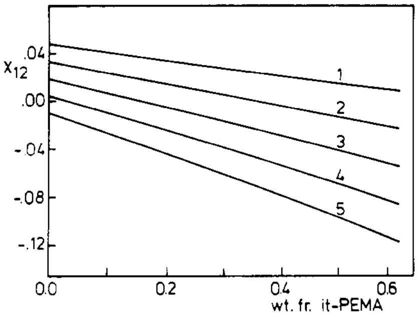

Figure 4. Flory–Huggins parameter vs. weight fraction of it-PEMA ($m_1/m_2 = 0.66$, $s_1/s_2 = 0.55$, $c_{12} = 0.02$): curve 1, $X_{12} = -0.5$; curve 2, $X_{12} = -1.0$; curve 3, $X_{12} = -1.5$; curve 4, $X_{12} = -2.0$; curve 5, $X_{12} = -2.5$ cal/cm^3.

to a calculated LCST at about 80 °C. This is, in accordance with earlier experimental observations,[6] far below the crystallization temperatures of PVF_2 in blends with it-PEMA.

As far as we know, the it-PEMA/PVF_2 system is the first polymer/polymer system exhibiting LCST behavior combined with an irregular asymmetry of the critical concentration. Mixtures of polyisobutylene ($\bar{M}_w = 250$) and poly(dimethylsiloxane) ($\bar{M}_w = 850$ and 1350) show upper critical solution temperature (UCST) behavior with an irregular asymmetric cloud point curve.[22] According to the results of Hamada et al.,[18] one should expect a positive c_{12} for this system. As the ratio of the masses per segment also satisfies $m_{PIB}/m_{PDMS} < 1$, it is tempting to attribute the observed skewness to the nonadditivity of the number of external degrees of freedom (cf. ref 9).

Conclusions

In this work we show that Flory's equation-of-state theory can reproduce the observed irregular asymmetry of the cloud point curve for blends of it-PEMA and PVF_2. The values of the mixing parameters necessary to obtain agreement between the experimental cloud point curve and the theoretical spinodal are in accordance with the observed absence of melting point depression. Moreover, the importance of the nonadditivity of the number of external degrees of freedom with respect to the skewness is demonstrated.

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Reviews

Polyquinolines

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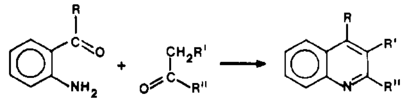
ABSTRACT: A review of the preparation and structure/property relationships of various polyquinolines is presented. The monomer and polymer syntheses and the kinetics, solution properties, morphology, thermal analyses, and cross-linking reactions of polyquinolines are discussed.

Introduction

The Friedländer reaction[1] is a base-catalyzed condensation of an *o*-amino aromatic aldehyde or ketone with a ketomethylene compound that produces a quinoline, usually in good yields. Although the reaction can be considered to be an aldol reaction followed by Schiff base formation at nitrogen or, alternatively, the reverse reaction sequence,[2,3] neither type of intermediate has been isolated, indicating that the second, cyclization step must be fast compared to the first reaction.



This type of base-catalyzed reaction has been applied to the synthesis of anthrazolines to obtain totally aromatic polymers.[4] The reaction of 4,6-diaminoisophthalaldehyde and a series of diacetyl aromatics in hexamethylphosphoric triamide gave a series of low molecular weight polyanthrazolines. Although these polymers showed reasonably

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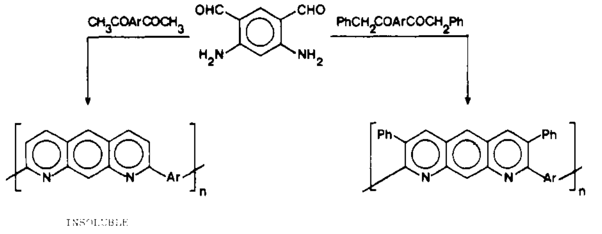
good thermal stability, they were soluble only in strong acid. A number of questions were raised as a result of this work: (1) Could the solubility of these polymers be improved by the substitution of pendent phenyl groups? (2) Could the solubility be improved by the synthesis of less rigid polymer structures? (3) Was the low molecular weight due to the premature precipitation of the polymers from the reaction medium because of poor solubility? (4) Was the reaction not good enough to afford high molecular weight polymer? The answer to all four of these questions is yes.



The base-catalyzed polymerizations of 4,6-diaminoisophthalaldehyde with diphenacetyl aromatic monomers gave polyanthrazolines of about the same molecular weight as the unphenylated analogues, even though these phenylated polyanthrazolines did not precipitate from the polymerization solvent, hexamethylphosphoric triamide.[5,6] Thus, the reason for the low molecular weight polymer in this case could be attributed to the reaction.

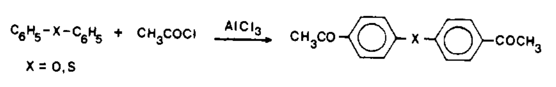
It was known[7,8] that the Friedländer reaction could also be catalyzed by acid, and in many cases, acid catalysis gave higher yields of quinolines than base catalysis. A study[9,10] of the model reactions of acetophenone and deoxybenzoin with *o*-aminobenzaldehyde and *o*-aminobenzophenone clearly demonstrated two requirements for high-yield (>98%) reactions: (1) *o*-Amino aldehydes could not be used since high enough yields of quinoline were not achieved (~80%). Apparently there is a damaging side reaction of the aldehyde function. (2) Acid catalysis was superior, consistently giving higher yields of quinoline, particularly with *o*-aminobenzophenone. Thus, the way was open for the synthesis of high molecular weight phenyl-substituted polyquinolines.

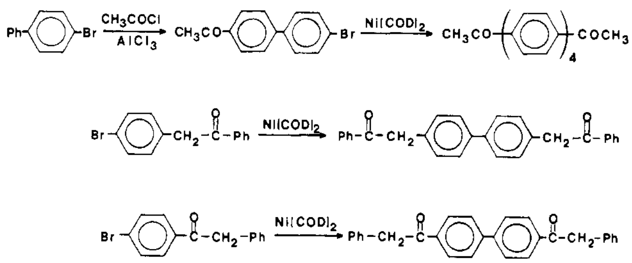
Monomer Synthesis

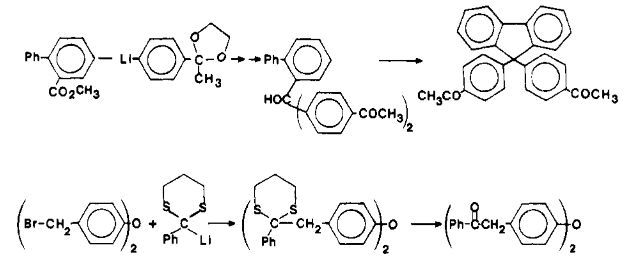
Monomers containing both the ketomethylene moiety and the amino ketone group in one molecule (A–B monomer) as well as bis(amino ketone) (A–A) and bis(ketomethylene) (B–B) monomers have been synthesized by a variety of diverse reaction sequences. Some representative syntheses of these compounds are outlined in the following sections.

Ketomethylene Monomers. A number of diacetyl or diphenacetyl monomers are commercially available. Because it was desirable to incorporate certain unique structural features into the polyquinolines, a variety of bis(ketomethylene) compounds that were not commercially available were synthesized.

