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Synthesis of Polyisoquinolines from Poly(ether ketone)s

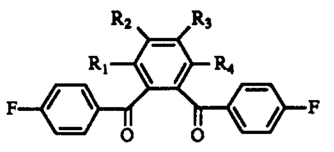
Introduction. In a recent paper,[1] we described the synthesis of 1,2-bis(4-fluorobenzoyl)benzenes 1-3 (Chart I), which upon reaction with bisphenates gave high molecular weight amorphous polyketones. We demonstrated[2] that the 1,2-dibenzoylbenzene moiety in the polyketone polymer chain undergoes an intramolecular ring-closure reaction with hydrazine monohydrate and a mild acid in chlorobenzene to give polyphthalazines. In this report, we describe another intramolecular ring-closure reaction of the 1,2-dibenzoylbenzene moiety, leading to the synthesis of a new class of amorphous, thermally stable polymers, polyisoquinolines, with high glass transition temperatures.

We would expect that polyisoquinolines would be similar in properties to polyquinolines,[3] which have previously been synthesized. Polyquinolines that have been prepared are either soluble in common organic solvents and have relatively low glass transition temperatures[4] (<250 °C) or are highly crystalline materials[5] insoluble in the common organic solvents with melting points greater than 500 °C. Because of the complexity of the synthesis and the cost of the starting materials, these materials have not been exploited. 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).

Results and Discussion. Treatment of the colorless poly(aryl ether ketone)s[7] 4–6 (Scheme I) with benzylamine in the presence of 1,8-diazabicyclo[5.4.0]undecene (DBU) in refluxing chlorobenzene[8,9] gave polyisoquinolines 7–9 as pale yellow polymers. The dramatic changes in properties that occurred upon ring closure of the poly(aryl ether ketone)s to their corresponding polyphthalazines[2] are also observed in the transformation of the poly(aryl ether ketone)s to the polyisoquinolines. Structurally this results in a significant straightening of the chain, which manifests itself in an increase in glass transition temperature, a large increase in solution viscosity, and a large increase in the apparent molecular weight as measured by gel permeation chromatography when compared to a polystyrene standard. The physical properties of the poly(aryl ether ketone)s 4–6 and their corresponding polyisoquinolines 7–9 are presented in Table I. Thermal stabilities of the polyisoquinolines were determined by TGA studies (5% weight loss) in air and in nitrogen and were found to be 500 °C or above. Figure 1 shows GPC traces of poly(aryl ether ketone)s 4 and the corresponding polyisoquinoline 7. The poly(aryl ether ketone) 4 appears at a retention time of 27.1 min with a $\bar{M}_w$ = 32 400, and the polyisoquinoline 7 appears at 24.9 min with a much larger $\bar{M}_w$ = 48 300. An increase in inherent viscosity for the polyisoquinoline 7 (0.59 dL/g) upon ring closure of the poly(aryl ether ketone) 4 (0.48 dL/g) is also observed. 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. Similar behavior was observed in the conversion of poly(aryl ether ketone)s 5 and 6 to polyisoquinolines 8 and 9. Tough and flexible yellow films of polymers 7–9 were obtained by casting from chloroform solution at room temperature.

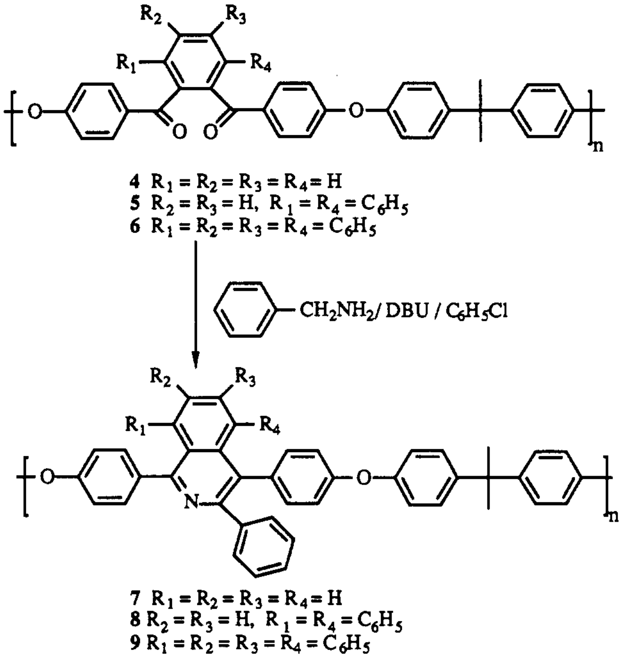
End-capped poly(aryl ether ketone)s 10–12 with terminal di-*tert*-butylphenyl groups that were prepared previously[10] with a degree of polymerization of ~50 monomer units/chain were converted to polyisoquinolines 13–15. The inherent viscosities, molecular weights determined by GPC, and number-average molecular weights determined by ^1H NMR for the capped materials are tabulated in Table II.

