## Synthesis of Polyphthalazines from Poly(ether ketone)s

**Introduction.** In our previous 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 poly(aryl ether ketone)s. Interestingly, the 1,2-dibenzoylbenzene moiety in the polymer chain introduces the possibility of further intramolecular ring closure with hydrazine in the presence of a mild acid, leading to the synthesis of polyphthalazines. This paper describes the synthesis and characterization of a new class of amorphous, thermally stable polymers, polyphthalazines, with high glass transition temperatures. Alternatively, the polyphthalazines can be synthesized by the reaction of a fluoro-substituted phthalazine monomer with a bisphenate.

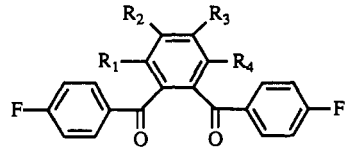
It has been shown[2] that heterocycles such as thiazole and phthalazine undergo electrochemical polymerization, providing a synthetic route to their corresponding polymers. Apart from the electrochemical polymerization reaction, polymers containing the phthalazine moiety have not been reported.

**Results and Discussion.** The colorless poly(aryl ether ketone)s[3] **4–6** (Scheme I) were treated with hydrazine monohydrate and acetic acid in refluxing chlorobenzene to give the polyphthalazines **7–9** as intensely yellow colored polymers. Essentially complete conversion to the polyphthalazines was indicated via $^1$H NMR studies. Depending on the amount of reagents used, the reaction temperature, the length of time of the reaction, and the solvent employed, copolymers can be readily synthesized.

Remarkable changes in properties occur upon ring closure of the poly(aryl ether ketone)s to their corresponding polyphthalazines. Structurally this transformation results in a significant straightening of the chain. The change in structure manifests itself in not only a significant increase in glass transition temperature but a large increase in the solution viscosity and a large increase in the apparent molecular weight as measured by gel permeation chromatography based on polystyrene standards. The structural modification to a more rigid molecule would take up more free volume and gives a polymer that appears to be higher in molecular weight since GPC separates molecules on the basis of size exclusion. The physical properties for the poly(aryl ether ketone)s **4–6** and their corresponding polyphthalazines **7–9** are presented in Table I. Figure 1 shows GPC traces of poly(aryl ether ketone) **5** and the corresponding polyphthalazine **8**. The poly(aryl ether ketone) **5** appears at a retention time of 24.8 min with a $\bar{M}_w$ = 85 400, and the polyphthalazine **8** appears at a shorter time, 14.5 min, with a much larger $\bar{M}_w$ = 125 200. Similar behavior was exhibited in the conversion of poly(aryl ether ketone)s **4** and **6** to polyphthalazines **7** and **9**. Tough and flexible yellow films of polymers **7–9** were obtained by casting from chloroform solution at room temperature.

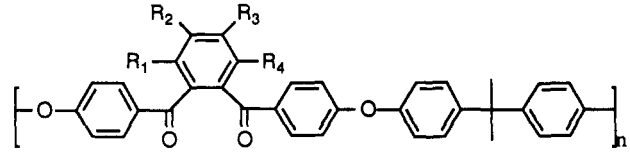
To demonstrate that neither chain scission nor branching had occurred during the synthesis of the polyphthalazines and to determine absolute molecular weights, end-capped poly(aryl ether ketone)s were prepared. The three monomers **1–3** were polymerized with excess anhydrous potassium carbonate in *N,N*-dimethylacetamide and toluene solution with 4,4′-(1-methylethylidene)bisphenol (BPA) in the presence of 3,5-di-*tert*-butylphenol as an end-capping agent to give poly(aryl ether ketone)s **10–12** with di-*tert*-butylphenyl terminal groups. Experiments were designed to give polymers with a degree of polymerization of 50 monomer units per polymer chain. $^1$H

