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Synthesis and Physical Properties of Amorphous Poly(aryl ether isoquinoline)s

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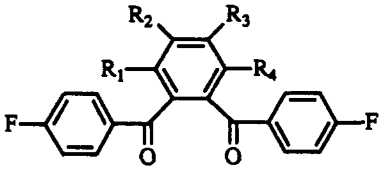
ABSTRACT: The synthesis of a new class of N-heterocyclic polymers, the poly(aryl ether isoquinoline)s, is described via an intramolecular ring-closure reaction of poly(aryl ether ketone)s containing the *o*-dibenzoylbenzene moiety with benzylamine in the presence of 1,8-diazabicyclo[5.4.0]undecene (DBU) in refluxing chlorobenzene. The synthesis of copolymers of poly(aryl ether ketone)s and poly(aryl ether isoquinoline)s is demonstrated, and the copolymer contents were determined by ^{1}H NMR studies. Ring-closure reactions of previously prepared end-capped poly(aryl ether ketone)s to poly(aryl ether isoquinoline)s were done to determine exact molecular weights of the resulting polymers. Various fluoro-substituted isoquinoline monomers were prepared and polymerized with bisphenols in *N*-methylcaprolactam (NMC) in the presence of excess base (K_2CO_3). The high molecular weight polymers showed T_g's ranging from 225 to 320 °C. Studies by TGA showed polymer 5% weight losses in air and nitrogen above 500 °C.

Introduction

Polyquinolines have been extensively studied by Stille et al.[1] These materials are thermally stable with high glass transition temperatures. Polyquinolines are synthesized by the polycondensation of bis(ketomethylene) compounds with a bis(*o*-benzoyl aromatic amine) compound using the Friedlander synthesis.[2] The polymerization reactions are conducted either in *m*-cresol or poly(phosphoric acid) at elevated temperatures to give high molecular weight materials. One of the approaches used to improve the solubility of the polyquinolines without a significant loss in thermal stability is the introduction of flexible groups into the polymer backbone.[4] High molecular weight polyquinolines have been synthesized with T_g's ranging from 250 to 400 °C[3] and with T_m's from 448 to 500 °C. The introduction of extra phenyl substituents in the polyquinoline backbone raises the T_g by 40–45 °C due to increased hindrance to rotation. Polyquinolines that have been prepared to date either are soluble in common organic solvents and have relatively low glass transition temperatures[4] (<250 °C) or are highly crystalline materials[5] that are insoluble in the common organic solvents and soluble only in acidic solvents. Due to the complexity of the synthesis and the cost of the starting materials, these materials have not been extensively exploited.

We would expect that polyisoquinolines would be similar in chemical and physical properties to polyquinolines. The introduction of isoquinoline moieties into polymers has recently been accomplished by Gibson,[6] who has synthesized bis(isoquinoline) polyesters exhibiting low glass transition temperatures (79–93 °C). We recently reported[7] the synthesis of 1,2-bis(4-fluorobenzoyl)benzenes **1–3** (Chart I), which upon reaction with bisphenates gave high molecular weight amorphous poly(aryl ether ketone)s. We demonstrated[8] that the 1,2-dibenzoylbenzene moiety in the polyketone polymer chain undergoes an intramolecular ring-closure reaction with hydrazine monohydrate in the presence of a mild acid in chlorobenzene to give poly(aryl ether phthalazine)s. Moreover, we described[9] another intramolecular ring-closure reaction of the 1,2-dibenzoylbenzene moiety in the polyketone polymer chain with benzylamine in a basic medium which led to a new class of amorphous, thermally stable polymers, the poly(aryl ether isoquinoline)s. In this paper we report our continued investigation of poly(aryl ether isoquinoline)s, their thermal and mechanical properties, and the synthesis of the polyisoquinolines via a halo displacement polymerization, where the fused pyridine ring is the activating group.

Chart I



1 $R_1 = R_2 = R_3 = R_4 = H$

2 $R_2 = R_3 = H, R_1 = R_4 = C_6H_5$

3 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

Results and Discussion

Treatment of the colorless poly(aryl ether ketone)s **4a–c**, **5a–c**, and **6a–e** (Scheme I) with benzylamine in the presence of 1,8-diazabicyclo[5.4.0]undecene (DBU) in refluxing chlorobenzene[10,11] gave poly(aryl ether isoquinoline)s **7a–c**, **8a–c**, and **9a–e**, respectively, as pale yellow polymers. The dramatic changes in physical and chemical properties that occurred upon ring closure of the polyketones to polyphthalazines[8] were also observed in the transformation of the polyketones to polyisoquinolines. Structurally this results in a significant straightening of the chain, which manifests itself in an increase in the glass transition temperature, a large increase in the solution viscosity (Table I), and a large increase in the apparent molecular weight as measured by gel permeation chromatography based on polystyrene standards.[9] The increase in molecular weight determined by GPC and the increase in inherent viscosity upon ring closure are indicative of structural changes arising from the conversion of a flexible molecule to a more rigid molecule that would have a greater hydrodynamic volume. Increases in the glass transition temperature from 15 to 45 °C occur when the polyketones are converted to the polyisoquinolines. Generally, all the poly(aryl ether isoquinoline)s synthesized were very soluble in chloroform at room temperature and the polymers (Table I) formed tough and flexible yellow films upon solution casting from chloroform. The unsubstituted poly(aryl ether isoquinoline)s **7b** and **7c** with

