Synthesis and Physical Properties of Poly(aryl ether phthalazine)s

Rina Singh† and Allan S. Hay*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

Received August 9, 1991; Revised Manuscript Received October 23, 1991

ABSTRACT: The synthesis of a new class of polymers, the poly(aryl ether phthalazine)s, is described via an intramolecular ring-closure reaction of poly(aryl ether ketone)s containing the *o*-dibenzoylbenzene moiety with hydrazine monohydrate. The synthesis of copolymers of poly(aryl ether ketone)s and poly(aryl ether phthalazine)s is demonstrated, and the copolymer ratios were determined by ^{1}H NMR studies. Various fluoro-substituted phthalazine monomers were prepared and polymerized with bisphenols in *N*-methyl-2-pyrrolidinone (NMP) in the presence of excess base (K_2CO_3). High molecular weight polymers were obtained, with glass transition temperatures in the 235–340 °C range. Thermal stabilities for the resulting materials by TGA showed polymer decomposition temperatures (5% weight loss) in air and in nitrogen ranging from 460 to 535 °C. The polymerization of 3,6-bis(4-fluorophenyl)pyridazine with 4,4′-(1-methylethylidene)-bisphenol (BPA) also afforded a new class of polymers, the poly(aryl ether pyridazine)s.

Introduction

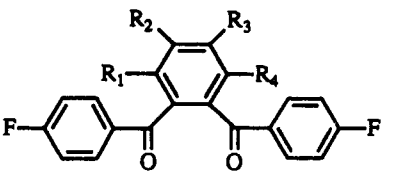
In the past, much effort has been expended toward the synthesis of polymers with heterocyclic functional groups[1] because such polymers are readily synthesized and they are very thermooxidatively stable due to their aromatic character. Poly(quinoline)s,[2] poly(quinoxaline)s,[3] and poly(benzoxazole)s[4] have limitied uses since they are soluble only in strong acids and cannot be processed from organic solvents. However, the introduction of ether linkages in the above classes of polymeric materials is known to improve the solubility characteristics of these highly rigid materials. The introduction of ether linkages results from a nucleophilic displacement polymerization reaction in heterocyclic monomers containing bishalide (nitro) groups with a bisphenate salt. As a result, the processability of these polymers is significantly improved without greatly sacrificing their thermal stability.

Recently, Hedrick et al.[5] demonstrated that fluoride groups para to a 2-benzoxazolyl group were readily displaced with phenoxides, resulting in high molecular weight poly(aryl ether benzoxazoles) that could be processed from common organic solvents. It has been shown also that quinoxaline-based poly(aryl ethers) can be synthesized via a halo displacement polymerization,[6] where the fused pyrazine ring is the activating group.

In our previous paper,[7] 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. The 1,2-dibenzoylbenzene moiety in the polymer chain introduced the possibility of further intramolecular ring closure with hydrazine in the presence of a mild acid, leading to the synthesis of a new class of amorphous, thermally stable polymers with high glass transition temperatures, the poly(aryl ether phthalazine)s.[8] Generally these materials were found to be readily soluble in ordinary organic solvents such as chloroform or methylene chloride at room temperature. Solution casting the materials at room temperature from chloroform gave clear yellow films. An alternative to the intramolecular ring-closure reaction of the 1,2-dibenzoylbenzene moiety in the polymer chain was reported by Singh and Hay,[8] in which the poly(aryl ether phthalazine)s can be synthesized by the reaction of a fluoro-substituted phthalazine monomer with a bisphenate.

It has been shown[9] that heterocycles such as thiazole and phthalazine undergo electrochemical polymerization,

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 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

providing a synthetic route to their corresponding polymers. Apart from the electrochemical polymerization reaction, polymers containing the phthalazine moiety have not been reported. In this paper we will describe further our investigation on poly(aryl ether phthalazine)s, including the results from thermal and mechanical properties of these materials.

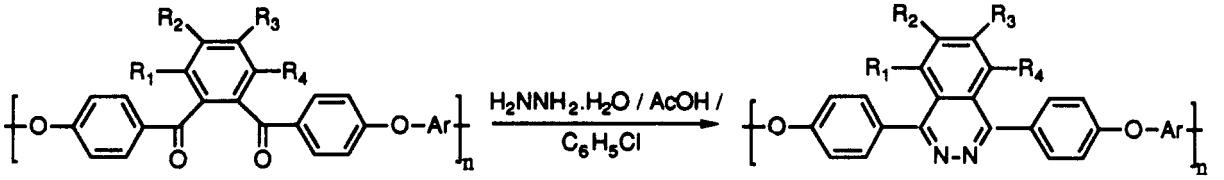
Results and Discussion

The colorless high molecular weight poly(aryl ether ketone)s[7] **4a–c**, **5a–c**, and **6a–e** (Scheme I) prepared previously were treated with excess hydrazine monohydrate and excess acetic acid in chlorobenzene to give the poly(aryl ether phthalazine)s **7a–c**, **8a–c**, and **9a–e**, respectively. The poly(aryl ether phthalazine)s were isolated as intensely yellow polymers. Essentially complete conversion to the poly(aryl ether phthalazine)s 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 from all of the poly(aryl ether ketone)s. As a result of the ring closure of the poly(aryl ether ketone)s to the poly(aryl ether phthalazine)s, dramatic changes in physical properties were observed. Structurally this transformation results in a significant straightening of the chain. The change in structure manifests itself in not only a significant increase in the glass transition temperature but also 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.[8] The structural modification to a more rigid molecule would take up more spatial volume, i.e., the radius of gyration and/or the end-to-end distance of the macromolecule increases, hence resulting in an increase in the solution viscosity and a higher apparent molecular weight as

† Central Research, Dow Chemical Co., Midland, MI 48674.

