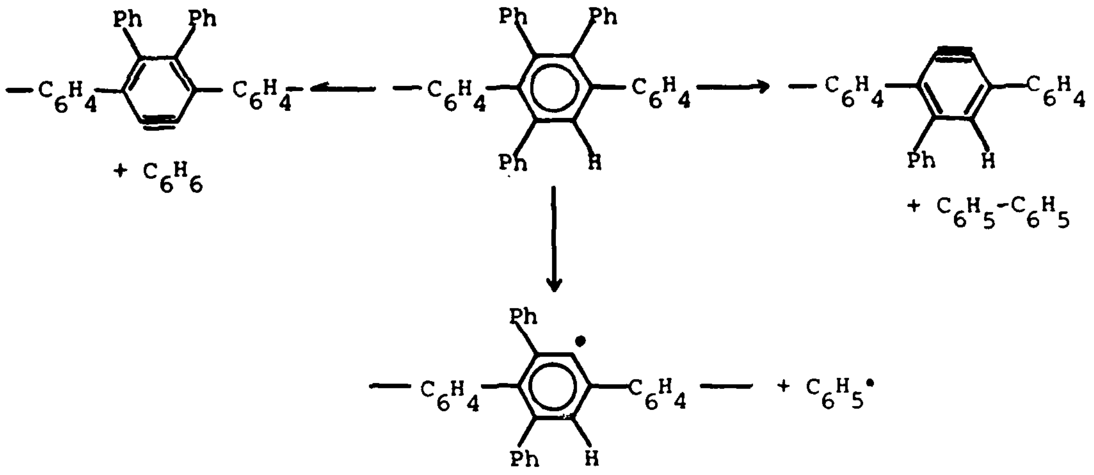
Fig. 7. E' of Copolymer **15b** vs Temperature

polyquinoxalines **15a** and **15b** studied here, the crosslinking does not have the same efficiency. In fact, in polymer **15b** a large increase in the Tg (365° vs 270°C) is observed by TMA after curing for 1 h at 380°C, and this is in accordance with the very high temperature at which the maximum in the loss modulus is observed after curing film samples (327° vs 270°C) (Fig 7). Such a high increase in the Tg is not observed in polymer **15a** . There is no obvious explanation for this difference, but it is apparent that with polymers containing such a small percentage of biphenylene units in the chain, the crosslinking probably occurs through a series of radical abstraction and coupling reactions, rather than tetrabenzocyclooctatetraene formation (dimerization). The radical reaction appears to be more favored in polymer **15b** containing biphenyl than in polymer **15a** containing diphenylether.

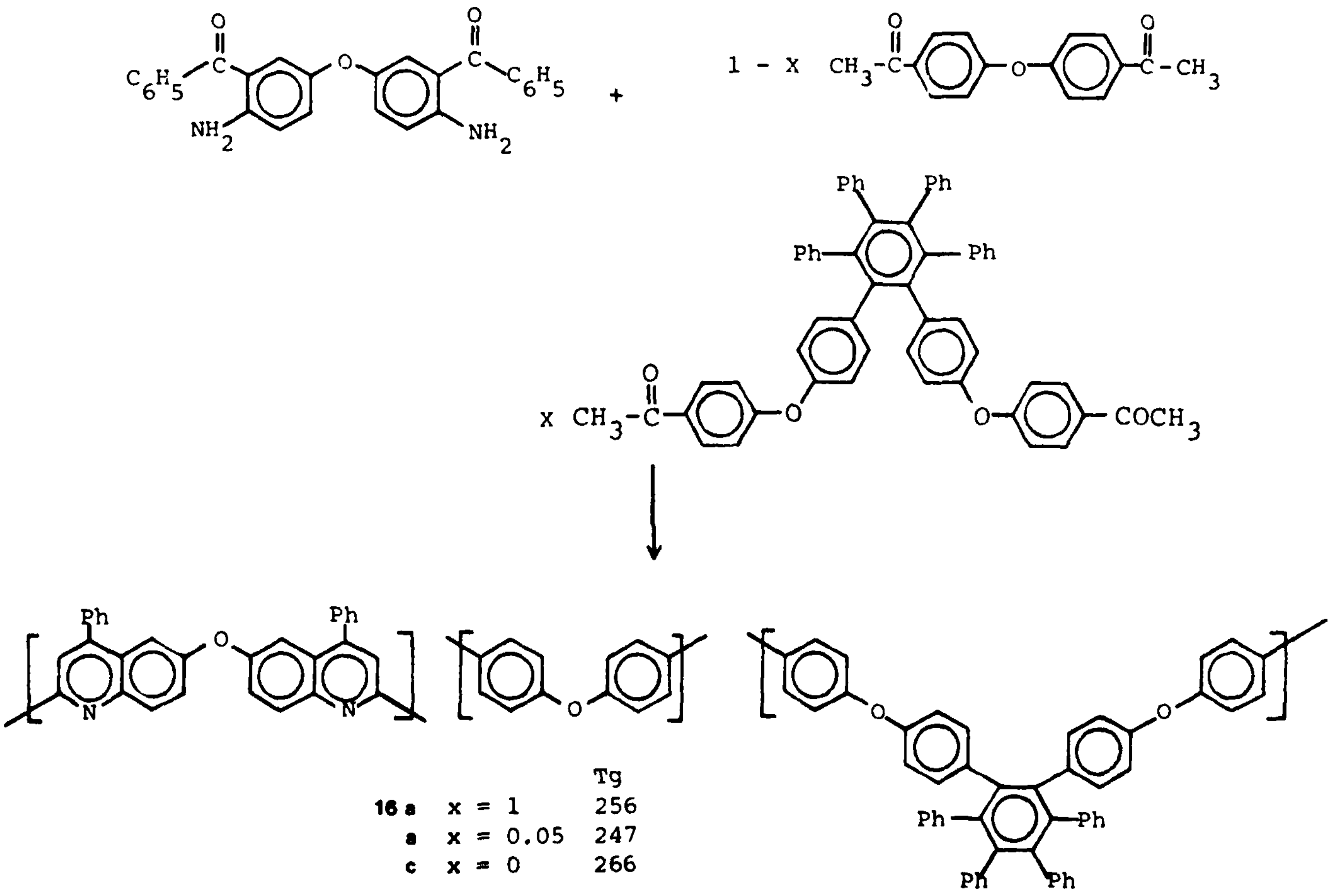
Hexaphenylbenzene Crosslinking.