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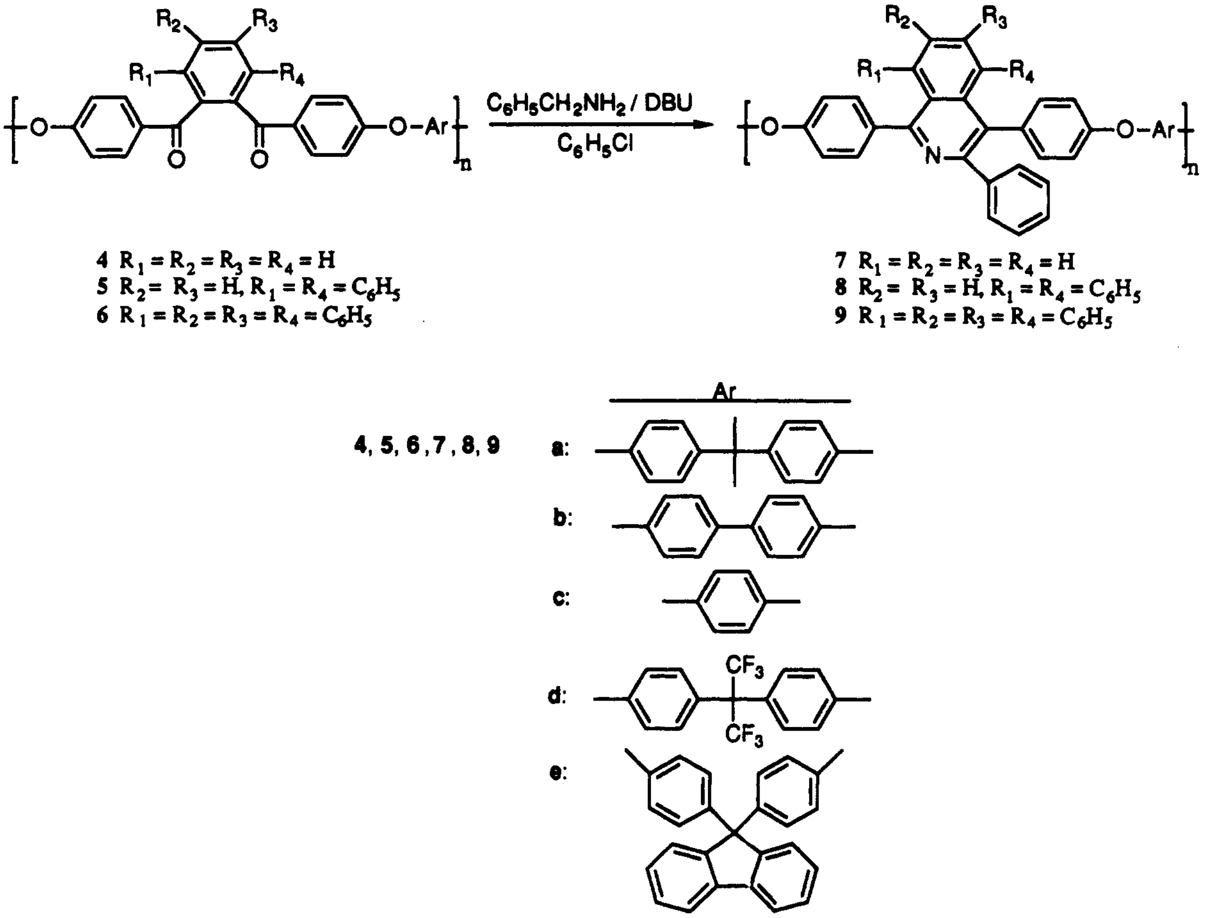
Scheme I



4 $R_1 = R_2 = R_3 = R_4 = H$
5 $R_2 = R_3 = H, R_1 = R_4 = C_6H_5$
6 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

7 $R_1 = R_2 = R_3 = R_4 = H$
8 $R_2 = R_3 = H, R_1 = R_4 = C_6H_5$
9 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

Table I
Physical Properties of Poly(aryl ether isoquinoline)s Compared to Poly(aryl ether ketone)s

polymer	η_{inh},[a] dL/g	T_g, °C	polymer	η_{inh},[a] dL/g	T_g, °C
4a	0.48	182	**7a**	0.59	226
4b	0.42	190	**7b**	0.54[b]	230
4c	0.43	185	**7c**	0.53[b]	220
5a	0.65	221	**8a**	0.68	234
5b	0.56	240	**8b**	0.88	275
5c	0.35	240	**8c**	0.51	260
6a	0.47	265	**9a**	0.65	280
6b	0.73	292	**9b**	0.98	320
6c	0.49	273	**9c**	0.58	297

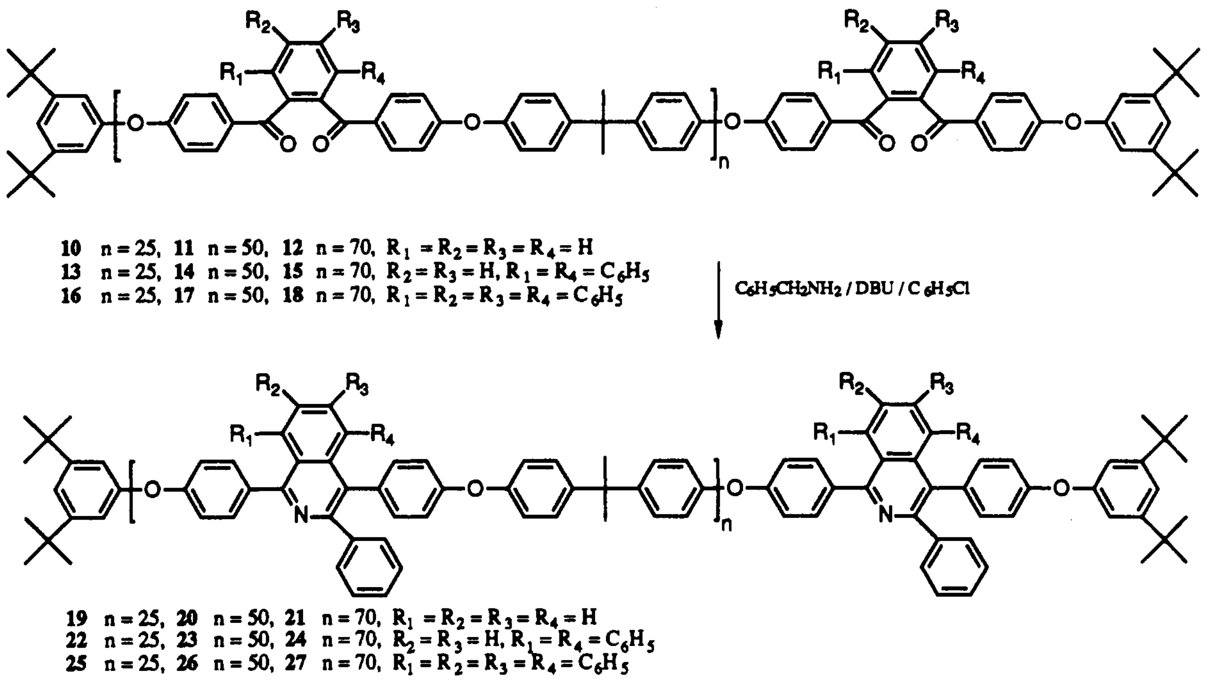
[a] Inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C. [b] Inherent viscosity measured at 25 °C in $CF_3COOH/CHCl_3$ (1/4, v/v).

either a hydroquinone or *p,p′*-biphenol moiety in the polyisoquinoline backbone are exceptions as they precipitate out of refluxing chlorobenzene during the ring-closure reaction and are not soluble in any of the chlorinated solvents at room temperature or at elevated temperatures in conventional solvents. A similar behavior was observed with the unsubstituted polyphthalazines with either a hydroquinone or *p,p′*-biphenol as the flexible linkage in the polymers.[12] From ^1H NMR studies these polymers (**7b** and **7c**) are copolymers resulting from partial ring closure to the polyisoquinolines. Inherent viscosities of the partially ring-closed polymers were determined at room temperature in a solvent mixture of chloroform and trifluoroacetic acid (4/1, v/v). Differences in reactivity were noted in the ring-closure reactions of the polyketones to the polyisoquinolines. The unsubstituted polyketones (**4a–c**) underwent intramolecular ring-closure reactions considerably faster (6–7 h) than the substituted polyketones (**5a–c** and **6a–e**) (~36 h). The differences in the rates of reactivity could be a result of the steric hindrance imposed on the central ring by the pendant phenyls in the substituted polyketones which could therefore retard the ring-closure reactions. However, in all cases completion of the reaction was indicated by ^1H NMR studies. The various flexible linkages in the polyisoquinolines had no effect on the rates of the intramolecular ring closure.