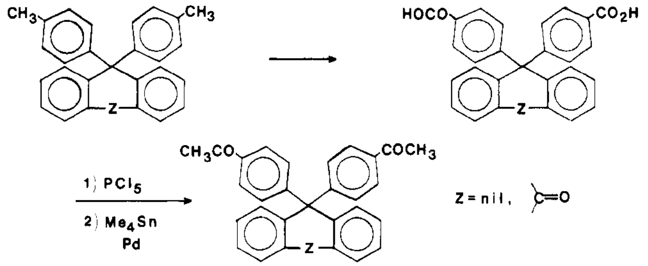
The Friedel–Crafts acylation or phenacylation of certain aromatics is a suitable method of obtaining pure bis(ketomethylene) compounds in high yields.[9] This method is particularly useful for the acylation of biphenyl, diphenyl ether, and diphenyl sulfide. The coupling reaction of an acyl aromatic compound can be an effective method of producing a bisacetyl monomer,[11,12] especially in an acylation reaction where the X group does not direct the substitution to the 4,4′-positions. In other syntheses, a lithium derivative bearing a protected acetyl group has been utilized in carbon–carbon bond-forming reactions.[11,13]



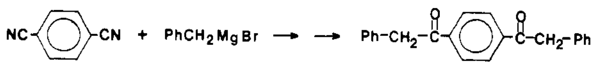




The conversion of an acid chloride to a methyl ketone by the palladium-catalyzed reaction of tetramethyltin proceeds in high yields under mild conditions with virtually no side reactions.[13,14]



The reaction of a Grignard reagent with a dinitrile also has been utilized for the synthesis of bis(ketomethylene) compounds, particularly for bis(deoxybenzoins).[9]



Amino Ketone Monomers. The direct benzoylation of a protected bis(aromatic amine) is not a satisfactory method of producing bis(*o*-amino ketone) monomers, since the yields are low and a variety of side reaction products are formed that make the desired amino ketone difficult to purify.[15,16] Furthermore, the oxidation reactions of a bisdioxindole obtained from a bisisatin do not give high yields of the desired bis(*o*-amino ketone).[17] Two different approaches to the introduction of *o*-aminobenzoyl functions into aromatic nuclei have been employed since both give high yields of pure monomers and involve relatively simple procedures.

The Friedel–Crafts reaction of a phthalic anhydride derivative followed by conversion of the remaining carboxylic acid function to an amine via a Hofmann degradation of the amide is a route to two amino ketone monomers.[9,18] The Friedel–Crafts reaction of pyromellitic dianhydride with benzene gives approximately equimolar amounts of the two isomeric dibenzoylphthalic acids that can be separated on the basis of their solubilities. Conversion of the acids to the pseudodibenzoylphthaloyl chlorides followed by the reaction with ammonia gives the

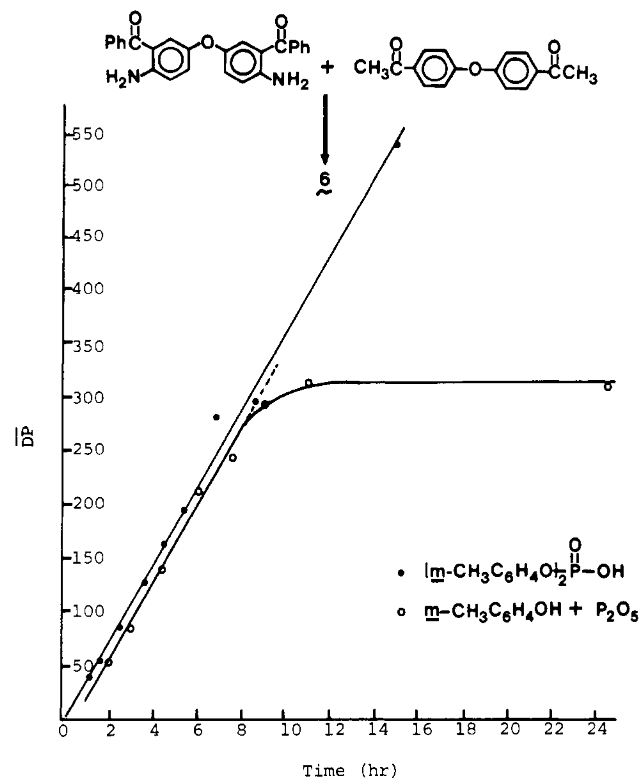
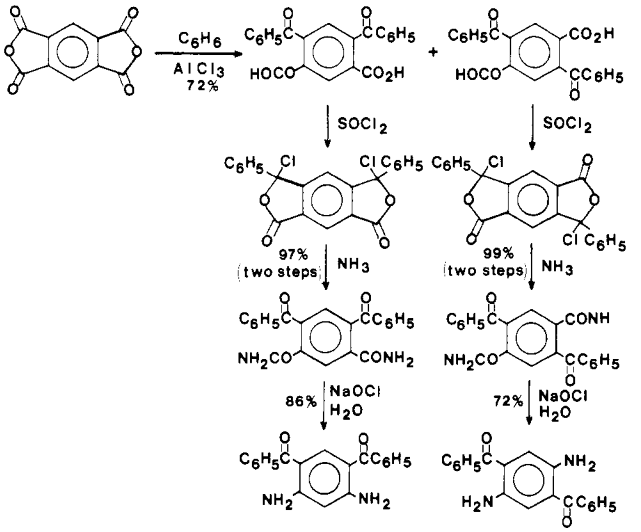
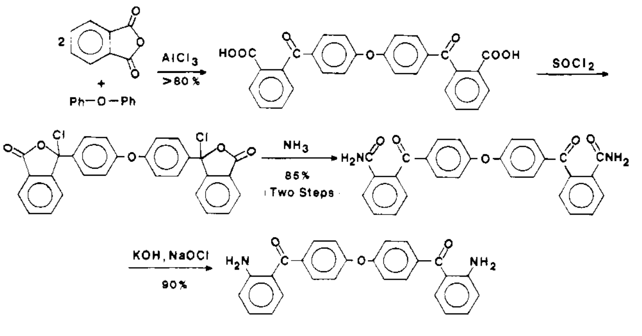


Figure 1. Kinetics of polymerization.

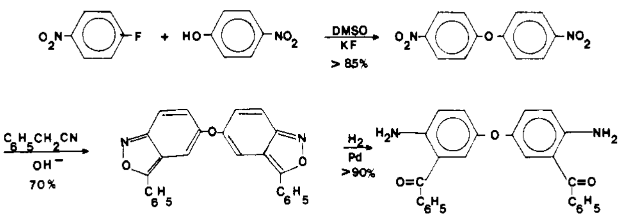
corresponding amides which are smoothly converted to the amine by a Hofmann reaction with sodium hypochlorite.