**Chart I**



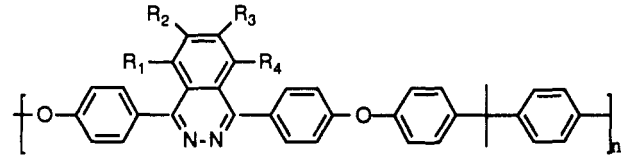
1 $R_1 = R_2 = R_3 = R_4 = H$
2 $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
3 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

**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 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

$H_2NNH_2 \cdot H_2O$ / AcOH/ $C_6H_5Cl$



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

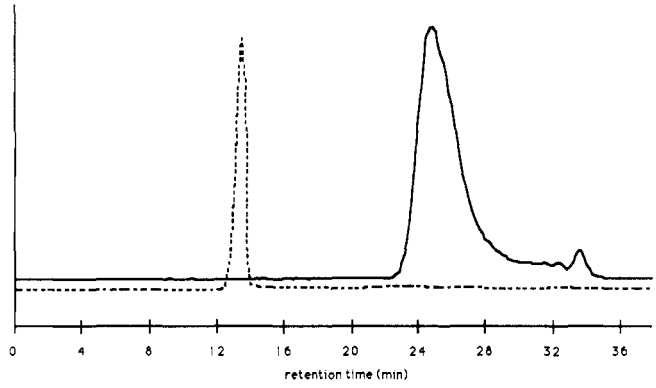



**Figure 1.** GPC trace for poly(aryl ether ketone) **5** (—) and the corresponding polyphthalazine **8** (- - -).

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

| poly(aryl ether ketone) | | | | | | polyphthalazine | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| polymer | $\eta_{inh}$,[a] dL/g | $T_g$, °C | $\bar{M}_w$[b] | $\bar{M}_n$[b] | TGA[c] for air/$N_2$, °C | polymer | $\eta_{inh}$,[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 | 0.72 | 236 | 47 900 | 19 110 | 463/468 |
| 5 | 0.65 | 221 | 85 400 | 51 600 | 512/512 | 8 | 0.89 | 250 | 125 200 | 62 100 | 309/508 |
| 6 | 0.47 | 268 | 44 000 | 27 300 | 520/523 | 9 | 0.64 | 283 | 162 300 | 38 500 | 516/513 |

[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. [c] 5% weight loss.

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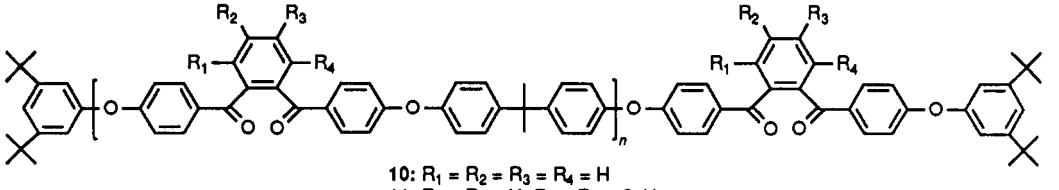
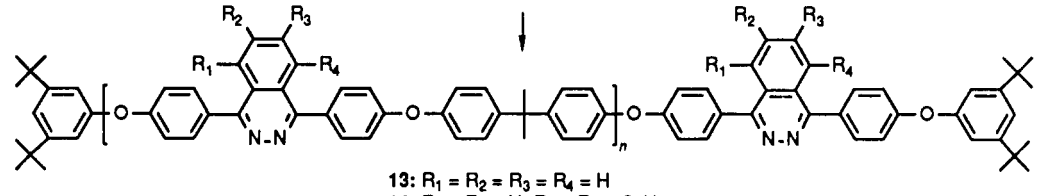
**Table II. Di-*tert*-butyl-Terminated Poly(aryl ether ketone)s and Polyphthalazines**