Hexaphenylbenzene decomposes rapidly at 450°C, a temperature well below that of biphenyl (550°C).[26] It has been observed that phenylated polyphenylenes decompose with the loss of benzene and biphenyl at 550°C, but that free radicals are produced at 350°C in these polymers, and crosslinking does occur. The mechanism of these decompositions and crosslinking is unknown, but in the case of the phenylated polyphenylenes, the main chain does not undergo appreciable scission; instead, the pendent phenyl groups are lost. Polyphenylenes that do not contain the pendent phenyl groups do not lose benzene or biphenyl at 550°C, and do not crosslink at temperatures below 500°C.[27-29] The homolytic bond breaking to form the free radical species and/or the formation of benzyne could explain these results. Presumedly the reaction of a hexaphenylated benzene in a polymer backbone would take place at lower temperatures.

The copolymerization of the diacetyl monomer containing a hexaphenylbenzene arrangement and 4,4'-diacetyldiphenylether with 3,3'-dibenzoylbenzidine gave polymers containing the desired perphenylated phenylene unit.[30]



The glass transition temperature of uncured samples of polymer containing 5% of the phenylated phenylene moiety was only slightly below the analogous polyquinoline homopolymer (255° vs 247°C). The cured polymers showed an increase or disappearance of the Tg, complete insolubility in all solvents, and higher moduli, particularly at temperatures above the original Tg.



		Tg
16 a	x = 1	256
a	x = 0.05	247
c	x = 0	266

REFERENCES

1. ARO Workshop, "New Directions in Fiber Research", Wrightville Beach, North Carolina, 24-27 October 1978.
2. J. K. Stille, J. F. Wolfe, S. O. Norris and W. Wrasidlo, Polymer Preprints, 17(1), 41 (1976).
3. J. F. Wolfe and J. K. Stille, Macromolecules, 9, 489 (1976).
4. S. O. Norris and J. K. Stille, Macromolecules, 9, 496 (1976).
5. W. Wrasidlo and J. K. Stille, Macromolecules, 9, 505 (1976).
6. W. Wrasidlo, S. O. Norris, J. F. Wolfe, T. Katto and J. K. Stille, Macromolecules, 9, 512 (1976).
7. J. K. Stille, J. Wolfe, S. Norris, Y. Imai, E. F. Johnson, T. Katto and M. Kurihara, "Advances in the Chemistry of Thermally Stable Polymers", Warszawa, 1977, p. 9.
8. W. H. Beever and J. K. Stille, J. Polymer Sci., Polymer Symposium, 65, 41 (1978).
9. J. Garapon, W. H. Beever and J. K. Stille, Polymer Preprints, 18(1), 138 (1977).
10. W. H. Beever and J. K. Stille, Macromolecules, 12, 1033 (1979).
11. V. V. Korshak, S. V. Vinogradova and Y. S. Vygodskii, J. Macromol. Sci., Rev. Macromol. Chem., C11(1), 45 (1974).
12. R. M. Harris, S. Padaki, P. Sybert and J. K. Stille, Polymer Preprints, 19(2), 7 (1978).
13. D. F. Lindow and L. Friedman, J. Am. Chem. Soc., 89, 1271 (1967).
14. L. Friedman and P. W. Rabideau, J. Org. Chem., 33, 451 (1968).
15. L. Friedman and D. F. Lindow, J. Am. Chem. Soc., 90, 2324 (1968).
16. M. J. S. Dewar and G. J. Gleicher, Tetrahedron, 21, 1817 (1965).
17. T. C. W. Mark and J. Trotter, Proc. Chem. Soc., London, 163 (1961).
18. R. C. Cass, H. D. Springall and P. G. Quincey, J. Chem. Soc., 1188 (1955).
19. L. Cassar, P. E. Eaton and J. Halpern, J. Am. Chem. Soc., 92, 3515 (1970).
20. J. K. Stille, Pure and Appl. Chem., 50, 273 (1978).
21. J. Garapon and J. K. Stille, Macromolecules, 10, 627 (1977).