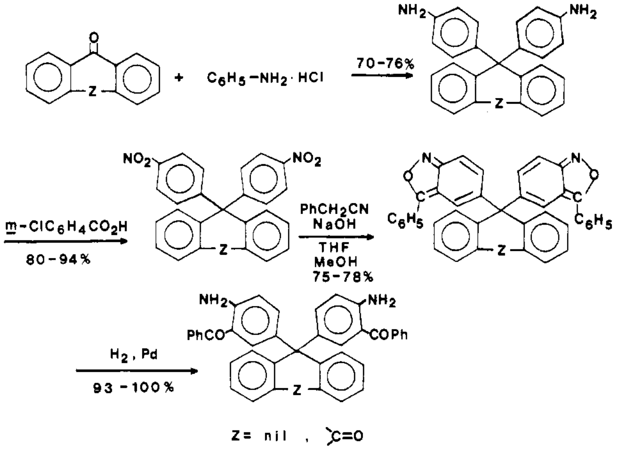
An analogous synthetic procedure has been carried out starting from phthalic anhydride and diphenyl ether, the resulting bis(carboxybenzoyl) diphenyl ether being converted to the corresponding amide.



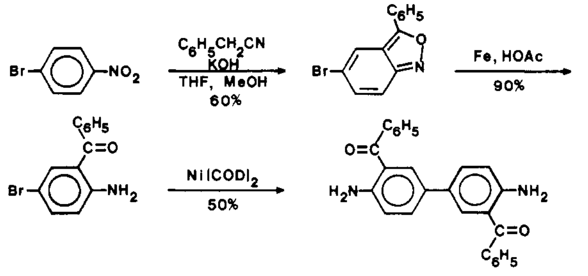
The generation of benzisoxazole from an aromatic nitro compound followed by reductive cleavage of the benzisoxazole has proven to be the most versatile and generally useful method of *o*-amino ketone synthesis.[12,13,19,20] The reaction of 4,4′-dinitrodiphenyl ether with phenylacetonitrile in the presence of base yields a bisbenzisoxazole that can be converted to the amino ketone by hydrogenation with a palladium catalyst. This catalyst does not reduced the aryl ketone.[19]



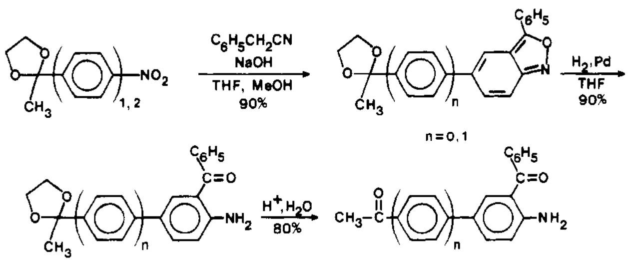
This sequence has also been employed in the latter stages of the synthesis of two cardo monomers.[13] In this series, the generation of nitro compounds from the corresponding aromatic amines was necessary since the earlier stages of the synthesis required electrophilic substitution reactions on aniline.



The formation of a benzisoxazole in good yields is very sensitive to electronic effects. Thus, the reaction of phenylacetonitrile with 4,4′-dinitrobiphenyl does not give the desired product. To circumvent this, a benzisoxazole has been obtained from *p*-bromonitrobenzene. Reduction of the benzisoxazole ring was carried out chemically to avoid removal of the bromide function. Coupling of the 2-benzoyl-4-bromoaniline was then accomplished with nickel.[12]



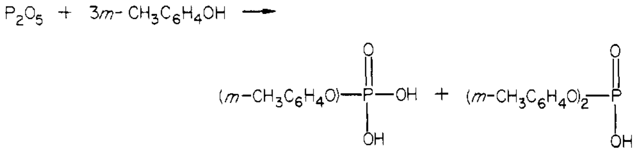
The synthesis of A–B monomers has been accomplished by the benzisoxazole synthesis.[12,19] Protection of the acyl group was necessary since the reaction of the nitro aromatic with phenylacetonitrile is carried out with strong base. Hydrogenation of the benzisoxazole ring was then followed by removal of the ketone protecting group.



Polymerization Reaction

Of the various acid catalysts and reaction conditions examined initially,[9,10] poly(phosphoric acid) in *m*-cresol gave the highest molecular weight materials.[9,10,17,21,22] The product of the reaction of phosphorus pentoxide with *m*-cresol was an even better catalyst,[18,19] although with both catalysts, the reaction stopped after achieving a moderate molecular weight ($\bar{M}_n \simeq 80000$). The polymerization reaction in these media followed second-order kinetics, first order each in ketomethylene and amino ketone functions (Figure 1). Most of the polymerization reactions were carried out at 135 °C.

The product of the reaction of *m*-cresol with phosphorus pentoxide was shown to consist of di-*m*-cresyl phosphate and mono-*m*-cresyl phosphate plus minor amounts of phosphoric acid and tri-*m*-cresyl phosphate.[22,23] Identification of the two major products was accomplished by a comparison of their ^{31}P chemical shifts in the reaction mixture with those of the authentic, independently synthesized phosphate esters.



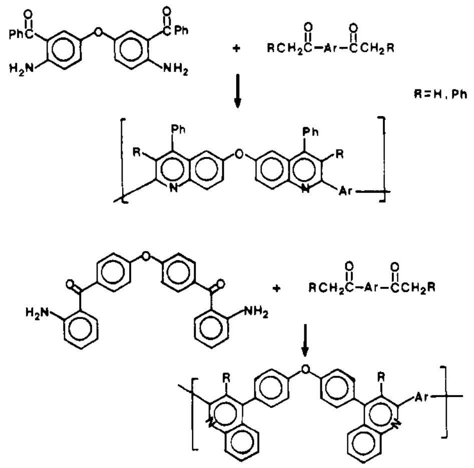
$$P_2O_5 + 3\,m\text{-}CH_3C_6H_4OH \longrightarrow (m\text{-}CH_3C_6H_4O){-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH + (m\text{-}CH_3C_6H_4O)_2{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}$$

Although the independently synthesized mono-*m*-cresyl phosphate was a poor acid for use in the polymerization, di-*m*-cresyl phosphate was an excellent acid in combination with the *m*-cresol solvent medium. The initial rate constants for the phosphorus pentoxide–*m*-cresol and the di-*m*-cresyl phosphate–*m*-cresol media were identical. One added advantage of using pure di-*m*-cresyl phosphate in *m*-cresol is that much higher molecular weights could be achieved. 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. Polymerization in a mixture of *m*-cresol and di-*m*-cresyl phosphate, however, gives a $\overline{DP} > 550$ in 14 h, and the polymerization reaction continues.

Structure and Properties: Solution Morphology and Thermal and Mechanical Properties

The wide variety of ketomethylene and amino ketone monomers that could be synthesized, and the ability of the quinoline-forming reaction to generate high molecular weight polymers under relatively mild conditions, allowed the synthesis of a series of polyquinolines with a wide structural variety. Polyquinolines with a range of chain stiffness that could be altered from a semirigid chain to rodlike macromolecules could be synthesized. Since the monomers were designed to produce only thermally stable polyaromatics, all the resulting polymers had excellent thermal stability, with initial weight losses occurring between 500 and 600 °C in air (TGA). Under nitrogen, the polyquinolines exhibited initial weight loss at about 600 °C and a 20% weight loss up to 800 °C. Isothermal aging of certain polymer samples showed them to be among the most thermally stable organic polymers known (vide supra). Because of the wide structural variety and the resulting wide variation in properties, the polyquinolines will be discussed in three separate categories: semirigid, cardo, and rigid rod.