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 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

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 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

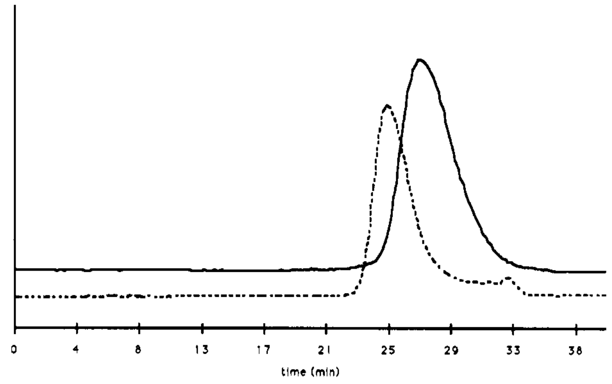


Figure 1. GPC trace for poly(aryl ether ketone) 4 (—) and the corresponding polyisoquinoline 7 (- - -).

A large increase in viscosity and molecular weight (by GPC) is observed for the conversion of the capped poly(aryl ether ketone)s to polyisoquinolines, as for the uncapped materials. From ^1H NMR studies,[11] the number of monomer units (*n*) in the polyisoquinoline chain was determined, and their exact molecular weights are tabulated in Table II. The degrees of polymerization of the polymers, e.g., poly(aryl ether ketone) 10 (*n* = 64) upon ring closure to the polyisoquinoline 13 (*n* = 65), remain

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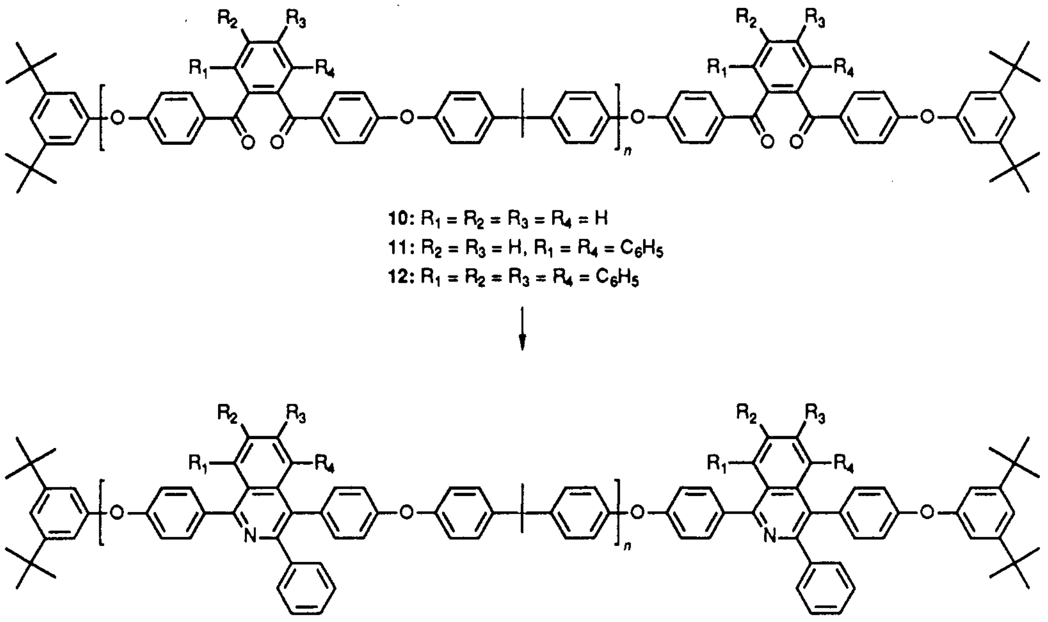
Table I
Physical Properties of Polyisoquinolines Compared to the Precursor Poly(aryl ether ketone)s

