

SYNTHESIS OF POLYMERS CONTAINING N–N LINKAGES

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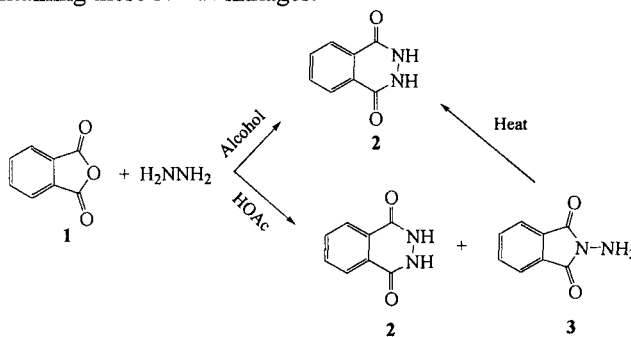
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Abstract The N–N linkage in hydrazine is thermally stable when it is tetrasubstituted and there are electron-withdrawing groups attached to the nitrogen atoms. Our research on the synthesis of polymers containing N–N linkages is reviewed. The *N,N*-bisimide structure has been introduced in the backbone of polymers as well as a pendant group in poly(aryl ether)s to give very thermoxidatively stable polymers with very high glass transition temperatures. Most of the polymers form tough, flexible films. *N*-Aminotriazoles also form stable imides by reaction with anhydrides and these *N*-imidotriazole groups have been introduced as pendent groups on poly(aryl ether)s. The polymers are highly fluorescent materials. Three methods for the synthesis of polymers containing the tetrasubstituted-azine structure will be discussed: (1) oxidative coupling of bisimines; (2) condensation of bishydrazones with diketones; (3) poly(aryl ether azines) from the azine formed from 4-fluorobenzophenone by reaction with salts of bisphenols.

Keywords Hydrazine, *N,N*-linkage, *N*-aminoimide, Poly(imidoaryll ether), *N*-aminotriazole, Polyazine

INTRODUCTION

Drew and coworkers^[1] found that phthalic anhydride **1** reacts with hydrazine to give phthalhydrazide **2** or a mixture of **2** with *N*-aminophthalimide **3**, depending on the conditions (Scheme 1). *N*-Aminophthalimide **3** converts readily to **2** simply by heating. They also found when there are substituents *X*, *Y* in the 3- or 3,5-positions that only the *N*-amino compound **4** was produced^[2]. Naphthalic anhydrides gave only the 6-membered *N*-amino compound **5**^[3]. The *N*-aminoimides behave like ordinary primary amines and readily form *N,N*-bisimides by reaction with anhydrides. The N–N linkage in these molecules is very stable and we have synthesized polyimides containing these N–N linkages.



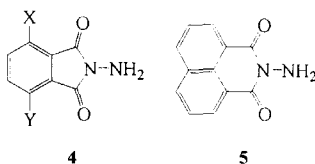
Scheme 1

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linkage is in the polymer chain or in a pendent group as a means to attach functional groups to the polymer chains.



POLYMERS CONTAINING THE *N,N*-BISIMIDE STRUCTURE IN THE BACKBONE

The bis-*N*-aminoimides **6–8** were prepared in high yield by direct reaction of the dianhydrides with hydrazine^[4–7]. Dine-Hart^[3] had previously prepared **6** and attempted unsuccessfully to synthesize polyimides by reaction with dianhydrides. Only insoluble, infusible products were obtained. We also found that only insoluble materials were obtained by reaction of **6** with a variety of dianhydrides^[5]. However, we were able to synthesize high molecular weight copolymers **9** that were soluble. Polymers **9a–c** had either a very high T_g or undetectable T_g and they were very thermally stable as indicated by their 5% weight losses around 500°C (Table 1).