Semirigid Polyquinolines. High molecular weight semirigid polyquinolines can be obtained from the bis(amino ketone) monomers containing an oxygen link between the aromatic units (Table I).[18,19] In *m*-cresol–phosphorus pentoxide mixtures, a $\overline{DP}$ of 300 (corresponding to a 99.7% extent of reaction) can be obtained for polymer **6**, for example. The dispersity of this polymer is $\bar{M}_w/\bar{M}_n = 3.75$. In the *m*-cresol–di-*m*-cresyl phosphate mixture, a number-average molecular weight of 162000 can be obtained in 14 h.



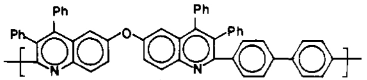
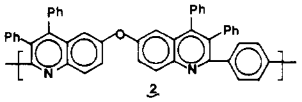
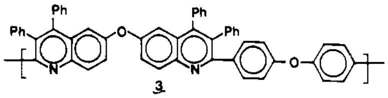
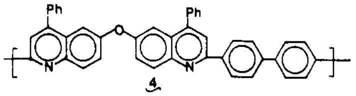
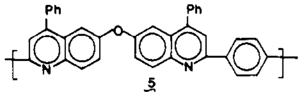
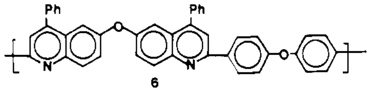
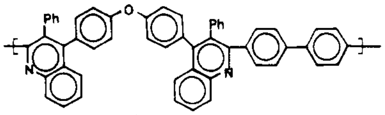
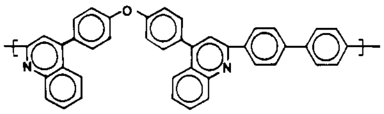
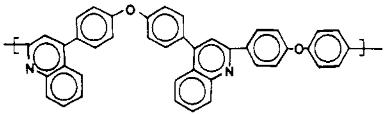
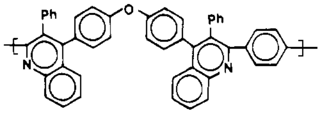
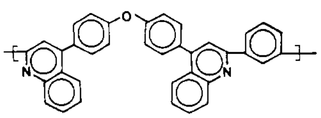
The semirigid polymers are soluble in chloroform, *sym*-tetrachloroethane, *m*-cresol, and other common organic solvents. Solutions of polymers **1–7** in chloroform or tetrachloroethane will precipitate polymer on prolonged standing. The amorphous precipitate is insoluble in the solvent from which it precipitated but will redissolve in *m*-cresol. Precipitation from *m*-cresol by a nonsolvent gives a polymer which will redissolve in chloroform or *sym*-tetrachloroethane and then precipitate on standing. This behavior has been attributed to the formation of aggregates in solution.

Polymer **6** has a molecular weight–viscosity relationship corresponding to $[\eta] = (9.0 \times 10^{-4})\bar{M}_n^{0.7}$. The value of 0.7 for *a* is lower than might be expected for a polymer of this structure; however, this value may be in error due to the tendency of these polymers to aggregate in solution. Low second virial coefficients were obtained for solutions of polymer **6** in chloroform ($\Gamma = 0.3\text{–}0.5$ cm^3/g).

By reversing the position of the methylene and carbonyl functions in the ketomethylene monomer, one can synthesize polyquinolines having 3,6-catenation (Table II).[11] These polymers (**12–14**) showed improved solubilities over the analogous polyquinolines with 2,6-catenation on the quinoline unit (**1–3**), being readily soluble in chloroform or *sym*-tetrachloroethane. A 10–15 wt % solution of polyquinoline **14** in chloroform, however, did precipitate polymer on standing, whereas polyquinolines **12** and **13** did not. Polyquinolines **15–17** containing quinoline units connected directly rather than by an oxygen link exhibited lower solubility, as expected.

Clear, transparent films of polyquinolines **1–14** could be cast from solutions of chloroform or tetrachloroethane.

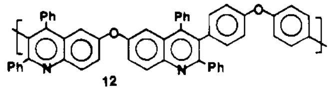
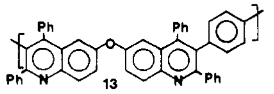
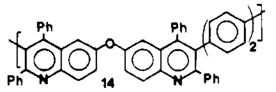
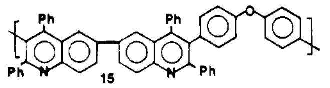
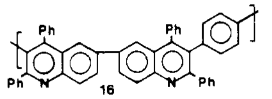
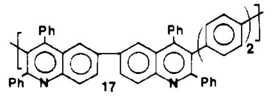
Table I
Intrinsic Viscosities and Phase Transition Temperatures of Semirigid 2,6-Polyquinolines

	$[\eta]_{\text{inh}}$, dL/g	T_g, °C	T_m, °C	T_g/T_m	T_d, °C	$(\Delta C_p)_{T_g}$, cal/(mol-deg)
 1	4.10	351	480	0.83		5.10
 2	3.40	345	475	0.82		6.0
 3	2.00	305	476	0.77		5.20
 4	3.10	308	480	0.77		4.00
 5	1.10	300	455	0.79		3.85
 6	1.80	266	448	0.75		3.00
 7	0.57	345	500	0.80	540	4.10
 8	0.38	326	475	0.80	575	
 9	0.62	276	483	0.73	565	4.95
 10	0.26	273	amorphous		520	
 11	0.36	268	amorphous		520	

Films of polyquinolines **15** and **17** were cast from *m*-cresol.

Although most of the semirigid polyquinolines (Tables I and II) are largely amorphous (<10%), crystalline transition temperatures could be detected.[11,24,25] These polymers are characterized by high glass transition temperatures ranging from 255 to 390 °C. It is interesting to compare the T_g's of 2,6-polyquinolines with and without the phenyl substituent in the 3-position. Polyquinolines **4–6** have T_g's 40–45 °C lower than the analogous polyquinolines **1–3**, respectively, containing a phenyl substituent in the 3-position. The increase in T_g of polymers **1–3** has been attributed to added steric hindrance presented by the phenyl substituent, retarding free rotation at the position of catenation and thus providing reduced chain mobility.[23] Polymers **15** and **16** exhibited heats of crystallization (T_c) in addition to crystalline transition temperatures. When these polymers were annealed at their respective T_c's for 1 h, the magnitude of T_g (DSC) decreased and the percent crystallinity increased to about 30%.

Table II
Properties of Semirigid 3,6-Polyquinolines

	solubility[a]	[η], dL/g (solvent)	T_g, °C DSC	T_g, °C E''_{max}	T_c, °C	T_m, °C
 12	$CHCl_3$	1.2 ($CHCl_3$)	255	250		
 13	$CHCl_3$	0.7 ($CHCl_3$)	312	310		
 14	TCE[b]	3.6 (*m*-cresol)	325	335		
 15	*m*-cresol	0.8 (*m*-cresol)	305	310	415	475
 16	H_2SO_4	0.5 (H_2SO_4)	370		437	550
 17	*m*-cresol	2.4 (*m*-cresol)	390	420		530

[a] Solubility defined as the ability to dissolve 10% by wt of polymer. [b] *sym*-Tetrachloroethane.