It is conceivable that, during the intramolecular ring-closure reactions in the polymer chains, one or more isomer(s) can be generated in the polymer backbone due to the nonselectivity of the isoquinoline ring formation. Attempts to determine the isomeric selectivity by 2D ^1H NMR studies (NOE experiments) were unsuccessful. If a random formation of the isoquinoline ring occurs in the polymer chain, then this would give rise to a more disordered chain packing which would greatly influence the solubility property of the resulting polymer.

The glass transition temperatures (T_g's) for the poly(aryl ether isoquinoline)s synthesized (Scheme I) were determined by differential scanning calorimetry (DSC) at a heating rate of 20 °C/min under an atmosphere of nitrogen and are tabulated in Table I. In all cases, the midpoint of the change in the slope of the base line was taken as the T_g. Polyisoquinoline series **9** containing four phenyl substituents on the central ring showed the highest T_g's (220–323 °C). As was expected, the polyisoquinolines (**7a–c**) without any phenyl substituents around the central aromatic ring displayed the lowest T_g's with the various flexible linkages and the glass transition temperatures of the polyisoquinolines increase with two pendant phenyls on the central benzene ring, intermediate between the unsubstituted and fully substituted polymers. A similar pattern was observed in the poly(aryl ether ketone)s[7] and the poly(aryl ether phthalazine)s.[8]

Scheme II



10 n = 25, **11** n = 50, **12** n = 70, $R_1 = R_2 = R_3 = R_4 = H$
13 n = 25, **14** n = 50, **15** n = 70, $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
16 n = 25, **17** n = 50, **18** n = 70, $R_1 = R_2 = R_3 = R_4 = C_6H_5$

19 n = 25, **20** n = 50, **21** n = 70, $R_1 = R_2 = R_3 = R_4 = H$
22 n = 25, **23** n = 50, **24** n = 70, $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
25 n = 25, **26** n = 50, **27** n = 70, $R_1 = R_2 = R_3 = R_4 = C_6H_5$

Table II
3,5-Di-*tert*-butyl-Terminated Poly(aryl ether ketone)s and Poly(aryl ether isoquinoline)s

poly(aryl ether ketone)			poly(aryl ether isoquinoline)					
polymer	$n^{a,b}$	η_{inh},[c] dL/g	polymer	n^b	$\bar{M}_n$, × 10^4	$\bar{M}_w$,[d] × 10^4	$\bar{M}_n$,[d] × 10^4	η_{inh},[c] dL/g
10	36	0.19	19	38	2.29	5.03	2.09	0.23
11	64	0.21	20	65	3.85	5.32	2.13	0.41
12	79	0.44	21	78	4.61	5.91	2.11	0.65
13	36	0.30	22	38	2.88	5.33	1.40	0.45
14	48	0.38	23	51	3.61	13.94	3.30	0.51
15	69	0.49	24	69	5.15	18.69	5.19	0.86
16	36	0.25	25	38	3.47	9.82	4.46	0.37
17	55	0.30	26	53	5.15	16.9	7.34	0.48
18	81	0.49	27	81	7.28	43.2	13.9	0.61

[a] The number of monomer units (n) was experimentally designed for 25 units for polymers 10, 13, and 16, 50 units for polymers 11, 14, and 17, and 70 units for polymers 12, 15, and 18. [b] The exact number of monomer units (n) was determined by ^1H NMR measurements. [c] Inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C. [d] Determined by GPC measurements using polystyrenes as standards.

End-capped poly(aryl ether ketone)s 10–18 (Scheme II) with 3,5-di-*tert*-butylphenyl terminal groups that were prepared previously[12] with a degree of polymerization of $n \sim 25$, 50, and 70 monomer units/chain were converted to poly(aryl ether isoquinoline)s 19–27 having di-*tert*-butylphenyl as terminal groups. The inherent viscosities, apparent molecular weights determined by gel permeation chromatography using polystyrenes as standards, and the exact number-average molecular weights determined by ^1H NMR for the capped polyisoquinolines are presented in Table II. A large increase in the inherent viscosity and molecular weight (by GPC) is observed for the conversion of the capped polyketones to polyisoquinolines, as was determined for the uncapped materials. From ^1H NMR studies,[13] the number of monomer units (n) in the polyisoquinoline chain was determined, and the exact molecular weight was calculated (Table II). The degrees of polymerization of the polymers, e.g., poly(aryl ether ketone) 11 ($n = 64$) upon ring closure to the polyisoquinoline **20** ($n = 65$), remain constant, indicating no side reactions such as chain scission or branching had occurred during the synthesis of the polyisoquinolines. Attempts to correlate the apparent molecular weights determined by GPC with the exact molecular weights determined by ^1H NMR failed. Solution casting polyisoquinoline 19 with a degree of polymerization of $n = 38$ from chloroform gave a brittle film, as did its precursor polyketone 10, whereas all other higher molecular weight polyisoquinolines (20–27) formed flexible films. The increases in the chain length with increases in the degree of polymerization (n) of the capped polyisoquinooines (19–21, 22–24, and 25–27) are reflected in the increases in inherent viscosities. The capped polyisoquinolines (Table II) and the uncapped ones (Table I) having similar inherent viscosities had identical glass transition temperatures. The spectra of the capped polyketones show chemical shifts for the di-*tert*-butyl group at δ 1.29 and the isopropylidene moiety at δ 1.68. A downfield shift of the protons in the di-*tert*-butyl group (δ 1.32) and the resonance due to the protons in the isopropylidene moiety (δ 1.72) occur in all of the ^1H NMR spectra of the poly(aryl ether isoquinoline)s. The exact number-average molecular weights for the polyketones and the polyphthalazines were also determined from the ratios of the peak areas of the di-*tert*-butyl group and the isopropylidene moiety. From ^1H NMR studies, the results confirmed that the overall ring-closure reactions were complete and the pyridine ring in the polyisoquinolines exerts a deshielding effect in the ^1H NMR spectra.