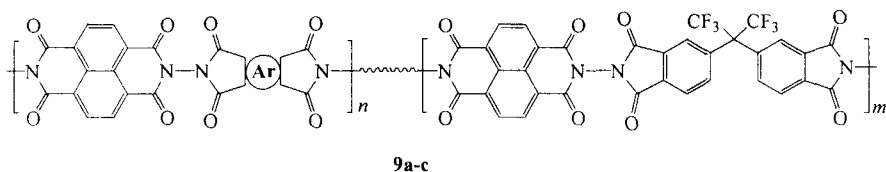
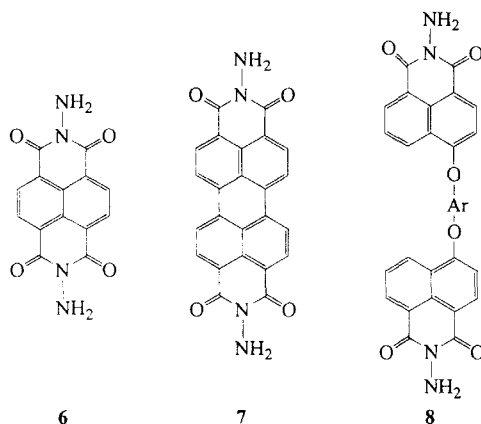
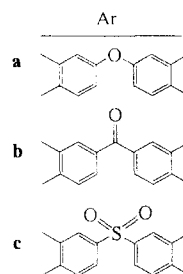


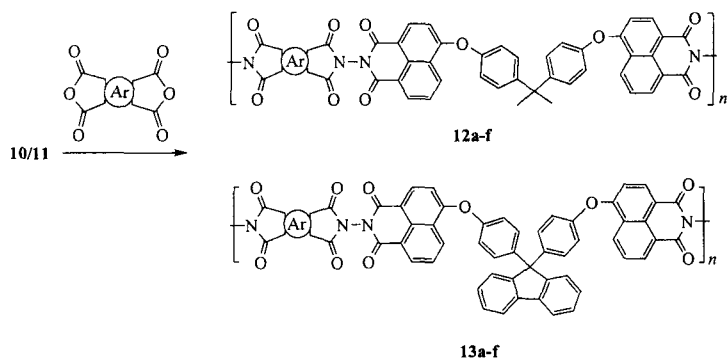
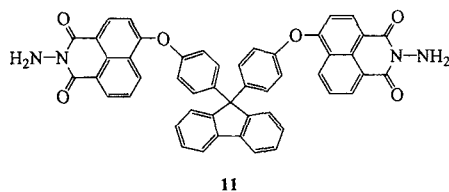
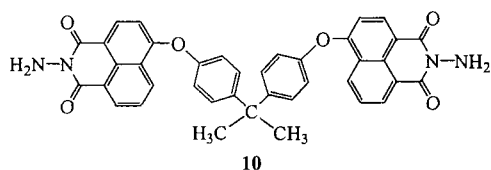
Table 1. Properties of copolymers **9a–c**

Polymer	η_{inh} (dL/g)	T_g (°C)	TGA (°C) ^a	
			N ₂	Air
9a	0.65	438	500	506
9b	0.56	ND	495	526
9c	0.41	ND	497	–

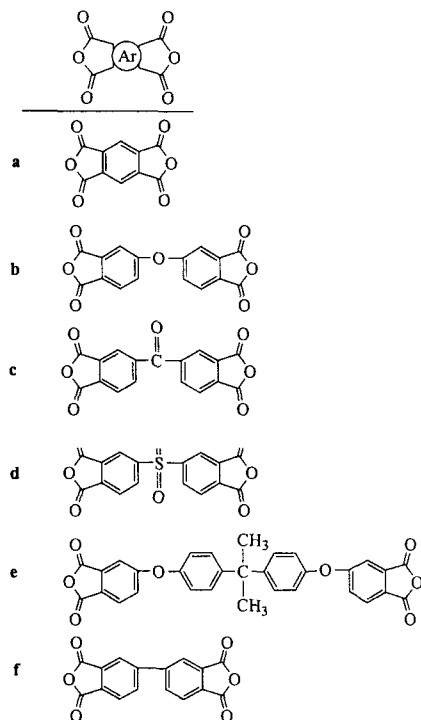
^a 5% weight loss



Very flexible bis-*N*-aminoimides **10**, **11** were synthesized from 4-chloronaphthalic anhydride and the corresponding bisphenols^[4, 7]. Soluble polymers **12a–f** and **13a–f** were obtained with the properties shown in Table 2.