poly(aryl ether ketone)						polyisoquinoline					
polymer	η_{inh},[a] dL/g	T_g, °C	$\bar{M}_w$[b]	$\bar{M}_n$[b]	TGA[c] for air/N_2 °C	polymer	η_{inh},[a] dL/g	T_g, °C	$\bar{M}_w$[b]	$\bar{M}_n$[b]	TGA[c] for air/N_2, °C
4	0.48	182	32 400	17 100	483/483	7	0.59	226	48 300	21 000	510/513
5	0.65	221	85 400	51 600	512/512	8	0.68	234	93 200	33 200	501/500
6	0.47	268	44 000	27 300	520/523	9	0.65	280	225 000	52 200	535/537

[a] Inherent viscosities were measured at a concentration at 0.5 g/dL in chloroform at 25 °C. [b] Determined by GPC based on polystyrene standards. [c] 5% weight loss.

Table II
Di-*tert*-butyl-Terminated Poly(aryl ether ketone)s and Polyisoquinolines



10: $R_1 = R_2 = R_3 = R_4 = H$
11: $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
12: $R_1 = R_2 = R_3 = R_4 = C_6H_5$

13: $R_1 = R_2 = R_3 = R_4 = H$
14: $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
15: $R_1 = R_2 = R_3 = R_4 = C_6H_5$

poly(aryl ether ketone)						polyisoquinoline					
polymer	n[a]	$\bar{M}_n$	$\bar{M}_w$[b]	$\bar{M}_n$[b]	η_{inh},[c] dL/g	polymer	n[a]	$\bar{M}_n$	$\bar{M}_w$[b]	$\bar{M}_n$[b]	η_{inh},[c] dL/g
10	64	33 300	9 600	4 300	0.21	13	65	38 500	53 200	21 300	0.41
11	48	32 600	42 700	16 000	0.38	14	51	36 100	39 400	33 000	0.51
12	55	45 700	32 800	13 600	0.27	15	53	51 500	168 900	73 400	0.48

[a] The number of monomer units (n) was designed experimentally for 50 units and determined by ^1H NMR measurements. [b] Determined by GPC measurements using polystyrenes as standards. [c] Inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

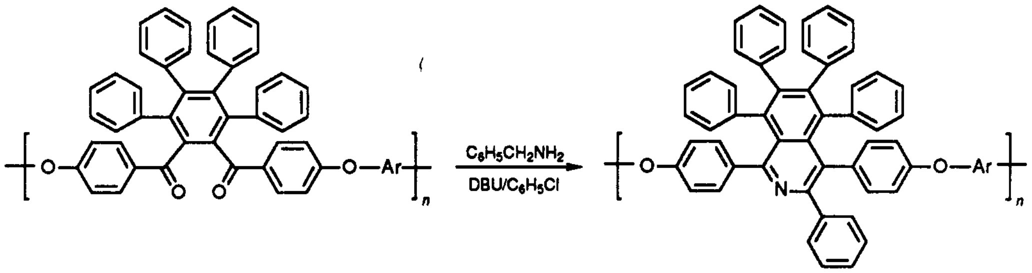
constant, indicating no side reactions occur in the conversion.