By controlling the amounts of reagents used in the conversion reaction or the reaction time and temperature, copolymers of poly(aryl ether ketone)s and poly(aryl ether isoquinoline)s could readily be synthesized. The fully

Table III
Copolymers of Polyketones and Polyisoquinolines

copolymer	percent compsn[a] for polyketone/polyisoquinoline, %	T_g,[b] °C
28	25/75	213
29	88/12	222
30	68/32	270

[a] Determined by ^{1}H NMR studies. [b] DSC measurements.

characterized ^{1}H NMR spectra of the poly(aryl ether ketone) 11, the copolymer **28** (made by partial ring-closure reaction of poly(aryl ether ketone) 11), and the poly(aryl ether isoquinoline) **20** were described previously.[9] From the ^{1}H NMR spectrum of copolymer **28**, the compositions of polyketone 11 (25%) and polyisoquinoline **20** (75%) were determined. The glass transition temperature of the copolymer **28** was observed at 213 °C, which corresponds to the calculated value. Copolymers **29** and **30** consisting of polymers **14** and **23**, **17** and **26**, respectively, were prepared, and the resulting compositions were determined from ^{1}H NMR studies (Table III). The glass transition temperatures for the copolymers **29** and **30** were found to be 222 and 270 °C, respectively, which correspond to the calculated figures.

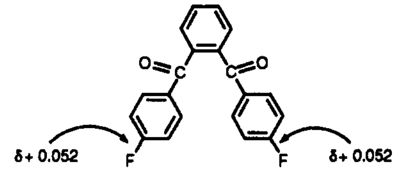
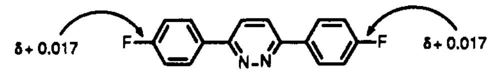
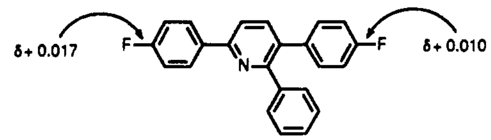
Heterocyclic ring systems, such as pyridazines,[8,12] benzoxazoles,[14] and quinoxalines,[15] activate haloaromatic rings toward nucleophilic substitution. The 1,2-bis(4-fluorobenzoyl)benzene monomer **1**, however, is much more reactive than these heterocyclic monomers in the polymerization reactions with bisphenates. In Table IV we have shown the calculated net charge density for **1** at the carbon atoms adjacent to the fluorine substituent.[16] The corresponding pyridazine monomer has a considerably lower net charge density at the CF carbon and the polymerization is also considerably slower. It has been previously demonstrated[9] that the polyisoquinoline ring also exerts a deshielding effect, which was illustrated in the ^{1}H NMR spectra of the copolymer **28** and the homopolymer polyisoquinoline **20**. The electron-deficient pyridine ring would be expected to activate halo groups toward nucleophilic substitution reactions.[17,18] From Table IV we see that the calculated charge density at the C–F bond para to the C=N moiety in the isoquinoline structure is the same as that for the pyridazine monomer; however, the net charge density at the other CF carbon is much lower, although still positive, and we therefore would predict that the polymerization of the isoquinoline monomers would be slower than the pyridazine monomers. This is borne out by experiment, since the reaction requires the use of *N*-methylcaprolactam as solvent in order to provide a higher reaction temperature to complete the reaction in a reasonable length of time. These activating groups can accept a negative charge, lowering the activation energy of the displacement reaction. During the displacement reaction, the negative charge on the expected Meisenheimer type transition state is well delocalized by resonance effects (Scheme III). Fluoro-substituted isoquinoline monomers, 1,4-bis(4-fluorophenyl)-3-phenylisoquinoline (**31**), 1,4-bis(4-fluorophenyl)-3,5,8-triphenylisoquinoline (**32**), and 1,4-bis(4-fluorophenyl)-3,5,6,7,8-pentaphenylisoquinoline (**33**), were prepared (Scheme IV) by treating the 1,2-bis(4-fluorobenzoyl)benzene monomers **1**–**3** (Chart I) with benzylamine and DBU in refluxing chlorobenzene. Isoquinoline monomer **31** was isolated in 93% yield, and the other two monomers **32** and **33** were isolated in considerably lower yields, 46% and 41%, respectively, and took longer times for the reactions to reach completion. The low yields of the monomers **32** and **33** could be due to steric hindrance caused by the presence of pendant phenyls on the central ring, which would retard the intramolecular reaction and simultaneously a gradual cleavage of the fluorines on the monomers by the base could be occurring.

Isoquinoline monomer **31** was subjected to polymerization reactions with bisphenols **34a**–**c** in an *N*-methylcaprolactam (NMC)/toluene (2/1) solvent mixture (Scheme V). The solid composition was maintained at 25 wt %, and any water present or generated during the bisphenoxide formation was removed as an azeotrope with toluene. The reactions were maintained at the reflux temperature of 140 °C for 30 min, and upon completion of bisphenoxide formation and dehydration, the polymerization reactions were heated to 230 °C to effect the displacement reaction. After a period of 24 h, high molecular weight poly(aryl ether isoquinoline) **7a** was achieved from monomer **31**. The dramatic increase in viscosity indicated the formation of high molecular weight material. Polyisoquinoline **7a** (η_{inh} = 0.43 dL/g) synthesized from monomer **31** has a ^{1}H NMR spectrum and glass transition temperature (226 °C) identical with those of polyisoquinoline **7a** (η_{inh} = 0.59 dL/g) synthesized from the intramolecular ring-closure reaction of polyketone **4a** (η_{inh} = 0.48 dL/g). The polyisoquinolines **7b** (η_{inh} = 0.46 dL/g, T_g = 234 °C) and **7c** (η_{inh} = 0.43 dL/g, T_g = 228 °C) containing the *p,p'*-biphenol and hydroquinone moieties synthesized from isoquinoline monomer **31** (Scheme V) demonstrated somewhat higher glass transition temperatures than polyisoquinolines **7b** (η_{inh} = 0.54 dL/g, T_g = 230 °C) and **7c** (η_{inh} = 0.53 cL/g, T_g = 220 °C) (Scheme I) obtained from the intramolecular ring-closure reactions. Presumably, the partial conversion of the polyketones **4b** and **4c** to polyisoquinolines **7b** and **7c** has the effect of giving materials with lower glass transition temperatures. Both methods gave polyisoquinolines (**7b** and **7c**) that were insoluble in chloroform but were found to be very soluble in a solvent mixture of chloroform and trifluoroacetic acid (4/1, v/v).