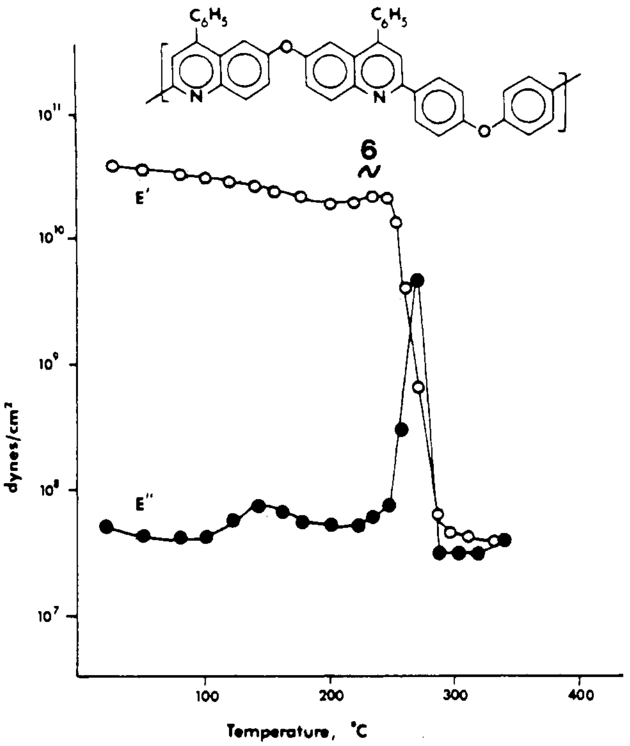


Figure 2. Dynamic storage and loss moduli vs. temperature: heating rate 5 °C/min, He atmosphere, frequency 35 Hz.

Table III
Properties of Unoriented Film Samples of Polyquinoline 6

thickness, mil	0.3–0.4
$[\eta]_{inh}$ (0.5% $CHCl_3$, 30 °C), dL/g	1.59 (M_n = 81 700)
density, g/cm³	1.174
X-ray	amorphous
T_g °C	266

tensile	23 °C	200 °C
modulus, psi	1.1 × 10⁶	0.74 × 10⁶
elongation, %	0.6	2.0
tensile strength, psi	3.2 × 10³	3.5 × 10³

Electrical Properties

dielectric strength, kV/mil	7.8
volume resistivity, (Ω-cm)/mil	2.5 × 10¹⁵
dielectric constant	2.6/2.5 (10²/10⁵ Hz)
dissipation factor	0.017/0.005 (10²/10⁵ Hz)

Thermal Stability

TGA (5% wt loss)	525 °C (air) 630 °C (N_2)
film failure (air aging)	2 h at 450 °C 20 h at 350 °C 11 days at 300 °C 6 months at 250 °C >10 years at 200 °C[a]

Permeability

O_2, cm³ (100 in²-24 h-atm)⁻¹	278
water vapor, g (100 in²-24 h-44 mm)⁻¹ mil⁻¹	9.4

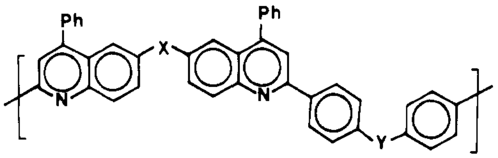
[a] Extrapolated from Arrhenius-type plot.

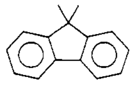
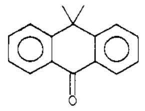
None of these semirigid polyquinolines were crystalline enough such that they maintained good mechanical properties above the glass transition temperature.[11,24,25] Under the mild tensile stresses required for dynamic mechanical testing the mechanical performance of films is relatively constant up to the glass transition temperature. Above T_g, mechanical losses become pronounced and a drop in Young's modulus, for polyquinoline 6, for example (Figure 2), from 5 × 10¹⁰ to less than 10⁸ dyn/cm², is observed.[8]

Because the semirigid polyquinolines are stable for short periods of time above 500 °C, are amorphous, and some have T_g's in the 250–300 °C range, they can be melt processed. Polyquinoline 9, for example, can be melt extruded through a large-bore capillary at 430 °C to give a 1-mm wire that was still soluble in chloroform.[18]

Unoriented films of those polyquinolines tested (e.g., polyquinoline 6) have high moduli, moderate tensile strength, and low elongation combined with good electrical properties (Table III).[23] Oxygen and water vapor

Table IV
Cardo Polyquinolines



	polyquinoline		solubility					
	X	Y	$CHCl_3$	TCE	$[\eta]$, dL/g	T_g, °C	T_d, °C	$E'_{25\,°C} \times 10^{-10}$, dyn/cm^2
18	 i	i	+	+	0.58^a	390	580	2.1
19	i	 ii	+	+	0.70^b	385	530	2.2
20	ii	i	+	+	1.30^b	405	540	2.6
21	ii	ii	+	+	0.53^b	390	520	1.5
22	nil	i	+	+	2.50^a	420	570	1.3
23	O	i	+	+	1.70^a	310	570	2.0
24	nil	ii	−	+	1.44^b	417	560	1.9
25	O	ii	+	+	0.87^b	340	580	1.8
26	i	nil	−	$-^d$	1.95^c	380	580	1.8
27	i	O	+	+	0.56^c	315	575	2.5
28	ii	nil	+	+	0.69^a	350	530	2.2
29	ii	O	−	$+^e$	0.97^c	320	535	

[a] $CHCl_3$. [b] $CHCl_2CHCl_2$. [c] *m*-Cresol. [d] Hot *m*-cresol. [e] Hot TCE.

permeabilities are relatively high. The thermal stability of **6** is excellent as determined by isothermal aging. A life in air (crease test) of about 10 years at 200 °C can be obtained by extrapolation of the Arrhenius data for isothermal aging.

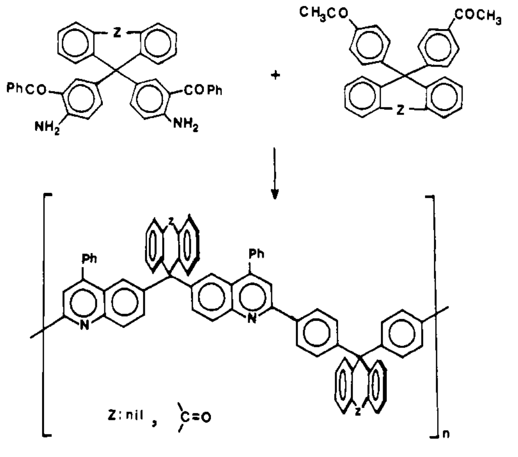
Fibers of **6** were spun from an *N*-methylpyrrolidinone dope containing 12% solids at 150 °C into concurrent nitrogen at 240 °C. The relatively low percentage of elongation did not allow draw ratios greater than about 2, and the drawn fiber did not show appreciable crystallinity. Tenacity and moduli of 3 and 45 g/denier, respectively, were obtained.

Cardo Polyquinolines.[13,20] It is evident that the amorphous, semirigid polyquinolines have a use temperature that is limited to their glass transition temperatures, a temperature 150–300 °C below the thermal decomposition temperature. One approach to this problem is to raise the glass transition temperature close to the thermal decomposition temperature while maintaining good solubility properties.