0024-9297/92/2225-1025$03.00/0

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 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

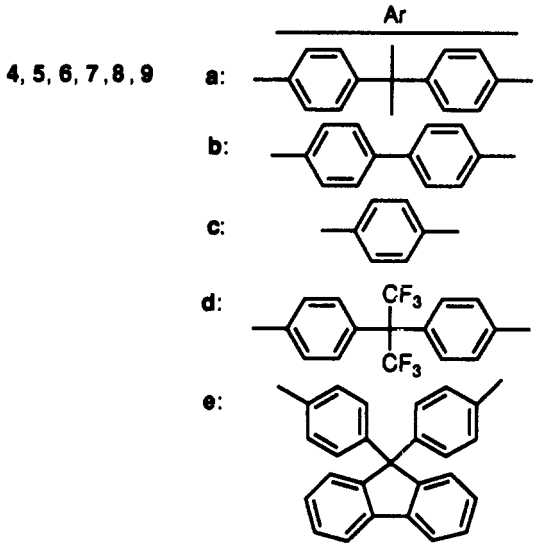


Table I
Physical Properties of Poly(aryl ether phthalazine)s Compared to Poly(aryl ether ketones)s

polymer	η_{inh},[a] dL/g	T_g, °C	polymer	η_{inh},[a] dL/g	T_g, °C
4a	0.48	182	**7a**	0.72	235
4b	0.42	190	**7b**	0.56[b]	255
4c	0.43	185	**7c**	0.54[b]	260
5a	0.65	221	**8a**	0.89	250
5b	0.56	240	**8b**	0.93	300
5c	0.35	240	**8c**	0.53	270
6a	0.47	265	**9a**	0.64	285
6b	0.73	292	**9b**	1.21	340
6c	0.49	273	**9c**	0.61	295
6d	0.44	278	**9d**	0.56	293
6e	0.55	313	**9e**	0.69	340

[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).

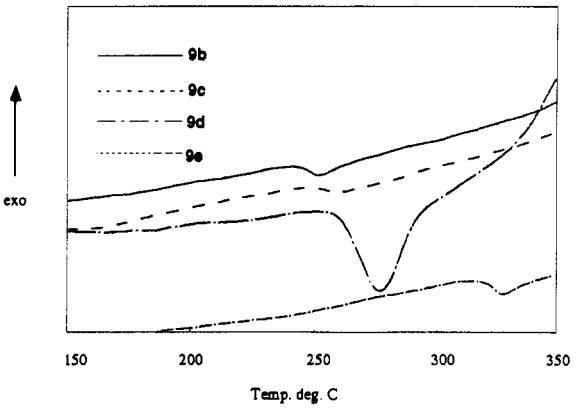


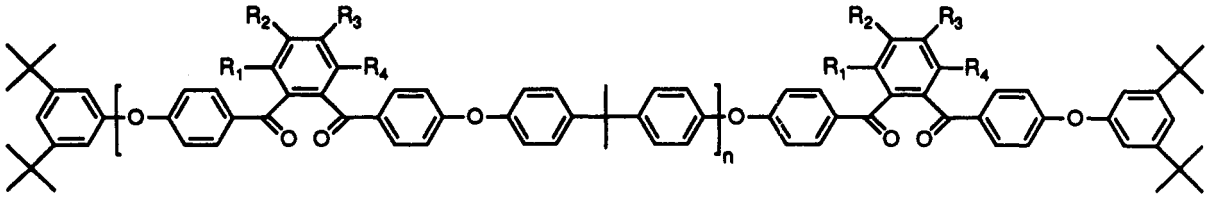
Figure 1. DSC analysis of polymers **9b–e** under an atmosphere of N_2.

measured by gel permeation chromatography. Increases in the glass transition temperature from 15 to 75 °C occur when the ketone polymers are converted to the polyphthalazines. Most of the poly(aryl ether phthalazine)s synthesized were very soluble in chloroform at room temperature, and all of the polyphthalazines (Table I) formed flexible, clear and yellow films upon solution casting from chloroform. The unsubstituted poly(aryl ether phthalazine)s **7b** and **7c** with either a hydroquinone or *p,p'*-biphenol moiety in the polymer backbone are exceptions since they come out of the hot solution during the ring-closure reaction and are not soluble in chloroform at room temperature nor at elevated temperatures in conventional solvents. To ensure total ring closure of these unsubstituted poly(aryl ether ketone)s **4b** and **4c** to the corresponding poly(aryl ether phthalazine)s **7b** and **7c**, the polyketones were subjected to ring-closure reactions in refluxing phenol to maintain solubility, and by ^1H NMR studies completion of the reaction was indicated. Inherent viscosities of polymers **7b** and **7c** were determined at room temperature in a solvent mixture of chloroform and trifluoroacetic acid (4/1, v/v). These polymers are amorphous, and, even after annealing experiments above the glass transition temperatures of the two polymers (**7b** and **7c**), no sign of crystallinity was observed.

The glass transition temperatures (T_g's) are reported in Table I. Poly(aryl ether phthalazine)s with a range of glass transition temperatures of 235–340 °C have been synthesized (Table I) via the intramolecular ring-closure reaction. Polymer series **9** showed the highest T_g's (285–340 °C). As was observed with the polyketones,[10] increases in the glass transition temperatures of the poly(aryl ether phthalazine)s occur with the addition of each pair of phenyl substituents on the central benzene ring. Figure 1 shows the DSC curves of poly(aryl ether phthalazine)s **9b–e**.

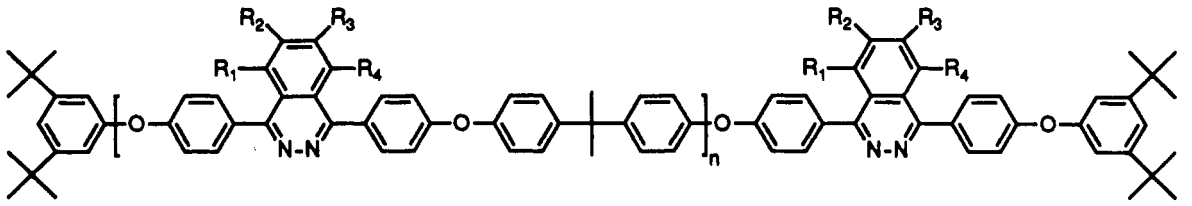
Apparent molecular weights determined by GPC using polystyrenes as standards have been reported for the poly(aryl ether phthalazine)s shown in Table I.[7,8] To demonstrate that neither chain scission nor branching had occurred during the synthesis of the poly(aryl ether ph-

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

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



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
Poly(aryl ether ketone)s and Poly(aryl ether phthalazine)s Terminated with 3,5-Di-*tert*-butylphenoxy Groups

poly(aryl ether ketone)			poly(aryl ether phthalazine)					
polymer	$n^{a,b}$	η_{inh},[c] dL/g	polymer	n^b	$\bar{M}_n$, ×10⁴	$\bar{M}_w$,[d] ×10⁴	$\bar{M}_n$,[d] ×10⁴	η_{inh},[c] dL/g
10	36	0.19	**19**	34	1.79	4.36	3.96	0.28
11	64	0.21	**20**	65	3.20	5.63	5.16	0.33
12	79	0.44	**21**	79	4.07	6.04	5.03	0.68
13	36	0.30	**22**	32	2.39	5.88	1.48	0.46
14	48	0.38	**23**	51	3.31	13.01	3.94	0.66
15	69	0.49	**24**	70	4.69	20.62	5.89	0.97
16	36	0.25	**25**	36	3.02	9.60	8.73	0.30
17	55	0.30	**26**	53	4.26	10.72	9.92	0.39
18	81	0.49	**27**	79	6.50	21.30	14.2	0.62