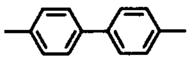
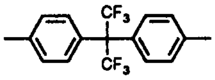
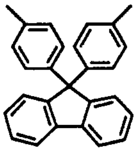
By controlling the amounts of reagents used in the conversion reaction or the time and reaction temperature, copolymers of poly(aryl ether ketone) and polyisoquinoline could readily be isolated. The fully characterized NMR spectra of the poly(aryl ether ketone) **10**, the copolymer **16** (made by partial ring-closure reaction of poly(aryl ether ketone) **10**), and the polyisoquinoline **13** are shown in Figure 2. The ^1H NMR spectrum of polymer **10** is easily identified due to its symmetrical appearance;[12] however, those of the copolymer **16** and polyisoquinoline **13** appear more complex. ^1H–^1H COSY and decoupling NMR studies were used to assign the chemical shifts. The singlet observed for the protons designated H_a at δ 7.56 in the spectrum of polymer **10** is still very prominent in the spectrum of copolymer **16** at δ 7.56. In the spectrum of copolymer **16**, a new set of multiplets appear at δ 7.33 and 7.36–7.68, along with a pronounced doublet appearing downfield δ 8.13 (J_{ortho} = 8.2 Hz), which is just as prominent in the spectrum of polyisoquinoline **13** and is designated H_1. A downfield shift of the protons in the di-*tert*-butyl group occurs in the copolymer **16**, and the resonance due to the protons in the isopropylidene moiety broadens. The *tert*-butyl group shows resonances at δ 1.29 and 1.31. The spectrum of the homopolymer (polyisoquinoline **13**) shows a complete conversion, the peaks for the di-*tert*-butyl group coalesce into a singlet at δ 1.32, and a sharp singlet for the isopropylidene moiety at δ 1.72 results. The ^1H–^1H COSY spectrum of polyisoquinoline **13** shown in Figure 3 confirms the chemical shift assignment for the ^1H NMR spectrum shown in Figure 2c.

The ^1H NMR spectrum of polymer **16** (Figure 2b) is a copolymer of polyketone **10** and polyisoquinoline **13**. From the spectrum the compositions of polyketone **10** (25%) and polyisoquinoline **13** (75%) were determined. The glass transition temperature of the copolymer **16** was observed as 213 °C, which corresponds to the calculated value.

Various high molecular weight, high glass transition temperature poly(aryl ether ketone)s synthesized previously[1] were converted to the polyisoquinolines (**17**–**20**). The results for the conversion reactions are presented in Table

Table III
Physical Properties of Polyisoquinolines Obtained from Poly(aryl ether ketone)s



poly(aryl ether ketone)			polyisoquinoline					
Ar	η_{inh},[a] dL/g	T_g, °C		η_{inh},[a] dL/g	T_g, °C	$\bar{M}_w$[b]	$\bar{M}_n$[b]	TGA for air/N_2, °C
	0.49	273	17	0.58	297	208 000	53 400	558/559
	0.73	292	18	0.98	320	180 900	37 700	548/548
	0.44	278	19	0.63	294	3 860 400	1 300 800	525/520
	0.55	313	**20**	0.72	323	3 480 700	1 520 000	510/513

[a] Inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C. [b] Determined by GPC based on polystyrene standards.

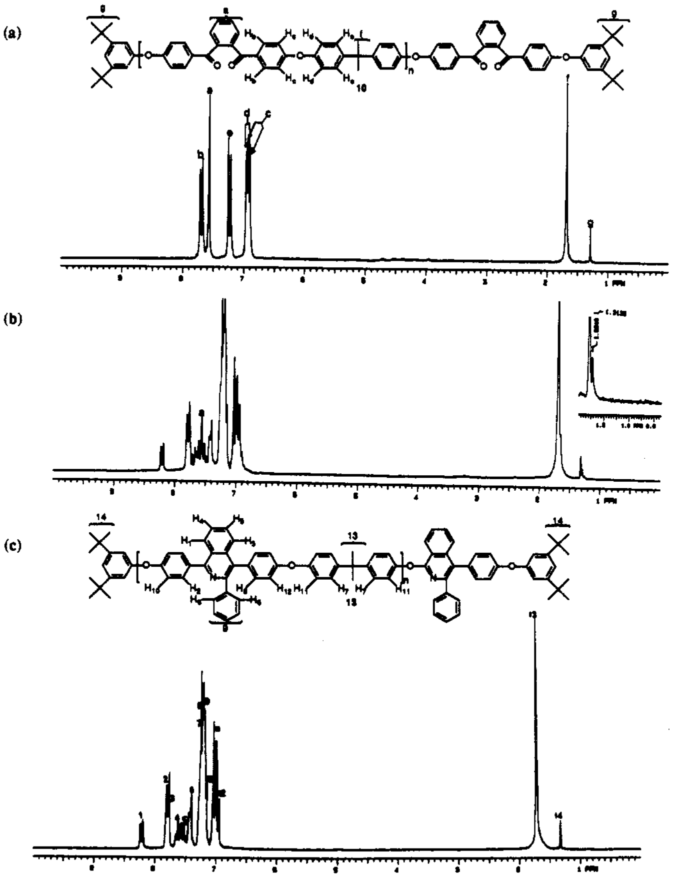


Figure 2. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of (a) capped poly(aryl ether ketone) **10**, (b) the capped copolymer **16**, and (c) polyisoquinoline **13**.