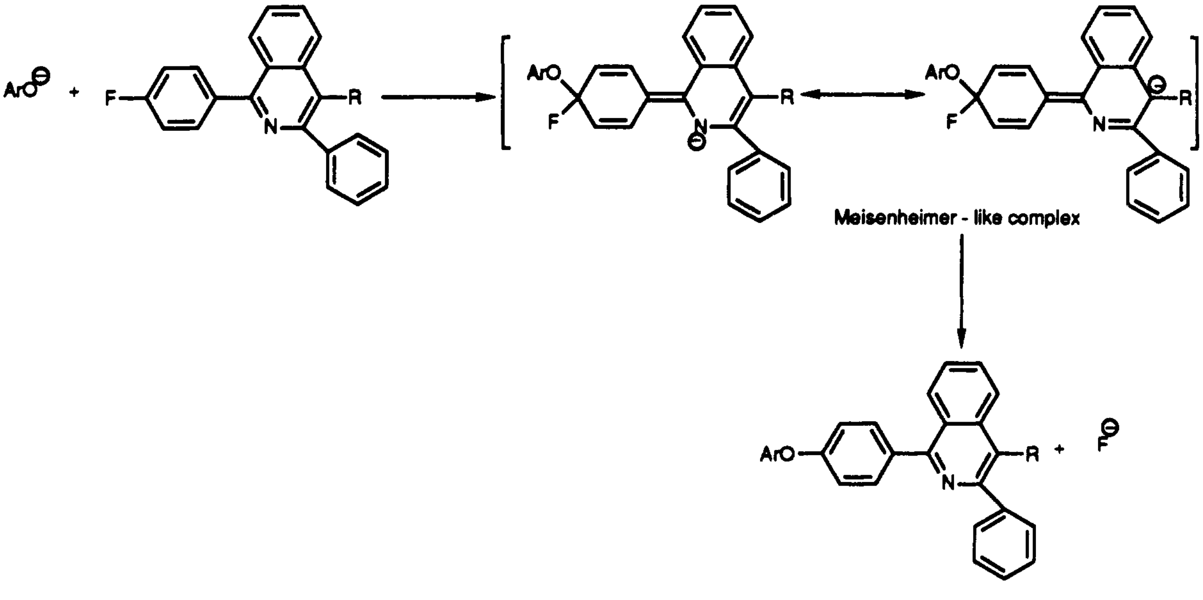
Poly(aryl ether isoquinoline)s **8a** and **9a** synthesized from isoquinoline monomers **32** and **33** with 4,4'-(1-methylethylidene)bisphenol (BPA), respectively, have glass transition temperatures (Table V) and ^{1}H NMR spectra identical with those of the polyisoquinolines **8a** and **9a** synthesized from intramolecular ring-closure reactions of polyketones **5a** and **6a**. Both methods afforded high molecular weight materials. All three isoquinoline monomers were subjected to polymerization reactions in NMC at 230 °C with the bisphenoxides shown in Scheme V. Isoquinoline **31** reacted with bisphenols **34a**–**c** to give polymers **7a**–**c**, and isoquinoline **32** and **33** reacted with bisphenol (BPA) **34a** to give polymers **8a** and **9a**, respectively. Since the polymers synthesized by direct nucleophilic displacement of the isoquinoline monomers with bisphenoxides have equivalent physical properties to those synthesized from intramolecular ring-closure reactions of the poly(aryl ether ketone)s, this further confirms that the reactions are complete and that no side reactions or branching occurs during the transformation.

Except for the pendant phenyl groups in the polyisoquinolines, structurally these materials are very similar to the polyphthalazines synthesized previously.[12] Earlier, it was demonstrated[12] that the unsubstituted polyphthalazines analogous to polyisoquinolines **7b** and **7c** synthesized by direct nucleophilic displacement polymerization in NMP at 180 °C with biphenol or hydroquinone as flexible linkages were of low molecular weight because they separated from solution during the reaction. On the other hand, the unsubstituted polyphthalazine containing the

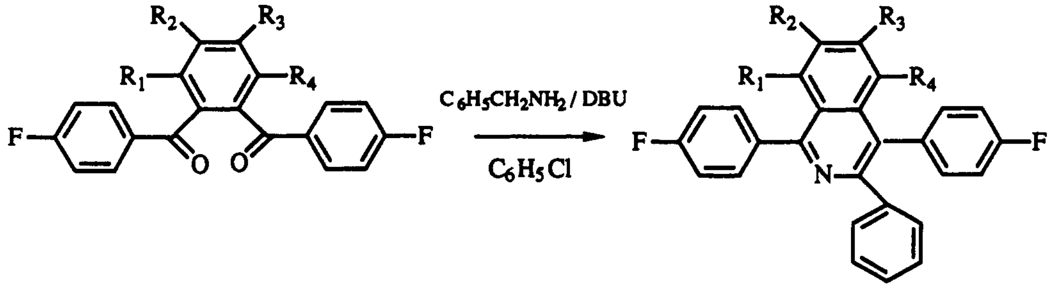
Table IV
Polymerization Time vs Net Charge Density at the C–F Bond

	solvent	temp, °C	time, h
	NMP	165	1
	NMP	180	18
	NMC	230	24

Scheme III



Scheme IV



1 $R_1 = R_2 = R_3 = R_4 = H$
2 $R_2 = R_3 = H, R_1 = R_4 = C_6H_5$
3 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

31 $R_1 = R_2 = R_3 = R_4 = H$
32 $R_2 = R_3 = H, R_1 = R_4 = C_6H_5$
33 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

flexible BPA moiety, having a structure similar to polyisoquinoline **7a** synthesized in NMP, was of high molecular weight. Interestingly, the polyisoquinolines **7a–c** synthesized in NMC at 230 °C were all of high molecular weight. As noted elsewhere,[19] polyisoquinolines containing a carbon–carbon linkage which were prepared by nickel-catalyzed coupling of the corresponding chloro-substituted monomers are also considerably more soluble than their phthalazine analogues.