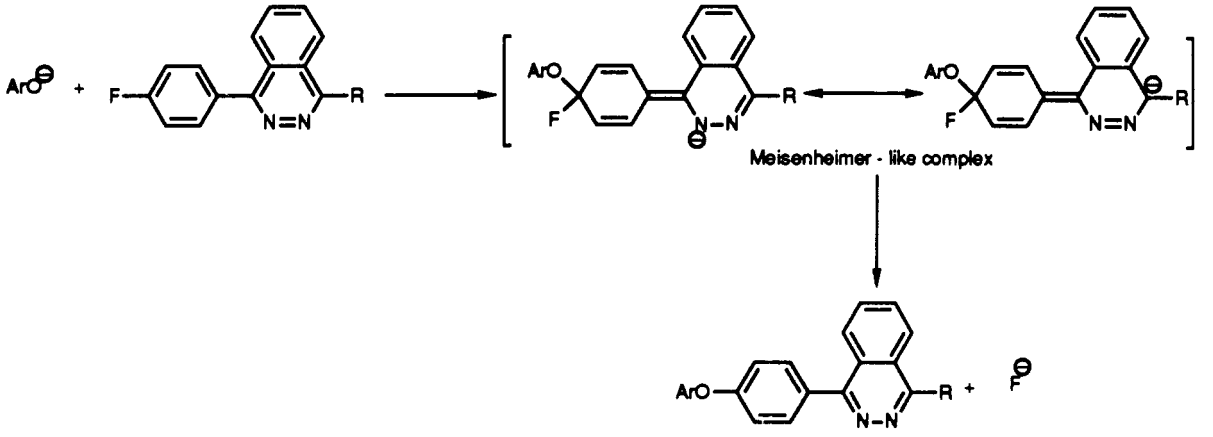
[a] The number of monomer units (n) was experimentally designed for 25 units for polymers **10**, **13**, and **16**, 50 units for polymers **11**, **14**, and **17**, and 70 units for polymers **12**, **15**, and **18**. [b] The exact number of monomer units (n) was determined by ^{1}H NMR measurements. [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.

thalazine)s and to determine absolute molecular weights, end-capped poly(aryl ether ketone)s with 3,5-di-*tert*-butylphenyl terminal groups prepared previously[10] were converted to poly(aryl ether phthalazine)s. The end-capped poly(aryl ether ketone)s **10**–**18** (Scheme II) with a degree of polymerization of $n \sim 25$, 50, and 70 monomer units/chain were converted to poly(aryl ether phthalazine)s **19**–**27** having di-*tert*-butylphenyl as terminal groups. The exact number-average molecular weights determined by ^{1}H NMR studies[11] for the capped poly(aryl ether phthalazine)s and apparent molecular weights determined by gel permeation chromatography using polystyrenes as standards are shown in Table II. Attempts to correlate the apparent molecular weights determined by GPC with the exact molecular weights determined by ^{1}H NMR failed. Solution casting the low molecular weight end-capped poly(aryl ether phthalazine) **19** from chloroform gave a brittle film as did its precursor polyketone **10**, whereas all other polyphthalazines (**20**–**27**) formed flexible films. The increases in chain length of the capped polyphthalazines (**19**–**21**, **22**–**24**, **25**–**27**) are reflected in the increases in inherent viscosities (Table II). The glass transition temperatures of the capped materials were observed to be identical to the uncapped materials shown in Table I. In all of the intramolecular ring-closure reactions of the capped polyketones to polyphthalazines (Talbe II) downfield shifts of the protons in the *tert*-butyl group and isopropylidene moiety are exhibited in the ^{1}H NMR spectra. The *tert*-butyl groups in the polyketones show a resonance at δ 1.27 and the isopropylidene moiety at δ 1.68. The ^{1}H NMR spectra of the polyphthalazines show a prominent downfield shift of the *tert*-butyl group (δ 1.32) and the isopropylidene moiety (δ 1.72) as compared to their precursor polyketones. In both classes of polymers, the polyketones and polyphthalazines, the exact number-average molecular weights for the polymers were calculated from the ratios of the peak areas of the di-*tert*-butyl group and the isopropylidene moiety. From ^{1}H NMR, the results confirmed that the overall ring-closure reactions were complete and that no side reactions or branching occur during the transformation.

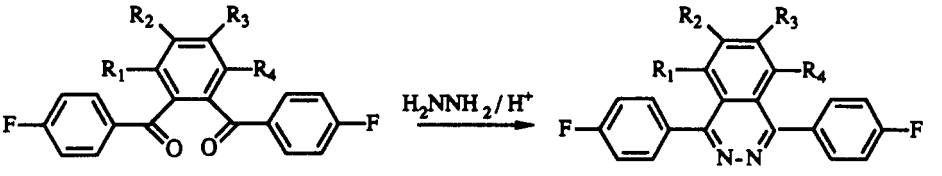
Copolymers **28**–**30** consisting of polymers **12** and **21**, **15** and **24**, and **18** and **27**, respectively, were prepared, and the resulting compositions were determined[11] from ^{1}H NMR studies (Table III). The glass transition temperatures for the copolymers **28**–**30** were found to be 230, and 240,[12] and 271 °C, respectively, which correspond to the calculated figures.