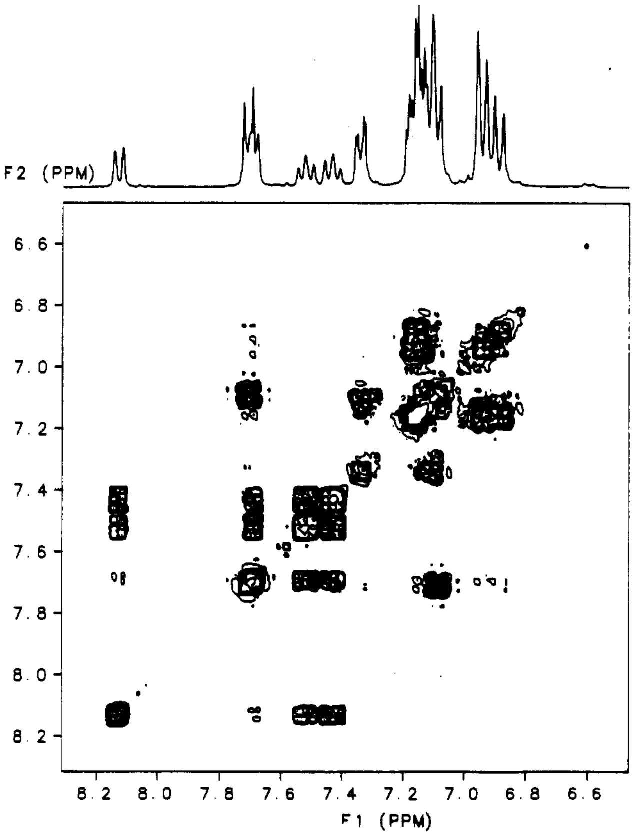


Figure 3. 2D ^{1}H–^{1}H COSY spectrum (δ 6.5–8.3) of polyisoquinoline **13** acquired at 300 MHz ($CDCl_3$). Diagonal proton resonances are labeled in the 1D ^{1}H NMR spectrum shown in Figure 2c.

III. In all instances, the polymers showed a large increase in molecular weight, inherent viscosity, and glass transition temperature. The glass transition temperatures for these materials were all above 290 °C, and they were all found to be thermooxidatively stable. TGA studies showed 5% weight losses in air and nitrogen above 500 °C.

In this study, we have synthesized a new class of high-temperature, high-T_g polymers, the polyisoquinolines, by an intramolecular ring-closure reaction of poly(aryl ether ketone)s containing the 1,2-dibenzoylbenzene moiety with benzylamine in a basic medium. The synthesis of other high-temperature, high molecular weight polyisoquinolines is being pursued. In addition, the mechanical and thermal properties of these materials are presently being investigated.

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References and Notes

(1) Singh, R.; Hay, A. S. Submitted for publication in *Macromolecules*.

(2) Singh, R.; Hay, A. S. Submitted for publication in *Macromolecules*.

(3) Stille, J. K. *Macromolecules* **1981**, *14*, 870 and references herein.

(4) Stille, J. K.; Wolfe, J. F. *Macromolecules* **1976**, *9*, 489.

(5) Stille, J. K.; Sutherlin, D. M. *Macromolecules* **1985**, *18*, 2669.

(6) Gibson, H. W.; Guilani, B. *Macromolecules* **1990**, *23*, 4339.

(7) The batch of poly(aryl ether ketone)s used were those synthesized in ref 1.

(8) Tashiro, M.; Tsuda, Y.; Takahashi, K.; Mataka, S. *Heterocycles* **1980**, *14*, 789.

(9) The methodology in ref 8 uses toluene as the solvent. We have found that solvents such as chlorobenzene or ethylbenzene are preferable.

(10) The capped poly(aryl ether ketone)s used were those synthesized in ref 2.

(11) The integral blanking technique (^1H NMR, 200 MHz, $CDCl_3$) was used to determine the exact number of protons under a given integral.

(12) Two-dimensional experiments (COSY and COLOC) were done to confirm the chemical shift assignments in the one-dimensional spectrum of polymer **10** shown in Figure 2a.

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