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

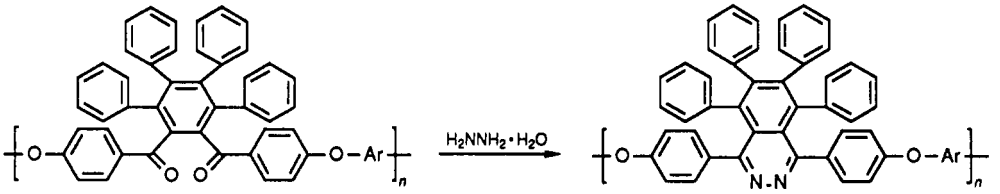


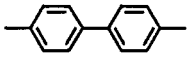
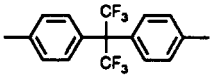
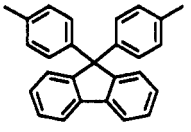
**13**: $R_1 = R_2 = R_3 = R_4 = H$
**14**: $R_2 = R_3 = H$, $R_1 = R_4 = C_6H_5$
**15**: $R_1 = R_2 = R_3 = R_4 = C_6H_5$

| poly(aryl ether ketone) | | | | | | polyphthalazine | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| polymer | $n^a$ | $\bar{M}_n$ | $\bar{M}_w{}^b$ | $\bar{M}_n{}^b$ | $\eta_{inh}$,[c] dL/g | polymer | $n^a$ | $\bar{M}_n$ | $\bar{M}_w{}^b$ | $\bar{M}_n{}^b$ | $\eta_{inh}$,[c] dL/g |
| **10** | 64 | 33 300 | 9 600 | 4 300 | 0.21 | **13** | 65 | 32 000 | 56 300 | 51 650 | 0.33 |
| **11** | 48 | 32 600 | 42 700 | 16 000 | 0.38 | **14** | 51 | 33 100 | 130 100 | 39 400 | 0.66 |
| **12** | 55 | 45 700 | 32 800 | 13 600 | 0.27 | **15** | 53 | 42 600 | 107 200 | 99 250 | 0.39 |

[a] The number of monomer units ($n$) was experimentally designed 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.

**Table III. Physical Properties of Polyphthalazines Obtained from Poly(aryl ether ketone)s**



| poly(aryl ether ketone) | | | polyphthalazine | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ar | $\eta_{inh}$,[a] dL/g | $T_g$, °C | | $\eta_{inh}$,[a] dL/g | $T_g$, °C | $\bar{M}_w{}^b$ | $\bar{M}_n{}^b$ | TGA for air/$N_2$, °C |
|  | 0.49 | 273 | **17** | 0.61 | 296 | 153 000 | 63 200 | 536/533 |
|  | 0.73 | 292 | **18** | 1.21 | 340 | 402 000 | 95 600 | 517/512 |
|  | 0.44 | 278 | **19** | 0.56 | 293 | 883 000 | 717 800 | 533/531 |
|  | 0.55 | 313 | **20** | 0.69 | 340 | 696 000 | 565 700 | 520/520 |

[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.

NMR[4] analysis was used to determine the exact number of units per chain. For example, in poly(aryl ether ketone) **11**, the intensities of the protons in the isopropylidene moiety at $\delta$ 1.66 (89%) and the di-*tert*-butyl group at $\delta$ 1.29 (11%) were measured. From this information the number of monomer units in the polymer chain **11** was calculated ($n$ = 48 units) to give a number-average molecular weight of 32 600. Similarly, the number-average molecular weights for the other poly(aryl ether ketone)s **10** and **12** were determined. The three poly(aryl ether ketone)s **10–12** were then converted to polyphthalazines **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. Ring closure of capped polymer **11** to polymer **14** gives a large increase in the apparent molecular weight from GPC studies; however, $^1H$ NMR indicates that the molecular weights of polyphthalazines are essentially the same as those of the poly(aryl ether ketone)s they were derived from (polymer **11–14**) as shown in Table II.