Polymers that contain pendent loops attached to the polymer backbone, "cardo" polymers, give chain-enhanced rigidity. 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 polymerization. Polymers containing the cardo structure generally possess greater rigidity while maintaining the good solubility of their more flexible analogues. Most of these polymers are amorphous as a result of the bulky pendent loops.

Polymers from cardo monomers having the largest value of reduced volume of the loop to molecular weight—for example, fluorene, $Ki/M = 1.58$—exhibit the highest heat distortion temperatures. Polymers containing cardo monomers derived from anthraquinone show slightly lower heat distortion temperatures ($Ki/M = 1.56$).

Polyquinolines containing pendent cardo fluorene and anthrone units can be prepared through the step-reaction polymerization of the appropriate monomers.[13,20]



Cardo polyquinolines **18**–**29** (Table IV) were all amorphous and showed good solubility in *sym*-tetrachloroethane and chloroform, with a few exhibiting good solubility only in *m*-cresol. Tough, transparent films could be cast from 10–15% (w/v) solutions in *sym*-tetrachloroethane, with the exception of **26**. Small structural changes displayed large effects on the solubility of the cardo polyquinolines and were dependent on the location of the cardo group in the repeat unit. For example, if the fluorenyl group is present only in the bis(*o*-aminobenzophenone) group (X) and not in the 4,4′-biphenylene unit of the diacetyl monomer (Y = nil, **26**), low solubility is observed (hot *m*-cresol). The polymer containing the reverse placement of the cardo group (X = nil, Y = fluorenyl, **22**) showed good solubility in chloroform.

The glass transition of the various cardo polyquinolines ranged from 310 to 420 °C. The dicardo polyquinolines (X, Y = cardo units) had higher T_g's than the rigid-rod polyquinolines (vide supra). An increase of T_g of 40–70 °C was observed when one ether link in polyquinoline **6** (X = Y = O, T_g = 266 °C) was replaced by either a fluorenyl or an anthronyl group. A second increase in T_g of 60–95 °C resulted from the introduction of a second cardo group for the remaining ether functionality.

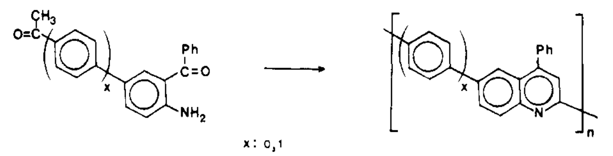
The glass transition temperature of the cardo polyquinolines containing one pendent loop per repeat unit is dependent not only on the stiffness of the linkages along the main chain but on the location of that loop in the repeat unit. For example, in the cardo polyquinolines containing biphenylene linkages, interchanging the fluorenyl or 10-anthronyl groups from positions between the quinoline units (**26**, T_g = 380 °C; **28**, T_g = 350 °C) to positions between the biphenylene units (**22**, T_g = 420 °C; **24**, T_g = 417 °C) increases T_g by 40–67 °C.

The storage moduli (E') of these polymers remained fairly constant ($\sim 10^{10}$ dyn/cm^2) up to their glass transition temperatures, where a significant loss occurred, with E' falling to 10^7–10^8 dyn/cm^2. The thermal stabilities of this series of polyquinolines were excellent, with the onset of decomposition occurring at 500–540 °C in air. Even though the cardo units contain an sp^3 carbon, that carbon has no hydrogen available for the initiation of oxidative degradation. Thus, by incorporating cardo units into the polyquinoline backbone, the use temperature, as governed by T_g, can be raised to within 100 °C of the oxidative decomposition temperature.

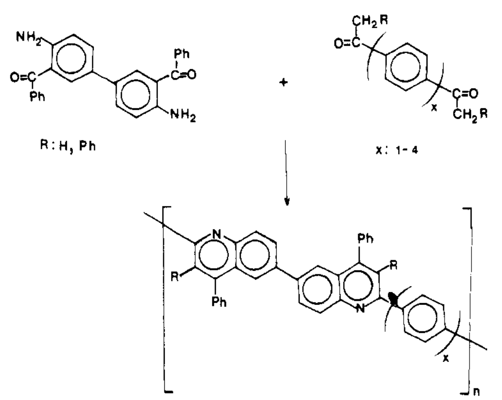
Rigid-Rod Polyquinolines. In a second approach to raising the use temperature of polyquinolines up to the decomposition temperature, the synthesis of a series of crystalline polyquinolines having crystalline transition temperatures near 500 °C was undertaken. Rigid-rod polymers generally possess higher phase transition temperatures and mechanical properties than the more flexible chain macromolecules. Especially high moduli and tensile strengths in one direction can be obtained when the rods are oriented along that direction as a result of shear from the melt or alignment in solution coupled with further orientation during extrusion. The prediction[26,27] that, above a certain concentration, the random arrangement of rigid rods in solution would become impossible and anisotropic domains would be formed in which the axes of the rods are preferentially oriented has been realized.

Initially, polymerization reactions of 4,6-dibenzoyl-1,3-phenylenediamine and 2,5-dibenzoyl-1,4-phenylenediamine were carried out with 4,4′-diacetylbiphenyl to give polyanthrazoline and polyisoanthrazoline structures, respectively (**30** and **31**).[9] These polymers did not achieve the high molecular weights, in part because the polymerizations were run in the phosphorus pentoxide–*m*-cresol reaction medium instead of the di-*m*-cresyl phosphate–*m*-cresol medium. Although the high molecular weights necessary for the observance of good physical properties were not realized, these two samples are included for comparison of their phase transition temperatures (Table V). Also, included for comparison are some of the slightly more flexible analogues of the rigid-rod polymers, polyanthrazoline **32** and isoanthrazoline **33**.

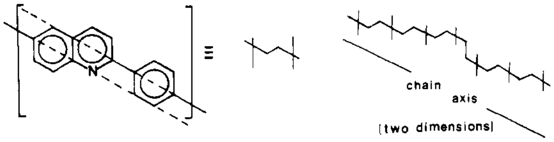
The self-polymerization of 5-acetyl-2-aminobenzophenone and 4-amino-4′-acetyl-3-benzoylbiphenyl along with a copolymerization of these two monomers was conducted with the di-*m*-cresyl phosphate–*m*-cresol mixture.[12,19]



The polymerization of 3,3′-dibenzoylbenzidine with diacetyl and diphenacetyl *p*-phenylene monomers was also carried out in the same reaction medium.[12,20] In both types of polymerizations A–B and A–A + B–B, the resulting polymer dope could be used directly for casting films or wet spinning fibers.

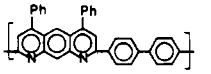
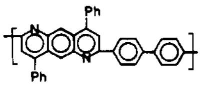
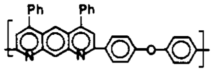
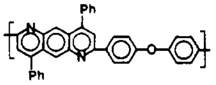
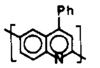
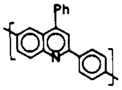
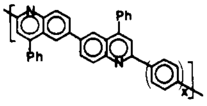
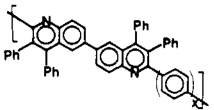
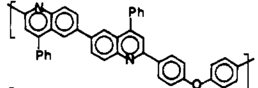
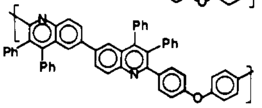


Whereas the homopolymers from the A–B monomers were soluble only in the polymerization solvent and strong mineral acids, the A–B copolymer was also soluble in trifluoroacetic acid. The A–A and B–B rigid-rod polymers were soluble in the polymerization medium and trifluoromethanesulfonic acid. Very high intrinsic viscosities of these polymers were observed. Note that in the structural recurring unit of the rigid-rod polymers, each quinoline unit introduces a lateral but parallel displacement in the polymer chain direction but does not change the direction. Although free rotation about the single bonds in the chain produces a displacement in the direction perpendicular to the chain direction, the end-to-end distance in the direction of the chain axis cannot change (the ultimate crankshaft).