It has been demonstrated that other heterocyclic ring systems, such a benzoxazoles[5] and quinoxalines,[6] activate haloaromatic rings toward nucleophilic aromatic substitution by phenoxides. It has been previously demonstrated

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 $R_1 = R_2 = R_3 = R_4 = C_6H_5$

Table III
Copolymers of Polyketones and Polyphthalazines

copolymer	percent compsn[a] for polyketone/polyphthalazine, %	T_g,[b] °C
28	10/90	230
29	33/67	240
30	78/22	271

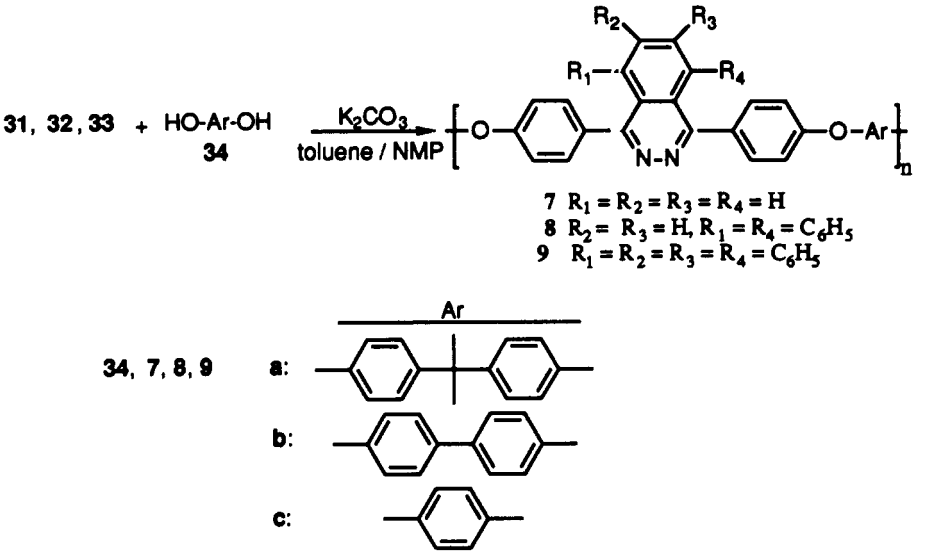
[a] Determined by ^1H NMR studies. [b] DSC measurements.

that the polyphthalazine ring also exerts a deshielding effect, which was illustrated in the ^1H NMR spectra of the copolymer **29** and the homopolymer polyphthalazine **24**.[12] The electron-poor pyridazine ring would also be expected to activate halo groups toward nucleophilic substitution reactions.[13,14] In addition, 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). The electron-withdrawing effect of the pyridazine ring which activates the aryl halide toward an aromatic nucleophilic displacement polymerization reaction is comparable to a ketone, a sulfone, and other activating groups. Fluoro-substituted phthalazine monomers, 1,4-bis(4-fluorophenyl)phthalazine (**31**), 1,4-bis(4-fluorophenyl)-5,8-diphenylphthalazine (**32**), and 1,4-bis(4-fluorophenyl)-5,6,7,8-tetraphenylphthalazine (**33**), were prepared (Scheme IV) by treating the 1,2-bis(4-fluorobenzoyl)benzene monomers **1–3** with hydrazine in an acidic medium.[15] The three phthalazine monomers were isolated in excellent yields.

Polymerization of phthalazine monomer **31** with bisphenols **34a–c** was carried out in an *N*-methyl-2-pyrrolidinone (NMP)/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 180 °C to effect the displacement reaction. After a period of 18 h, high molecular weight poly(aryl ether phthalazine) **7a** was achieved from monomer **31**. The dramatic increase in the viscosity indicated the formation of high molecular weight material. Polyphthalazine **7a** (η_{inh} = 0.56 dL/g) synthesized from phthalazine monomer **31** has ^1H NMR spectrum and glass transition temperature (236 °C) identical with those of polyphthalazine **7a** (η_{inh} = 0.72 dL/g) synthesized from intramolecular ring-closure reaction of polyketone **4a** (η_{inh} = 0.48 dL/g). The 1D ^1H NMR spectrum of polyphthalazine **7a** is shown in Figure 2a, and the 2D ^1H–^1H COSY spectrum (6.8–8.2 ppm) shown in Figure 2b confirms the chemical shift assignment for the aromatic region shown in the 1D ^1H NMR spectrum. The polyphthalazines **7b** (η_{inh} = 0.21 dL/g, T_g = 215 °C) and **7c** (η_{inh} = 0.22 dL/g, T_g = 226 °C) containing the *p,p'*-biphenol and hydroquinone moieties synthesized from phthalazine monomer **31** (Scheme V) precipitated from solution during polymerization. These low molecular weight polymers, inferred from their low inherent viscosities (Table IV), were found to be very soluble in chloroform, unlike the higher molecular weight polyphthalazines **7b** (η_{inh} = 0.56 dL/g, T_g = 250 °C) and **7c** (η_{inh} = 0.54 dL/g, T_g = 260 °C) (Scheme I and Table I) obtained from the intramolecular ring-closure reactions. Higher molecular weight polymers can probably be synthesized using a higher boiling solvent (>200 °C) to maintain a homogeneous solution.

Poly(aryl ether phthalazine)s **8a** and **9a** synthesized from phthalazine monomers **32** and **33** with 4,4'-(1-methylethylidene)bisphenol (BPA), respectively, have glass transition temperatures (Table IV) and ^1H NMR spectra identical with those of the polyphthalazines **8a** and **9a** synthesized from intramolecular ring-closer reactions of polyketones **5a** and **6a**. Both methods gave high molecular weight materials. All three phthalazine monomers were subjected to polymerization reactions in NMP at 180 °C with the bisphenoxides shown in Scheme V. Ph-

Scheme V



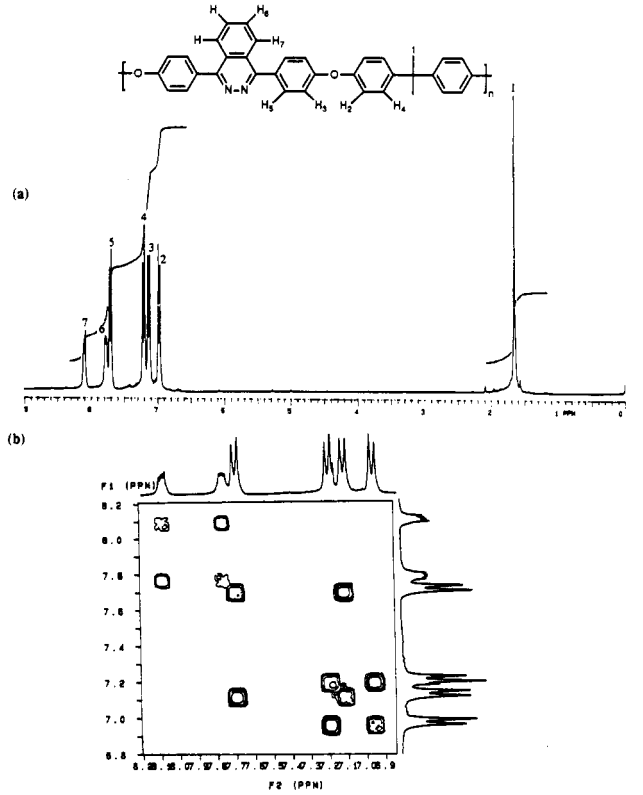


Figure 2. (a) 1D ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of poly(aryl ether phthalazine) **7a**. (b) 2D ^{1}H–^{1}H COSY spectrum (6.8–8.2 ppm) of poly(aryl ether phthalazine) **7a** acquired at 300 MHz ($CDCl_3$). Diagonal aromatic proton resonances in the 2D ^{1}H NMR spectrum are labeled in the 1D ^{1}H NMR spectrum.

thalazine **31** reacted with bisphenol **34a–c** to give polymers **7a–c**, and phthalazines **32** and **33** reacted with bisphenol (BPA) **34a** to give polymers **8a** and **9a**, respectively. Since the polymers synthesized by direct polymerization of the phthalazine monomers with bisphenoxides are identical to those synthesized from intramolecular ring-closure reactions of the poly(ether ketone)s, it further confirms that the reactions are complete and that no side reactions or branching occur during the transformation.