The $^1H$ NMR spectra of the capped poly(aryl ether ketone) **11**, the polyphthalazine **14** obtained from **11**, and the copolymer **16** are shown in Figure 2. A downfield shift of the protons in the di-*tert*-butyl group and isopropylidene moiety is exhibited in the spectrum of copolymer **16** (from partial ring-closure reaction of poly(aryl ether ketone) **11**). The *tert*-butyl group shows resonances at $\delta$ 1.27 and 1.31 and the isopropylidene moiety at $\delta$ 1.68 and 1.72. A prominent downfield shift arises in the copolymer

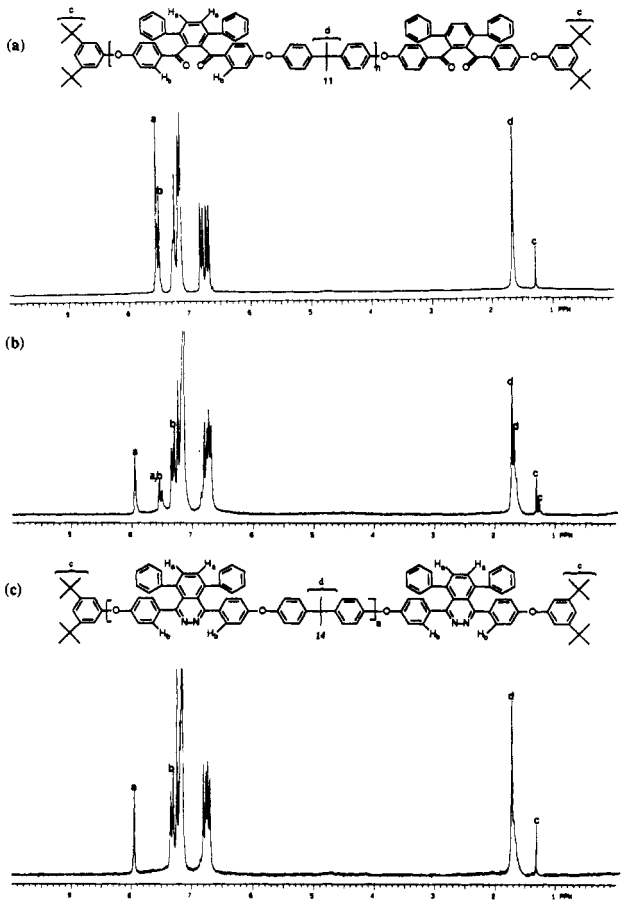
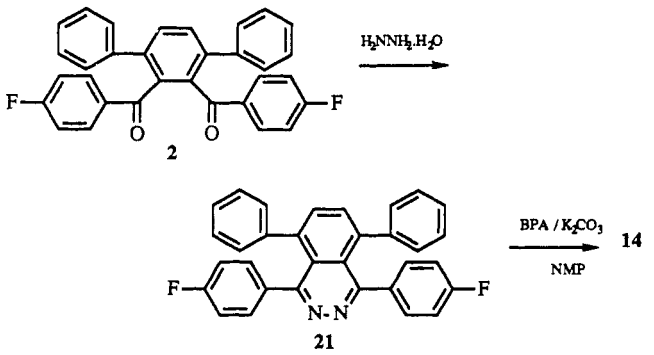


Figure 2. $^1$H NMR (200 MHz, $CDCl_3$) spectrum of (a) capped poly(aryl ether ketone) 11, (b) the capped copolymer 16, and (c) polyphthalazine 14.

**Scheme II**



spectrum due to the protons designated $H_a$ $\delta$ 7.95, and gradual disappearance of the doublet $H_b$ protons at $\delta$ 7.5 ($J_{ortho}$ = 9.3 Hz) occurs. The spectrum of the homopolymer (polyphthalazine 14) shows a complete conversion, and the double peaks seen for the *tert*-butyl and isopropylidene groups in the copolymer spectrum coalesce into definite singlet peaks $\delta$ 1.32 ($C(CH_3)_3$) and $\delta$ 1.72 ($C(CH_3)_2$). These results confirm that the overall ring closure is complete and that no side reactions or branching occur during the transformation.