The poly(aryl ether isoquinoline)s (**7a–9e**) have excellent dimensional stability over a wide temperature range observed. For example, the dynamic mechanical analysis of polyisoquinoline **9a** is shown in Figure 1. The glass transition temperatures for the polyisoquinolines determined by dynamic mechanical analysis were in agreement with those determined by DSC (Table I). None of the poly(aryl ether isoquinoline)s synthesized show any crystalline behavior even after extensive annealing above the T_g. The modulus data for the films from poly(aryl ether isoquinoline)s synthesized by intramolecular ring-closure reactions of the polyketones and direct displacement reactions of the bisphenoxides with the difluoride iso-

Scheme V

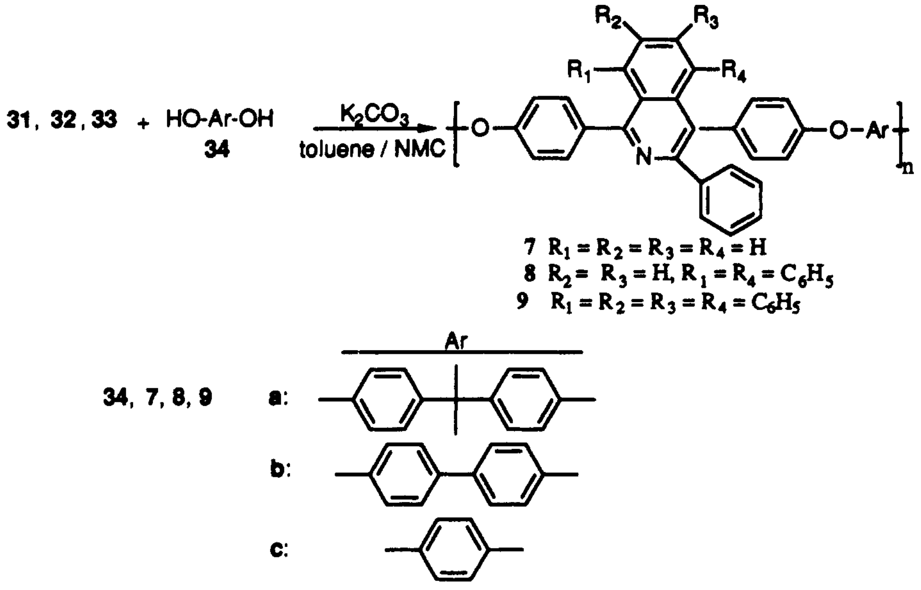


Table V
Properties of Poly(aryl ether isoquinoline)s Synthesized from Isoquinoline Monomers

poly(aryl ether isoquinoline)	η_{inh},[a] dL/g	T_g, °C
7a	0.43	226
7b	0.46[b]	234
7c	0.43[b]	228
8a	0.50	234
9a	0.43	275

[a] Inherent viscosities were measured at a concentration of 0.5 g/dL in $CHCl_3$ at 25 °C. [b] Inherent viscosities were measured in $CF_3COOH/CHCl_3$ (1/4, v/v).

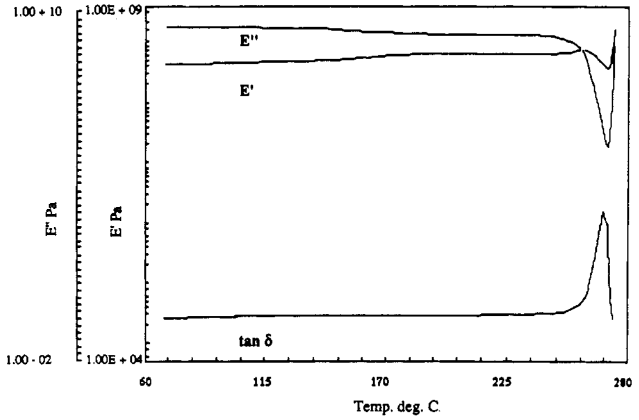


Figure 1. Thermomechanical analysis for poly(aryl ether isoquinoline) **9a**: (a) modulus (E') vs temperature; (b) storage modulus (E'') vs temperature; (c) tan δ vs temperature.

quinoline monomers are presented in Table VI. The moduli of the materials range from 2.29 to 3.98 GPa at 25 °C and 1.42 to 2.32 GPa at 200 °C. Films prepared from the poly(aryl ether isoquinoline)s are all tough and show ductile mechanical behavior with no failure at 40% elongation. The moduli of the polyisoquinolines are comparable to other engineering thermoplastics such as poly(aryl ether phthalazine)s,[12] poly(aryl ether benzoxazole)s,[14] and poly(aryl ether phenylquinoxaline)s[15] (~2.5 GPa). The moduli of the poly(aryl ether isoquinoline)s are all a little higher than their precursors, the poly(aryl ether ketone)s,[12] which is indicative of the chain straightening that results upon ring closure of the polyketones which results in a more rigid and a stiffer backbone.

Table VI
Moduli of Poly(aryl ether isoquinoline)s at 25 and 200 °C

polymer	modulus for temp 25 °C/200 °C, GPa	polymer	modulus for temp 25 °C/200 °C, GPa
7a	2.54/1.49	9a	2.31/1.72
7b	2.72/1.42	9b	2.62/1.99
7c	2.62/1.52	9c	2.65/1.62
8a	3.98/2.12	9d	2.51/2.01
8b	3.35/2.32	9e	2.29/1.87
8c	3.38/2.21		

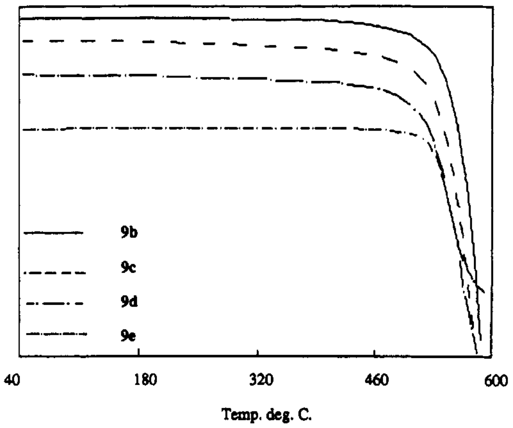


Figure 2. TGA thermograms (weight loss versus temperature) for poly(aryl ether isoquinoline)s **9b–e** under an atmosphere of N_2.

The poly(aryl ether isoquinoline)s showed excellent thermooxidative stability by thermogravimetric analysis, with 5% weight losses above 500 °C under atmospheres of air and nitrogen[9] as shown in Figure 2. Since the poly(aryl ether isoquinoline)s **9b–e** synthesized from poly(aryl ether ketone)s **6b–e** (Scheme I) are the most thermally stable by TGA studies, isothermal aging (TGA) was done at 400 °C under an atmosphere of nitrogen over an 8-h period to assess the thermal stability of the polymers (Table VII). From the aging experiments, the uncapped materials show weight losses ranging from 0.63 to 1.21%/h under nitrogen. Polyisoquinolines **9b** and **9c** are the most thermally stable by isothermal aging experiments, and these results are in agreement with the variable-temperature TGA results.