We have also synthesized the poly(aryl ether pyridazine)[16] **38** from 3,6-bis(4-fluorophenyl)pyridazine (**37**; Scheme VI). Fluorobenzene and fumaryl chloride were reacted in a Friedel–Crafts reaction to give *trans*-1,2-bis(4-fluorobenzoyl)ethylene (**35**)[17] which is known to undergo photochemical isomerization[18] to the cis isomer **36**. As depicted in Scheme VI, a one-pot reaction in which the thermal transformation of the trans isomer **35** in excess hydrazine monohydrate and acetic acid to the cis intermediate is accomplished, which then undergoes an intramolecular ring-closure reaction to the 3,6-bis(4-fluorophenyl)pyridazine (**37**). Polymerization of the pyridazine monomer **37** with BPA (**34a**) in an NMP/toluene (2/1) solvent mixture in the presence of potassium carbonate at 180–190 °C for 24 h, to effect the displacement reaction, afforded high molecular weight polymer **38** (T_g = 202 °C, η_{inh} = 0.43 dL/g in chloroform at 25 °C).

Table IV
Properties of Poly(aryl ether phthalazine)s Synthesized from Phthalazine Monomers

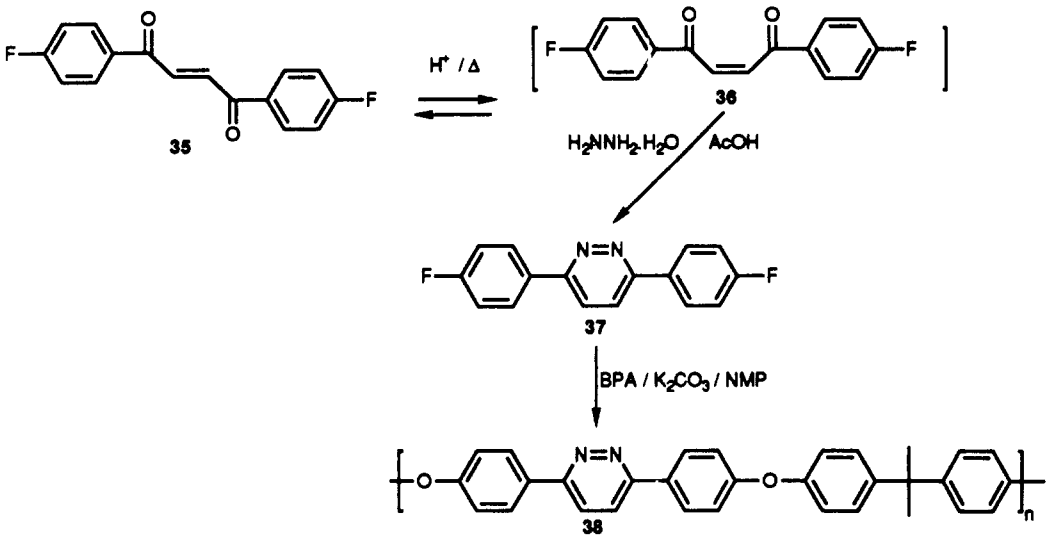
poly(aryl ether phthalazine)	η_{inh},[a] dL/g	T_g, °C
7a	0.56	236
7b	0.21	215
7c	0.22	226
8a	0.66	250
9a	0.49	285

[a] Inherent viscosities were measured at a concentration of 0.5 g/dL in chloroform at 25 °C.

The poly(aryl ether phthalazine)s demonstrated excellent thermooxidative stability by thermogravimetric analysis, with 5% weight losses above 500 °C under atmospheres of air and nitrogen[8] (Figure 3). The poly(aryl ether phthalazine)s **9b–e** synthesized from poly(aryl ether ketone)s **6b–e** (Scheme I) are the most thermally stable by TGA. Isothermal aging (TGA) was done under an atmosphere of nitrogen over an 8-h period to assess the thermal stability of the polymers (Table V). From the aging experiments, the uncapped materials show weight losses of ~1.0%/h under nitrogen, and for polyphthalazine **9b** end-capped using 4-phenylphenol the weight loss measured under air was 1.5%.

The glass transition temperatures determined by DSC for the poly(aryl ether phthalazine)s (Table I) were in good agreement with those determined from dynamic mechanical analysis as shown, for example, for polyphthalazine **9e** in Figure 4. None of the polymers synthesized show any crystalline behavior even after extensive annealing above the T_g. Table VI presents modulus data for the films from poly(aryl ether phthalazine)s synthesized from intramolecular ring-closure reactions of the polyketones. The moduli of the materials range from 2.11 to

Scheme VI



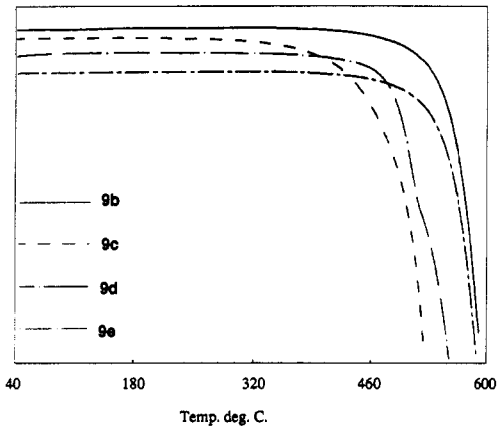


Figure 3. TGA thermograms (weight loss vs temperature) for poly(aryl ether phthalazine) **9b–e** under an atmosphere of N_2.