A copolymer consisting of 11 and 14 was prepared, and its composition was determined[4] from the $^1$H NMR (Figure 2b) spectrum to have 67% polyphthalazine polymer units and 33% polyketone units. The glass transition temperature for the copolymer 16 was found to be 240 °C, which corresponds to the calculated figure.

Other high molecular weight poly(aryl ether ketone)s[5] were converted to the polyphthalazines (17–20) as shown in Table III. All polymers showed a large increase in molecular weight, inherent viscosity, and glass transition temperature. The increase in $T_g$ was in the range of 15–55 °C. The polyphthalazine polymers are all very thermooxidatively stable. From TGA studies 5% weight losses in air and in nitrogen are above 500 °C.

It has been demonstrated that other heterocyclic ring systems, such as quinoxalines[6] and benzoxazoles,[7] activate haloaromatic rings toward nucleophilic aromatic substitution by phenoxides. The polyphthalazine ring also exerts a deshielding effect as illustrated in the $^1$H NMR spectra of the copolymer 16 and the homopolymer polyphthalazine 14 (Figure 2b,c). The electron-poor pyridazine ring would also be expected to activate halo groups toward nucleophilic substitution reactions.[8,9] Fluoro-substituted phthalazine monomer 21 was prepared by the reaction of monomer 2 with hydrazine in acetic acid. Polymerization of 21 with BPA and excess $K_2CO_3$ in NMP at 180 °C gave polyphthalazine 14 (Scheme II). Polyphthalazine 14 (from phthalazine monomer 21) shows a glass transition of 250 °C and an inherent viscosity of 0.73 dL/g. The $^1$H NMR of polyphthalazine 14 from phthalazine 21 was identical with that of polyphthalazine 14 ($T_g$ = 250 °C, $\eta_{inh}$ = 0.66 dL/g) synthesized from poly(aryl ether ketone) 11 shown in Figure 2c.

A new class of high-temperature, high-$T_g$ polymers, the polyphthalazines, has been synthesized by the intramolecular ring closure of capped poly(aryl ether ketone)s containing the 1,2-dibenzoylbenzene moiety with hydrazine or via the direct reaction of fluoro-substituted phthalazines with bisphenates.

Further work on polyphthalazines is in progress involving the synthesis of other phthalazine monomers and their polymers. In addition, the mechanical and thermal properties of these materials are being investigated.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada and the General Electric Co. for generous financial support.

## References and Notes

(1) Hay, A. S.; Singh, R., submitted for publication in *Macromolecules*.
(2) Aldissi, M.; Nyitray, A. M. *ACS Symp. Ser.* **1988**, *346*, 559–67.
(3) The batch of poly(aryl ether ketone)s used were the ones synthesized in ref 1.
(4) The integral blanking technique ($^1$H NMR, 200 MHz, $CDCl_3$) was used to determine the exact number of protons under a given integral.
(5) The same batch of high molecular weight, high-$T_g$ poly(aryl ether ketone)s was employed for each conversion reaction (see ref 1).
(6) Hedrick J. L.; Labadie, J. W. *Macromolecules* **1988**, *21*, 1883. Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23*, 1561.
(7) Hedrick, J. L.; Labadie, J. W.; Hilborn, J. G. *Macromolecules* **1990**, *23*, 2854.
(8) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Polym. Chem. Sci.* **1967**, 2375.
(9) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1096. Attwood, T. E.; Barr, D. A.; Feasey, G. G.; Leslie, V. J.; Newton, A. B.; Rose, J. B. *Polymer* **1977**, *17*, 354.

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*Received December 7, 1990*
*Revised Manuscript Received February 25, 1991*