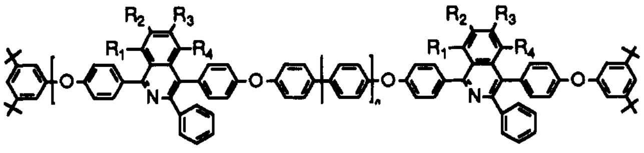
Like the poly(aryl ether ketone)s and poly(aryl ether phthalazine)s, the poly(aryl ether isoquinoline)s are all amorphous and the glass transition temperatures increase

Table VII
Thermal Properties of Poly(aryl ether isoquinoline)s 9b–e under an Atmosphere of N_2

poly(aryl ether isoquinoline)	isothermal aging at 400 °C,[a] wt loss %/h	TGA for N_2,[b] °C
9b	0.80	548
9c	0.63	559
9d	1.12	520
9e	1.21	513

[a] Isothermal aging experiments were performed on materials that were not end-capped. [b] Reported for 5% weight loss.

Table VIII
Oxygen Permeation at 20 °C of Poly(aryl ether isoquinoline)s



poly(aryl ether isoquinoline)	$P^a \times 10^{13}$
21 ($R_1 = R_2 = R_3 = R_4 = H$)	0.33
24 ($R_2 = R_3 = H$; $R_1 = R_4 = C_6H_5$)	1.15
27 ($R_1 = R_2 = R_3 = R_4 = C_6H_5$)	3.04

[a] P in cm³·cm/cm²·s·Pa.

with increasing numbers of pendant phenyl groups. Since the free volume in the polyketones and polyphthalazines was found to increase[12] as the bulky phenyl groups are added, it was of interest to determine if a similar behavior would occur in the polyisoquinolines. This was done by determining the oxygen permeation in films of the poly(aryl ether isoquinoline)s **21**, **24**, and **27**. Oxygen permeation (Table VIII) at 20 °C increases with increasing phenyls in the polymer chain which is indicative of the larger free volume associated with poly(aryl ether isoquinoline) **27** containing four phenyls, which has an O_2 permeation value of 3.04. Polyisoquinoline **24** which has two pendant phenyls has an O_2 permeation of 1.15, and polymer **21** having no pendant phenyl groups has an even lower O_2 permeation, 0.33. From these O_2 permeation results it can be concluded that polyisoquinoline **21**, having no pendant phenyls, has the smallest free volume, which probably results from closer interchain packing. As was observed in the polyphthalazine series, polyisoquinoline **21** has approximately half the O_2 permeation of its precursor, poly(aryl ether ketone) **12** (1.03),[12] which again is indicative of the resulting chain straightening that occurs in the polyisoquinolines and polyphthalazines. Polyisoquinoline **27** (four pendant phenyls) unlike polyisoquinoline **24** (two pendant phenyls)[20] has a slightly higher penetrant diffusion rate than its precursor polyketone **18** (four pendant phenyl; 2.82). This could be a result of the extra pendant phenyl in the polyisoquinoline **27** polymer backbone, which has the net effect of increasing the free volume.

Conclusion

In this study, a new class of high-temperature, high-T_g, amorphous polymers, the poly(aryl ether isoquinoline)s, have been synthesized by the intramolecular ring closure of poly(aryl ether ketone)s containing the 1,2-dibenzoylbenzene moiety with benzylamine in a basic medium or via a nucleophilic aromatic substitution reaction of fluoro-substituted isoquinoline monomers with bisphenates. In the direct displacement polymerization reactions, the electron-deficient pyridine component of the isoquinoline ring activates the aryl fluoride substituents toward a nucleophilic displacement polymerization reaction. The nucleophilic displacement polymerization reactions were conducted in NMC in the presence of excess K_2CO_3 to afford high molecular weight polymers. Increases in glass transition temperatures occurred in the polyisoquinolines with an increasing number of pendant phenyls in the 1,4-bis(4-fluorophenyl)isoquinoline monomers. The materials had 5% weight losses above 500 °C by thermogravimetric analysis, indicative of high thermal stability. The moduli of the polyisoquinolines are comparable to other engineering thermoplastics such as poly(aryl ether phthalazine)s, poly(aryl ether benzoxazole)s, and poly(aryl ether phenylquinoxaline)s. All of the polymers could be readily processed from solution to give tough, flexible, yellow and transparent films.

Experimental Section

General Methods. The ^1H NMR 1D spectra (200 MHz) were recorded on a Varian XL-200 instrument using tetramethylsilane as the internal standard, in deuteriochloroform as the solvent. The chemical shift (δ) and coupling constant (J) data are quoted in ppm and hertz, respectively. The 2D experiments (COSY and COLOC) were done on a Varian XL-200 or XL-300 instrument. Mass spectra were recorded on a ZAB 2F HS spectrometer, ion source 240 °C and 70-eV electron impact, direct inlet: m/e (assignment). LRMS with specific ion monitoring to ascertain purity was performed. Thin-layer chromatography was performed on silica gel (Kieselgel 60F 254) aluminum-backed plates. Generally, all compounds isolated were solids. All solvents were reagent grade unless otherwise stated. *N*-Methylcaprolactam (NMC) was refluxed and distilled over barium oxide. Chlorobenzene, benzylamine, 1,8-diazabicyclo[5.4.0]undecene (DBU), and ethylbenzene were purchased from Aldrich and used without further purification. Bisphenols 4,4′-(1-methylethylidene)bisphenol (BPA) and 4,4′-dihydroxybiphenyl were kindly supplied by General Electric Co. and hydroquinone was purchased from Aldrich Chemical Co. Melting points were determined on a Fischer-Johns melting point apparatus and are uncorrected.

1,4-Bis(4-fluorophenyl)-3-phenylisoquinoline (31). To a solution of 1,2-bis(4-fluorobenzoyl)benzene (**1**; 22.4 mmol, 7.2 g) in chlorobenzene (200 mL) under an atmosphere of nitrogen was added 1,8-diazabicyclo[5.4.0]undecene (40.3 mmol, 6.7 mL) and benzylamine (22.4 mmol, 2.5 mL). The reaction mixture was refluxed for 18 h, and TLC (petroleum ether/ethyl acetate, 5/1) indicated completion of the reaction. The solvent was removed under reduced pressure, and the resulting residue was precipitated in petroleum ether. The yellow solid was filtered to give a 100% yield of crude isoquinoline **31**. Recrystallization of the crude solid from ethanol gave isoquinoline **31** as fine needlelike white crystals in 93% yield: mp 188–190 °C; ^1H NMR (200 MHz) δ 7.14 (d, J = 8.6 Hz, 2 H, ortho C_4H_2F), 7.21–7.26 (m, 6 H), 7.29–7.41 (m, 2 H), 7.54–7.77 (m, 4 H), 7.81–7.85 (m, 2 H), 8.17 (d, J = 8.3 Hz, 1 H); MS (EI) m/e (calcd for $C_{27}H_{17}NF_2$, 393.1329; found, 393.1329) 393 (58.4), 392 (100), 390 (10.3), 295 (10.1), 270 (9.8), 186 (2.3).