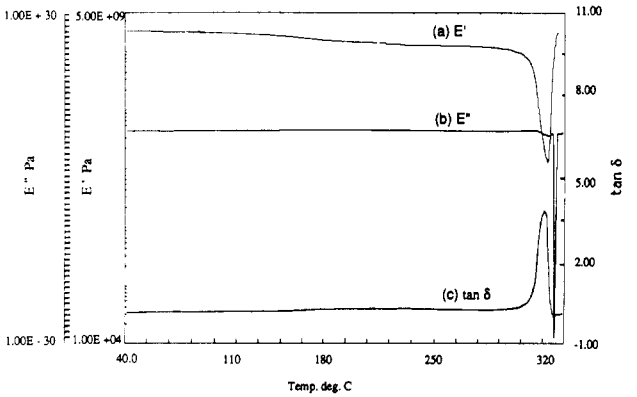


Figure 4. Thermomechanical analysis for poly(aryl ether phthalazine) **9e**: (a) modulus (E') vs temperature; (b) storage modulus (E'') vs temperature; (c) tan δ vs temperature.

Table V
Thermal Properties of Poly(aryl ether phthalazine)s 9b–e

poly(aryl ether phthalazine)	isothermal aging at 400 °C,[a] wt loss %/h	TGA for N_2,[b] °C
9b	1.07 (1.5)[c]	512
9c	0.98	533
9d	0.98	531
9e	1.01	520

[a] Isothermal aging experiments were performed under an atmosphere of N_2, on materials that were not end-capped. [b] Reported for 5% weight loss. [c] Aging experiments performed under an atmosphere of air with 4-phenylphenol as the end-capping agent.

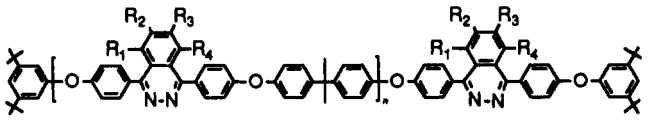
Table VI
Moduli of Polymers at 25 and 200 °C

polymer	modulus for temp 25 °C/200 °C, GPa	polymer	modulus for temp 25 °C/200 °C, GPa
7a	2.74/1.52	**9a**	2.32/2.10
7b	2.81/1.79	**9b**	2.73/2.05
7c	2.79/2.02	**9c**	2.78/2.01
8a	3.98/2.13	**9d**	2.49/1.97
8b	3.46/2.56	**9e**	2.11/1.83
8c	3.48/2.88		

3.98 GPa at 25 °C and 1.52 to 2.88 GPa at 200 °C. The moduli of the films from poly(aryl ether phthalazine)s synthesized from intermolecular nucleophilic displacement reactions of the bisphenoxides with the difluoride phthalazine monomers were the same. Films prepared from the poly(aryl ether phthalazine)s are all tough and show ductile mechanical behavior with no failure at 40% elongation. The moduli of the poly(aryl ether phthalazine)s are all higher than their precursors, the poly(aryl ether ketone)s.[10] The transformation to the polyphthalazines results in a chain straightening, hence resulting in a more rigid system and a stiffer backbone. The moduli of the polyphthalazines (2.11–3.98 GPa) are comparable to other engineering thermoplastics such as poly(aryl ether benoxazole)s[5] and poly(aryl ether phenylquinoxaline)s[6] (~2.5 GPa).

The poly(aryl ether phthalazine)s are amorphous, and the glass transition temperatures increase with increasing numbers of pendant phenyl groups, as was observed with the poly(aryl ether ketone)s. It might be expected that the free volume in the polyphthalazines would increase as the bulky phenyl groups are added. In order to confirm this, we determined the permeation of oxygen in the poly(aryl ether phthalazine)s **21**, **24**, and **27**. Oxygen permeation (Table VII) at 20 °C increases with increasing phenyls in the polymer chain which is indicative of the larger free volume associated with poly(aryl ether phthalazine) **27** containing four phenyls, which has an O_2 permeation value of 2.73. Polyphthalazine **24** which has two pendant phenyls has an O_2 permeation of 1.16, and polymer **21** having no pendant phenyls has an even lower O_2 permeation, 0.54. From these O_2 permeation results it can be concluded that polymer **21** has the smallest free volume, which results from closer interchain packing. Also, polyphthalazine **21** has approximately half the O_2 permeation of its precursor, poly(aryl ether ketone) **12** (1.03),[10] which again is indicative of the resulting chain straightening that occurs in the polyphthalazines, hence giving a more close chain packing than

Table VII
Oxygen Permeation at 20 °C of Poly(aryl ether phthalazine)s



poly(aryl ether phthalazine)	$P^a \times 10^{13}$
21 ($R_1 = R_2 = R_3 = R_4 = H$)	0.54
24 ($R_2 = R_3 = H$; $R_1 = R_4 = C_6H_5$)	1.16
27 ($R_1 = R_2 = R_3 = R_4 = C_6H_5$)	2.73

[a] P in $cm^3 \cdot cm/cm^2 \cdot s \cdot Pa$.

in the polyketones. Similar observations were made with the other polyphthalazines 24 (two pendant phenyls) and 27 (four pendant phenyls) which have lower penetrant diffusion rates than polyketones 15 (two pendant phenyls, 1.27) and 18 (four pendant phenyls, 2.82).

Conclusion

A new class of high-temperature, high-T_g polymers, the poly(aryl ether phthalazine)s, have been synthesized by the intramolecular ring closure of poly(aryl ether ketone)s containing the 1,2-dibenzoylbenzene moiety with hydrazine or via a nucleophilic aromatic substitution reaction of fluoro-substituted phthalazine monomers with bisphenates generating the aryl ether linkages. In the latter reaction, the electron-deficient pyridazine component of the phthalazine ring activates the aryl fluoride substituents toward a nucleophilic displacement polymerization reaction. The nucleophilic displacement polymerization reactions were conducted in NMP in the presence of K_2CO_3 to give high molecular weight polymers. Increases in glass transition temperatures occurred in the polyphthalazines with increasing pendant phenyls in the 1,4-bis(4-fluorophenyl)phthalazine monomers. The materials had 5% weight losses above 500 °C by thermogravimetric analysis, indicative of their high thermal stability. All of the polymers could be readily processed from solution to give 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*-Methyl-2-pyrrolidinone (NMP) was refluxed and distilled over barium oxide. Chlorobenzene, fluorobenzene, acetic acid, dioxane, 4-phenylphenol, and hydrazine monohydrate (98%) were purchased from Aldrich and used without further purification. Bisphenols 4,4'-(1-methylethylidene)bisphenol (BPA) and 4,4'-biphenol were kindly supplied by General Electric Co. and hydroquinone was purchased from Aldrich Chemical Co. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. UV spectra were performed on a SP 800 Unicam ultraviolet spectrophotometer with a deuterium lamp.