Both differential scanning calorimetry and dynamic thermomechanical analysis were used to determine the glass transition temperatures (Table V). These rigid-rod polyquinolines are characterized by high glass transition temperatures, from ~350 to ~420 °C, but not any higher than the T_g's for the polyquinolines containing two cardo units per recurring unit (Table IV). In some cases, T_g was not readily apparent due to the relatively high degree of crystallinity. A high degree of crystallinity and high crystalline transition temperatures, 500–580 °C, were observed, but in some cases no crystalline transition could be observed below the decomposition temperature. Thus, in these rigid-rod polyquinolines, the decomposition temperature and the use temperature, as defined by the loss of mechanical properties, coincide. The situation is exemplified by a comparison of the dynamic storage moduli (E') of a semirigid polyquinoline, **6**, and a rigid-rod polyquinoline, **36** (Figure 3). The other rigid-rod polymers that are crystalline exhibit similar behavior, retaining their mechanical properties above the glass transition temperature and up to 500 °C.

Table V
Rigid-Rod Polyquinolines

	[η], dL/g	T_g, °C		T_m, °C	E′, dyn/cm²	
		DSC	E''_{max}		25 °C	above T_g (T, °C)
 30	0.62	392	*a*	513	*a*	
 31	0.89	383	*a*	498	*a*	
 32	0.77	379	382	502	4.8 × 10^{10}	7.2 × 10^{7}
 33	0.59	362	368	490	3.5 × 10^{10}	2.4 × 10^{7}
 34	3.6	415	*a*	552	*a*	
 35	11.6	*b*	383	580	4.2 × 10^{10}	3.6 × 10^{9} (480)
1:1 copolymer 34 and 35	4.9	330	343	520	3.1 × 10^{10}	5.2 × 10^{9} (355)
 x = 1, 36	7.6	350	395	*c*	4.2 × 10^{10}	1.9 × 10^{10} (425)
x = 2, 37	26.0	340	360	500	3.9 × 10^{10}	1.8 × 10^{9} (440)
x = 3, 38	22.0	345	350	504	2.5 × 10^{10}	4.2 × 10^{9} (442)
x = 4, 39	*d*	350	*a*	*c*	*a*	
 x = 1, 40	17.0	370	400	555	2.5 × 10^{10}	1.9 × 10^{9} (502)
x = 2, 41	22.0	360	420	*c*	1.7 × 10^{10}	1.8 × 10^{9} (515)
 42	3.4	305	285	*e*	5.5 × 10^{10}	4.2 × 10^{8} (428)
 43	10.5	330	*a*	*e*	*a*	

[a] Suitable films could not be obtained. [b] T_g was not detectable by DSC. [c] No crystalline transition temperature was detected below T_d. [d] Insoluble in all solvents. [e] Amorphous.

In order to attain a high degree of orientation in solution (anisotropic), the following conditions must be met:[26,27] (1) The polymer must take on a rigid or extended-chain conformation in solution. (2) The polymer must exceed some minimum molecular weight. (3) The polymer must be sufficiently soluble to exceed a critical concentration, which is dependent on the axial ratio of the polymer.

Polymers **30** and **31** did not form anisotropic solutions, possibly because of the relatively low molecular weight. In addition, polyanthrazoline, **30**, cannot form an extended-chain conformation since each anthrazoline unit puts a 120° kink in the chain. Polyquinolines **34**, **35**, **36–38**, **40**, and **41** form anisotropic solutions in the polymerization dope (5:1 *m*-cresol–di-*m*-cresyl phosphate) at about 9 wt %. Even solutions of polymers at very low concentrations, ~1%, will give stable anisotropic solutions on shearing. These solutions become isotropic on heating but form anisotropic solutions again on shearing at ambient temperature.

Films of the rigid-rod polymers cast from 0.5–1.5 wt % solutions (isotropic) of the polymerization dope showed birefringence after evaporation of the *m*-cresol, extraction, and drying. The rigid-rod polyquinolines could be wet spun (8–18.5 wt % solids) from the *m*-cresol–di-*m*-cresyl phosphate solvent by using a 60–80-cm air gap and methanol as a nonsolvent. The resulting fibers possessed a high degree of crystallinity and an orientation of the rods along the direction of the fiber axis (Figure 4). Moderate tensile strengths and moduli could be obtained in these preliminary runs (Table VI); however, the ultimate mechanical properties of these fibers undoubtedly have not been achieved.

Cross-Linking Reactions of Polyquinolines

One approach to the problem of obtaining an easily processable polymer with a high use temperature is to cross-link the polymer after its fabrication. Unfortunately, because of the chemically inert structure and reduced chain mobility of polyaromatics, there are few good cross-linking reactions. Such a cross-linking reaction should take place without the evolution of volatiles to produce a thermally stable product through the generation of thermally stable links. The temperature of the cross-linking reaction should be above T_g but below the polymer decomposition tem-

Table VI
Mechanical Properties of Polyquinoline 37 Fiber

concn[a] of spin dope, wt %	heat treatment,[b] g/T, °C	denier, g	tenacity, g/denier	elongation to break, %	modulus, g/denier
9		350	3.8	12	98
	100/380	240	6.8	2.6	280
18.5		25			
	20/380	23	8.5	7.7	160
			9.0	2.5	340

[a] Mild drawing of the spun solution took place in the air gap prior to coagulation. [b] Heated for 1 h with the indicated stress.

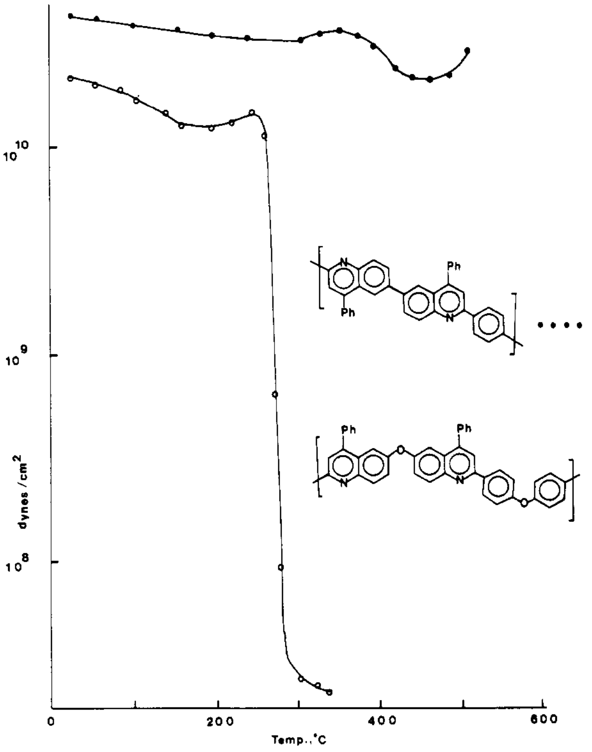


Figure 3. Thermomechanical properties of polyquinolines.