1,4-Bis(4-fluorophenyl)-3,5,8-triphenylisoquinoline (32). To a solution of 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene (**2**; 21.1 mmol, 10 g) in chlorobenzene (250 mL) under an atmosphere of nitrogen was added 1,8-diazabicyclo[5.4.0]undecene (42.2 mmol, 6.3 mL) and benzylamine (21.1 mmol, 2.3 mL). The reaction mixture was refluxed for 36 h, and TLC (petroleum ether/ethyl acetate, 20/1) indicated completion of the reaction. The solvent was removed under reduced pressure, and the resulting residue was precipitated in petroleum ether. The yellow solid was filtered to give 82% yield of crude isoquinoline **32**. Column chromatography (20/1, petroleum ether/ethyl acetate) of the crude solid gave a 46% yield of isoquinoline **32** as a white powder: mp 233–235 °C; ^1H NMR (200 MHz) δ 6.47 (dd, J = 8.5 Hz, 2 H), 6.52–6.84 (m, 4 H), 6.98–7.42 (m, 21 H), 7.61 (s, 2 H); MS (EI) m/e (calcd for $C_{39}H_{25}NF_2$, 545.1955; found, 545.1956) 545 (100), 468 (12), 448 (6.1), 374 (3.1).

1,4-Bis(4-fluorophenyl)-3,5,6,7,8-pentaphenylisoquinoline (33). To a solution of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**3**; 3.20 mmol, 2 g) in chlorobenzene (70 mL) under an atmosphere of nitrogen was added 1,8-diazabicyclo[5.4.0]undecene (6.4 mmol, 0.96 mL) and benzylamine (3.20 mmol, 0.35 mL). The reaction mixture was refluxed for 36 h, solvent was removed under reduced pressure, and the residue was diluted with a minimum amount of methylene chloride and precipitated in petroleum ether. The crude yellow solid recovered after filtration was obtained in 62% yield. Column chromatography of the crude material (5/1, petroleum ether/ethyl acetate) gave a 41% yield of isoquinoline **33** as a white solid: mp 298–300 °C; ^{1}H NMR (200 MHz) δ 6.26 (d, J = 8.7 Hz, 2 H), 6.75–6.87 (m, 24 H), 7.25–7.64 (m, 7 H); MS (EI) *m/e* (calcd for $C_{51}H_{33}NF_2$, 697.2331; found, 697.2332) 697 (52), 690 (25), 600 (12), 423 (23), 325 (12).

Polymer Characterization. Inherent viscosity measurements were determined by using a Ubbelohde dilution viscometer. Apparent molecular weights were determined by gel permeation chromatography using polystyrene standards with chloroform as the solvent on a Waters 510 HPLC with a UV detector and with four μ-Styragel columns (500, 10^4, 10^5, and 100 Å) in series. Glass transition temperatures were measured on a Mettler FP80 at a heating rate of 20 °C/min for the variable-temperature scans. Isothermal aging and variable-temperature scans (TGA) were performed on a Seiko TG/DTA 220. Dynamic mechanical behavior was measured on a Seiko 120 thermomechanical analyzer thermal stress–strain analyzer (TMA/SS) with a heating rate of 10 °C/min. Films for the mechanical analyzer were cast from chloroform at room temperature and were dried in an oven at 90 °C for 24 h. Oxygen permeation measurements were made on a Mocon's Ox-tran 100 twin, and the films employed for these measurements were developed and treated in a manner similar to that above.

Polymer Synthesis. Poly(aryl ether isoquinoline) 7a from Poly(aryl ether ketone) 4a. Intramolecular ring-closure reactions were conducted under an atmosphere of nitrogen. To a solution of poly(aryl ether ketone) **4a** (700 mg) in chlorobenzene (25 mL) was added excess 1,8-diazabicyclo[5.4.0]undecene (3 mL) and benzylamine (2.2 mL). The colorless reaction mixture was refluxed for 6 h. The resulting pale yellow reaction mixture was cooled, concentrated under reduced pressure, and diluted with a minimum amount of chloroform (5 mL). The polymer was then coagulated in methanol (50 mL) and filtered, redissolved in chloroform, and filtered hot through a thin layer of Celite. The chloroform solution was concentrated under reduced pressure and then coagulated in a large volume of methanol (60 mL). The pale yellow fibrous polymer was filtered and dried in a vacuum oven (120 °C) for 48 h to give poly(aryl ether isoquinoline) **7a** in quantitative yield.

Poly(aryl ether isoquinoline) 7b from 1,4-Bis(4-fluorophenyl)-3-phenylisoquinoline (31). A typical synthesis of a poly(aryl ether isoquinoline) from an isoquinoline monomer is described. The detailed synthetic procedure for the synthesis of poly(aryl ether isoquinoline) **7b** from monomer 1,4-bis(4-fluorophenyl)-3-phenylisoquinoline (**31**) is provided. To a three-neck flask equipped with a nitrogen inlet, Dean-Stark trap, and condenser was added 1,4-bis(4-fluorophenyl)-3-phenylisoquinoline (**31**; 2.54 mmol, 1 g) and bisphenol **34b** (2.54 mmol, 472 mg). Under an inert atmosphere *N*-methylcaprolactam (5.7 mL) and toluene (2.9 mL), followed by anhydrous potassium carbonate (3.05 mmol, 421 mg), were added. The reaction mixture was heated until the toluene began to reflux at 130–140 °C. Toluene was periodically removed from the Dean-Stark trap and replaced with dry toluene to ensure dehydration. The reaction mixture was maintained at ~140 °C until the presence of water was no longer observed in the Dean-Stark trap, which took 1–2 h. During this stage of the reaction, the solution underwent several color changes. During the initial formation of the phenoxide, a yellow color was observed, and as the refluxing proceeded the color changed to pale orange and then dark brown. Upon completion of dehydration and removal of toluene, the temperature of the reaction mixture increased to 230 °C. The reaction mixture was heated at 230 °C for 24 h. Completion of the reaction was qualitatively estimated by the point where the viscosity increased dramatically. The reaction mixture was diluted with chloroform (5 mL) and filtered hot through a thin layer of Celite. The solution was concentrated, coagulated in methanol (30 mL), and filtered to give a pale yellowish beige fibrous material. The material was redissolved in a minimum amount of chloroform, coagulated in methanol (30 mL), filtered, and dried in a vacuum oven (120 °C) for 48 h to give poly(aryl ether isoquinoline) **7b** in almost quantitative yield.

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