1,4-Bis(4-fluorophenyl)phthalazine (31). To a cooled solution of 1,2-bis(4-fluorobenzoyl)benzene (1; 46.6 mmol, 15 g) in glacial acetic acid (300 mL) was added hydrazine monohydrate (90 mL) over a period of 1 h. The reaction mixture was refluxed for 4 h and cooled, and the resulting precipitate was filtered. Recrystallization of the solid from ethanol gave phthalazine 31 as fine needlelike, pale yellow crystals in quantitative yield: mp 219–221 °C; ^1H NMR (200 MHz) δ 7.25 (dd, J = 8.5 Hz, 4 H, 2 ortho C_6H_2F), 7.79 (dd, J = 5.5 Hz, 4 H, 2 meta C_6H_2F), 7.87 (dd, J = 6.4 Hz, 2 H, C_6H_4), 8.13 (dd, J = 6.4 Hz, 2 H, C_6H_4); MS (EI) m/e (calcd for $C_{20}H_{12}N_2F_2$, 317.0889; found, 317.0889) 317 (100), 289 (5.2), 288 (17.3), 145 (10.7); UV (CCl_3H) λ_{max} 270 nm (ϵ 1.29 × 10^4).

1,4-Bis(4-fluorophenyl)-5,8-diphenylphthalazine (32). To a cooled solution of 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene (2; 4.2 mmol, 2 g) in dioxane (20 mL) and concentrated hydrochloric acid (3 mL) was added hydrazine monohydrate (10 mL) over a period of 15 min. The reaction mixture was refluxed for 8 h and cooled and the solvent removed under reduced pressure to give a solid. Recrystallization of the solid from toluene gave a pale yellow powder. Column chromatography 5/1, petroleum ether/ethyl acetate) of the pale yellow solid gave in 98% yield compound 32: mp 301–302 °C; ^1H NMR (200 MHz) δ 6.73 (dd, J = 8.7 Hz, 4 H, 2 ortho C_6H_2F), 7.12 (s, 10 H, 2 C_6H_5), 7.35 (dd, J = 8.7 Hz, 4 H, 2 meta C_6H_2F), 7.98 (s, 2 H, $CH(C_6H_5)_2$); MS (EI) m/e (calcd for $C_{32}H_{20}N_2F_2$, 470.1594; found, 470.1594) 470 (100), 469 (64.2), 393 (28.4), 348 (12.9), 346 (17.5); UV (CCl_3H) λ_{max} 305 nm (ϵ 2.13 × 10^4), 220 nm (ϵ 4.56 × 10^4).

1,4-Bis(4-fluorophenyl)-5,6,7,8-tetraphenylphthalazine (33). To a cooled solution of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (3; 6.4 mmol, 4 g) in dioxane (30 mL) and concentrated hydrochloric acid (3.5 mL) was added hydrazine monohydrate (20 mL) over a period of 1 h. The reaction mixture was refluxed for 18 h and cooled and the solvent removed under reduced pressure to give a solid. Recrystallization of the solid from toluene gave a pale yellow powder. Column chromatography (2/1; petroleum ether/ethyl acetate) of the pale yellow powder gave compound 33 in quantitative yield: mp 346 °C; ^1H NMR (200 MHz) δ 6.62–6.88 (m, 24 H, 4 C_6H_5 and 2 ortho C_6H_2F), 7.25 (dd, J = 8.6 Hz, 4 H, 2 meta C_6H_2F); MS (EI) m/e (calcd for $C_{44}H_{28}N_2F_2$, 622.2220; found, 622.2220) 622 (100), 546 (27.9), 545 (68.1), 517 (10.2), 499 (6.2), 418 (4.5), 302 (2.8); UV (CCl_3H) λ_{max} 245 nm (ϵ 3.48 × 10^4).

3,6-Bis(4-fluorophenyl)pyridazine (37). To a cooled solution of 1,2-bis(4-fluorobenzoyl)ethylene (35; 58.8 mmol, 16 g) in glacial acetic acid (300 mL) was added hydrazine monohydrate (30 mL) over a period of 1 h. The resulting red reaction mixture was heated until a yellow in the solution became persistent (4 h). The reaction mixture was cooled, and a pale yellow solid precipitated, which was filtered to give crude pyridazine 37 in 75% yield. The crude material was recrystallized from acetic acid to give pyridazine 37 as fine needlelike crystals in 48% yield: mp 258–259 °C; ^1H NMR (200 MHz) δ 7.23 (dd, J = 8.7 Hz, 4 H, 2 ortho C_6H_2F), 7.89 (s, 2 H, $C_4H_2N_2$), 8.15 (dd, J = 8.7 Hz, 4 H, 2 meta C_6H_2F); MS (EI) m/e (calcd for $C_{44}H_{28}N_2F_2$, 268.0812; found, 268.0812) 268 (46.1), 238 (3.1), 214 (1.3), 121 (13.3), 120 (100), 100 (1.7); UV (CCl_3H) λ_{max} 258 nm (ϵ 3.18 × 10^4).

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 phthalazine) 21 from Poly(aryl ether ketone) 12. Intramolecular ring-closure reactions were conducted under an atmosphere of nitrogen. A typical synthesis of an intramolecular ring-closure reaction based on a poly(aryl ether phthalazine) 7a is described from polyke-

tone 12 synthesized previously.[7] To a cooled solution of poly(aryl ether ketone) 4a (700 mg)in chlorobenzene (25 mL) and glacial acetic acid (5 mL) was added hydrazine monohydrate (5 mL) over a period of 30 min. The cloudy, colorless reaction mixture was heated at 90 °C for 10 h. The resulting straw yellow reaction mixture was cooled, concentrated under reduced pressure, and diluted in a minimum amount of chloroform (5 mL). The polymer solution 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 phthalazine) 21 in a quantitative yield. Using the above amounts of reagents, solvent, and temperature, copolymer 28 (from partial ring-closure reaction of poly(aryl ether ketone) 12) was isolated after a period of 7 h and its composition determined by ^{1}H NMR studies was found to be 10% polyketone and 90% polyphthalazine. The intramolecular ring-closure reactions of polyketones to polyphthalazines could just as well be conducted in refluxing dioxane with similar amounts of the reagents mentioned above. The intramolecular ring-closure reaction is much faster (5 h) in dioxane than in chlorobenzene, and copolymers require less reagents (acetic acid and hydrazine monohydrate) and shorter times. Syntheses of copolymers (partial ring closure of polyketones) and polyphthalazine homopolymers (from total ring closure of polyketones) conducted in dioxane as the solvent were worked up in a fashion similar to that of the reactions performed in chlorobenzene.