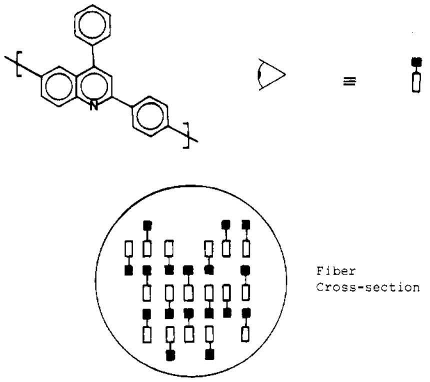
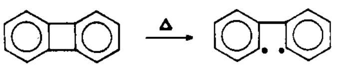


Figure 4. Orientation and packing of rigid-rod polyquinoline 35 in the fiber.

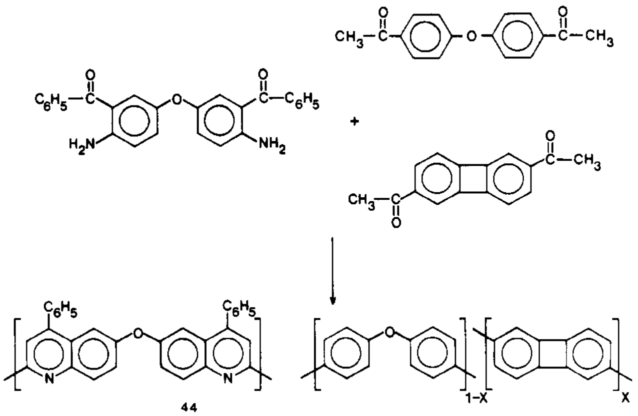
perature.

Such a reaction that is applicable to cross-linking polyquinolines is the ring-opening reaction of biphenylene.[22,28–30] The cross-linking presumably is accomplished by radical substitution and abstraction reactions that occur as the result of the generation of a diradical (thermal) and its reaction with any portion of an adjacent polymer chain. The cross-linking reaction also



can be catalyzed by group 8 transition metals, and the catalyzed reaction takes place more rapidly and at lower reaction temperatures.

A series of polyquinolines containing a range of biphenylene units in the polymer backbone has been prepared by balancing the appropriate amounts of 2,6-diacetylbiphenylene in place of 4,4′-diacetyldiphenyl ether under the standard polymerization conditions. A reaction exotherm signaling the cross-linking reaction takes place at about 300 °C but no cross-linking reaction takes place below T_g. This cross-linking reaction is catalyzed by rhodium and nickel, for example, and even though the catalyzed reaction occurs ~200 °C lower than the thermal reaction, a reaction temperature above T_g must be reached in order to effect cross-linking.

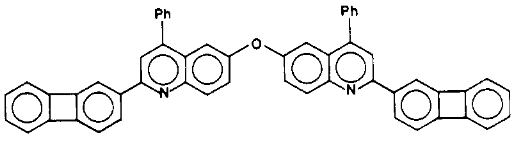


44

	T_g, °C
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

Cross-linking these polyquinolines has the effect of raising the glass transition temperature while decreasing the magnitude of the transition. The dynamic storage moduli of the cured polymers compared to uncured samples are higher up to the glass transition temperature. Above the glass transition temperature, the moduli of the cured polymers are much higher and are a function of the percent biphenylene in the copolymer. Even a low biphenylene incorporation (2.5%) is sufficient to raise the value from 2.4 × 10^7 (uncured) to 3.8 × 10^8 dyn/cm^2 at 400 °C.

This cross-linking reaction also has been applied to the reaction of polyquinolines with an added bisbiphenylene cross-linking agent.[30]



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Notes

Elastic Properties of a Polymer Chain with Excluded Volume: A Renormalization Group Theory

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The elastic behavior of a single polymer chain in a good solvent is related to a number of important problems, including the general problem of rubber elasticity of swollen networks. This behavior has been studied recently by using scaling arguments[2] and by Monte Carlo methods.[3] The scaling arguments can describe the elastic behavior only in the weak and strong stretching regimes; they cannot give information about the intermediate stretching regime, the crossover behavior. The intuitively appealing blob arguments do not work in this interesting crossover regime. The Monte Carlo calculations of Webman et al.[3] describe the response of a single chain to the whole range of the strength of stretching forces. The results of Webman et al. are in conformity with the general scaling arguments in limiting cases, and they suggest that the crossover behavior is fairly abrupt (see Figure 2 of ref 3).

This note provides for the first time the renormalization group calculation of the full range of elastic behavior, including crossover, for a polymer of fixed degree of polymerization with well-developed excluded volume.

In the presence of a stretching force **F**, the end-to-end vector **R** distribution function $f_{\mathbf{F}}(\mathbf{R})$ is proportional to $f(\mathbf{r}) \times \exp(\beta \mathbf{F} \cdot \mathbf{R})$, where $\mathbf{r} = \mathbf{R}/R_0$, $R_0 = \langle R^2 \rangle^{1/2}$ is the root-mean-square end-to-end distance without external forces, $f(\mathbf{r})$ is the end-to-end vector distribution for $\mathbf{F} = 0$, and $\beta = 1/kT$. We have calculated $f(\mathbf{r})$ to order $\epsilon = 4 - d$, d being the spatial dimension, in a preceding paper,[4] using a renormalization group approach with dimensional regularization which is formulated in chain configuration space in terms of full chain distribution functions. These calculations yield[4]

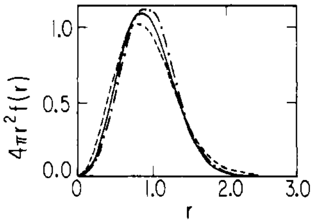

Figure 1. Distribution function for the magnitude of the end-to-end vector |**r**| in 3-space: (- - -) denotes the Gaussian distribution function, i.e., the distribution function for a simple random walk; (-·-) estimate of the distribution function for a self-avoiding walk on the simple cubic lattice;[5] (—) distribution function for a self-avoiding random walk from eq 2.

$$f(\mathbf{r}) = \left(\frac{2}{\pi}\right)^{2-\epsilon/2} 2^{\epsilon/8} \exp\left(\frac{1}{8}\epsilon\hat{\gamma} - \frac{3}{4}\epsilon\right) \times |\mathbf{r}|^{\epsilon/4} \exp\left[-(2\mathbf{r}^2)^{1+\epsilon/8}\left(1 - \frac{3}{8}\epsilon\right) + \frac{\epsilon}{4}(1 - \hat{\gamma})\mathbf{r}^2\right] \quad (1)$$

where $\hat{\gamma} \simeq 0.577...$ is Euler's constant. In 3-space the correctly normalized $f(r)$ is given by

$$f(r) = 0.33|\mathbf{r}|^{0.25} \exp(-1.5|\mathbf{r}|^{2.25} + 0.1|\mathbf{r}|^2) \quad (2)$$

The function $4\pi r^2 f(r)$ is compared in Figure 1 to the estimation obtained by Domb et al.[5] The agreement is good