22. A. Recca, J. Garapon and J. K. Stille, Macromolecules, 10, 1344 (1977).

23. A. Recca and J. K. Stille, Macromolecules, 11, 479 (1978).

24. C. Chiriac and J. K. Stille, Macromolecules, 10, 710 (1977).

25. C. Chiriac and J. K. Stille, Macromolecules, 10, 712 (1977).

26. I. B. Johns, E. A. McElhill and O. J. Smith, J. Chem. Eng. Data, 7, 277 (1962).

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

28. J. K. Stille and Y. K. Gilliams, Macromolecules, 4, 515 (1971).

29. H. F. Vankerckhoven, Y. K. Gilliams and J. K. Stille, Macromolecules, 5, 514 (1972).

30. G. Baker and J. K. Stille, Macromolecules, 12, 369 (1979).

APPENDIX I

List of Publications

ARO Support 1977-1979

J. Garapon, W.H. Beever and J.K. Stille, Polymer Preprints, 18(1), 138 (1977); "Polyquinolines: A Class of Rigid Chain Polymers".

J.K. Stille, J. Wolfe, S. Norris, Y. Imai, E.F. Johnson, T. Katto and M. Kurihara, "Polymers Containing Quinoline and Anthrazoline Units in the Main Chain" in "Advances in the Chemistry of Thermally Stable Polymers", Warszawa, 1977, p 9.

J. Garapon and J.K. Stille, Macromolecules, 10, 627 (1977); "Biphenylene as Cross-Linking Sites for Polyquinolines".

C. Chiriac and J.K. Stille, Macromolecules, 10, 710 (1977); "Aromatic Polyamides by a Direct Polycondensation Reaction".

C. Chiriac and J.K. Stille, Macromolecules, 10, 712 (1977); "Polyaramides Containing Sulfone Ether Units".

A. Recca, J. Garapon and J.K. Stille, Macromolecules, 10, 1344 (1977); "Biphenylene as a Cross-Linking Site. Curing Conditions, Glass Transition Temperatures and Moduli of High Molecular Weight Polyquinolines Containing Biphenylene Units in the Chain".

R.T. Kohl, T. Katto, J.N. Braham and J.K. Stille, Macromolecules, 11, 340 (1978); "Diels-Alder Reactions of Phenyl-Substituted 2-Pyrones: Direction of Addition with Phenylacetylene".

J.N. Braham, T. Hodgins, T. Katto, R.T. Kohl and J. K. Stille, Macromolecules, 11, 343 (1978); "Polyphenylenes via Bis(2-pyrones) and Diethynylbenzenes. The Effect of *m*- and *p*-Phenylene Units in the Chain".

A. Recca and J.K. Stille, Macromolecules, 11, 479 (1978); "Biphenylene as a Cross-Linking Site in Theramlly Stable Polymers".

J.K. Stille, Pure and Appl. Chem., 50, 273-80 (1978); "Polyquinolines: Versatile Aromatics with Diverse Properties".

W.H. Beever and J.K. Stille, Journal of Polymer Science: Polymer Symposium, 65, 41-53 (1978); "Polyquinolines: A Class of Rigid-Chain Polymers".

R.M. Harris, S. Padaki, P. Sybert and J.K. Stille, Polymer Preprints, 19(2), 7 (1978); "Polyquinolines: Rigid Rod Polymers and Chains Containing Pendent Spiro Units".

G.L. Baker and J.K. Stille, Macromolecules, 12, 369 (1979); "Hexaarylbenzene Units as Cross-Linking Sites for Polyquinolines".

W.H. Beever and J.K. Stille, Macromolecules, 12, 1033 (1979); "The Synthesis and Thermal Properties of Aromatic Polymers Containing 3,6-Quinoline Units in the Main Chain".

APPENDIX 2

List of Participating Scientific Personnel

NAME

Dr. J. K. Stille (Principal Investigator)

Dr. A. Recca

Dr. W. Vancraeynest

Dr. W. Beever (Ph.D. Colorado State 1979)

Mr. G. Baker

Mr. R. Harris

Mr. S. Padaki

Mr. P. Sybert

Mr. J. Droske