Poly(aryl ether phthalazine) 7a from 1,4-Bis(4-fluorophenyl)phthalazine (31). A detailed synthetic procedure designed to prepare poly(aryl ether phthalazine) 7a from 1,4-bis(4-fluorophenyl)phthalazine (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)phthalazine (31; 6.4 mmol, 2.0 g) and bisphenol (BPA) 34a (6.4 mmol, 1.45 g). Under an inert atmosphere, 1-methyl-2-pyrrolidinone (18 mL) and toluene (9 mL), followed by anhydrous potassium carbonate (19.2 mmol, 2.6 g), were added. Note that potassium carbonate could easily be used in 2–3-fold excess. The reaction mixture was heated until the toluene began to reflux. An optimum temperature range was reached 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 may take 1–2 h. During this stage of the reaction, the solution underwent several color changes. For example, during the initial formation of the phenoxide, a straw yellow was observed, and as the refluxing proceeded, the color changed to brown, green, and then dark brown. Upon completion of dehydration and removal of toluene, the temperature of the reaction mixture increased to 180 °C. The reaction mixture was heated at 180 °C for approximately 18–20 h. Completion of the reaction was qualitatively estimated by the point where the viscosity increased dramatically. The reaction mixture was diluted with chloroform (10 mL) and filtered hot through a thin layer of Celite. The solution was concentrated, coagulated in methanol (30 mL), and filtered to give a 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 phthalazine) 7a in almost quantitative yield.

Poly(aryl ether phthalazine) 21: ^{1}H NMR (200 MHz) δ 1.32 (s, 36 H, 4 $C(CH_3)_3$), 1.72 (s, 6 H, 2 CH_3), 6.97 (d, J = 8.5 Hz, 4 H, 2 meta $C_6H_2C(CH_3)_2$), 7.15 (d, J = 8.5 Hz, 4 H, 2 ortho C_6H_2O), 7.22 (d, J = 8.5 Hz, 4 H, 2 ortho $C_6H_2C(CH_3)_2$), 7.72 (d, J = 8.5 Hz, 4 H, 2 ortho $C_6H_2C_8H_4N_2$), 7.78 (dd, J = 6.1 Hz, 2 H, $C_8H_4N_2$), 8.11 (dd, J = 6.1 Hz, J = 6.3 Hz, 2 H, $C_8H_4N_2$); UV (CCl_3H) λ_{max} 310 nm (ϵ 6.80 × 10^5), 255 nm (ϵ 9.31 × 10^5).

Poly(aryl ether phthalazine) 24: ^{1}H NMR (200 MHz) δ 1.32 (s, 36 H, 4 $C(CH_3)_3$), 1.72 (s, 6 H, 2 CH_3), 6.76 (dd, J = 8.5 Hz, 4 H, 2 meta $C_6H_2C(CH_3)_2$), 6.81 (dd, J = 8.5 Hz, 4 H, 2 ortho C_6H_2O), 7.17–7.25 (m, 14 H, 2 C_6H_5 and 2 ortho $C_6H_2C(CH_3)_2$), 7.33 (d, J = 8.3 Hz, 4 H, 2 meta C_6H_2O), 7.97 (s, 2 H, $C_8H_2N_2(C_6H_5)_2$); UV (CCl_3H) λ_{max} 340 nm (ϵ 8.63 × 10^5), 247 nm (ϵ 2.25 × 10^6).

Poly(aryl ether phthalazine) 27: ^{1}H NMR (200 MHz) δ 1.32 (s, 36 H, 4 $C(CH_3)_3$), 1.72 (s, 6 H, 2 CH_3), 6.63–6.88 (m, 28 H, 4 C_6H_5, 2 meta $C_6H_2C(CH_3)_2$ and 2 ortho C_6H_2), 7.25–7.36 (m, 8 H, 2 ortho $C_6H_2C_8N_2(C_6H_5)_4$ and 2 ortho $C_6H_2C(CH_3)_2$); UV (CCl_3H) λ_{max} 245 nm (ϵ 1.69 × 10^6).

Acknowledgment. We thank Dr. Orval Mamer of the Biomedical Mass Spectrometry Unit for mass spectra, the Natural Sciences and Engineering Research Council of Canada, and General Electric Co. for generous financial support.

References and Notes

(1) Cassidy, P. E. *Thermal Stable Polymers*; Marcel Dekker: New York, 1980.
(2) Stille, J. K. *Macromolecules* **1981**, *14*, 870 and references herein.
(3) Hergenrother, P. M. *J. Appl. Polym. Sci.* **1984**, *18*, 1779. Wrasidlo, W.; Augl, J. M. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 3393.
(4) Arnold, C. *J. Polym. Sci., Macromol. Rev.* **1979**, *14*, 265. Kubota, T.; Nakanishi, J. *J. Polym. Sci., Part B* **1964**, *2*, 655. Moyer, W. W., Jr.; Cole, C.; Anyos, T. J. *J. Polym. Sci., Part A* **1965**, *3*, 2107.
(5) Hedrick, J. L.; Labadie, J. W.; Hilborn, J. G. *Macromolecules* **1990**, *23*, 2854.
(6) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1988**, *21*, 1883. Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23*, 1561.
(7) Singh, R.; Hay, A. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 393. Singh, R.; Hay, A. S. *Macromolecules* **1991**, *24*, 2637.
(8) Singh, R.; Hay, A. S. *Macromolecules* **1991**, *24*, 2640.
(9) Aldissi, M.; Nyitray, A. M. *ACS Symp. Ser.* **1988**, *346*, 559–67.
(10) Singh, R.; Hay, A. S., submitted for publication in *Macromolecules*.
(11) The integral blanking technique (^{1}H NMR, 200 MHz, $CDCl_3$) was used to determine the exact number of protons under a given integral.
(12) The ^{1}H NMR spectra for the homopolymers 15 and 24 and copolymer 29 were illustrated in an earlier publication (ref 8).
(13) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, 2375.
(14) 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**, 354.
(15) Regan, T. H.; Miller, J. B. *J. Org. Chem.* **1966**, *31*, 3053. Blicke, F. F.; Weinkauff, O. J. *J. Am. Chem. Soc.* **1932**, *54*, 1454.
(16) Studies related to the new class of material, the poly(aryl ether pyridazine)s, are presently in progress.
(17) Shephard, M. C.; Worthington, P. A. *U.S. Patent* 4,130,409, 1978.
(18) Pasto, D. J.; Duncan, J. A.; Silversmith, E. F. *J. Chem. Educ.* **1974**, *51*, 277.