Table 2. Properties of polymers **12a-f** and **13a-f**

Polymer	η_{inh} (dL/g)	T_g (°C)	TGA -5%	
			N ₂	Air
12a	0.47	ND		
12b	0.58	357		
12c	0.54	360		
12d	0.37	362		
12e	0.36	307		
12f	0.47	375		
13a	0.46	436	506	507
13b	0.44	398	510	520
13c	0.45	404	509	521
13d	0.34	400	500	510
13f	0.42	429	515	515



The bis-*N*-aminoimide obtained from perylene tetracarboxylic dianhydride was extremely insoluble and the rate of polymerization was extremely slow. High molecular weight homopolymers could only be synthesized using the very flexible dianhydride **e** (in Table 2) and this polymer was only soluble in solvents like *m*-cresol at elevated temperatures and it was semicrystalline^[6]. Copolymers with *m*-phenylene diamine gave polymers (**14b–c**) with greater solubility and flexible films could be obtained from them (Table 3). The polymers were red in color and fluorescent.

We also prepared a series of arylenebis-thioethernaphthalic anhydrides **15a–e** and the corresponding bis-*N*-amino derivatives **16a–e** (Scheme 2). High molecular weight bisimide polymers **17a–e** were synthesized by reaction of the thioether anhydrides **15a–e** with the bis-*N*-aminoimides **16a–e**^[8]. The properties of these polymers are given in Table 4.

Polyetherimides were also synthesized from the bischloronaphthalic bisimides **18** and **19**^[9] by a nucleophilic substitution reaction with bisphenoxides.

POLYMERS CONTAINING PENDENT *N,N*-BISIMIDE STRUCTURES

Strukelj *et al.*^[10–12] prepared a series of imidoarylbiphenols **20** with a variety of alkyl and aryl groups attached to the nitrogen. Poly(aryl ether)s **21** were synthesized from these monomers that had very high T_g s and were thermoxidatively stable (Scheme 3). Herbert^[13] found that stable *N*-amino derivatives **23** could be prepared from

these polymers by reaction with hydrazine, giving polymers that could be readily functionalized.

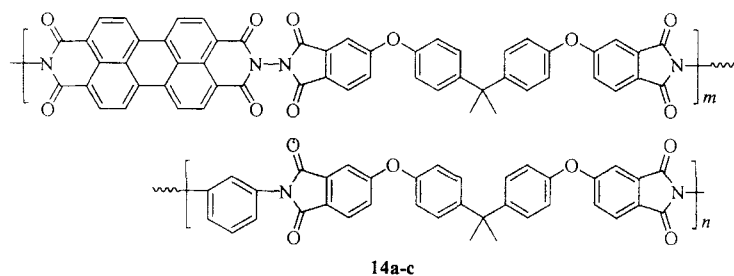


Table 3. Properties of polymers 14a-c

Polymer	<i>m</i> -PD (mol%)	η_{inh} (dL/g)	T_g (°C)	TGA (°C)		Modulus (GPa)		T (°C) $\tan \delta$ max	Solubility	Color
				N ₂	Air	25°C	200°C			
14a	0	0.48	ND	459	470	1.1	0.5	405	<i>m</i> -cresol	dk red
14b	20	0.43	359	453	468	1.5	1.1	366	<i>m</i> -cresol /TCE	dk red
14c	50	0.53	317	464	475	1.9	1.4	328	CHCl ₃	red

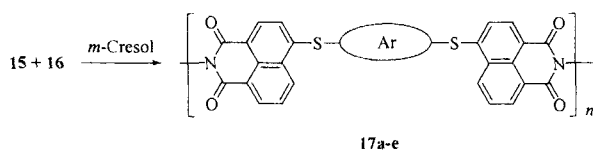
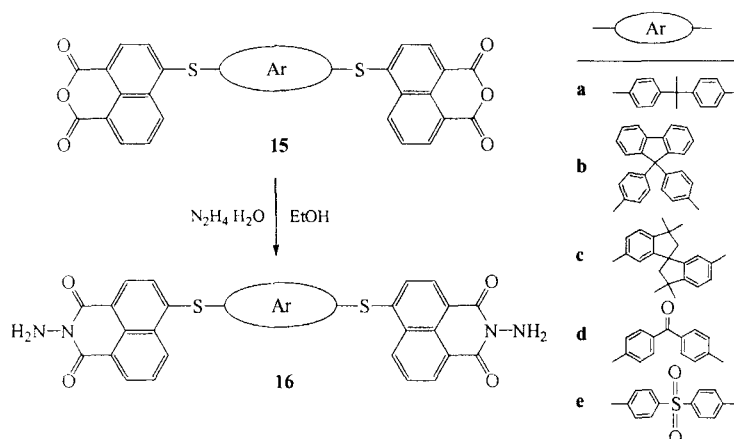


Table 4. Properties of poly(thioether naphthalimide)s 17a-e

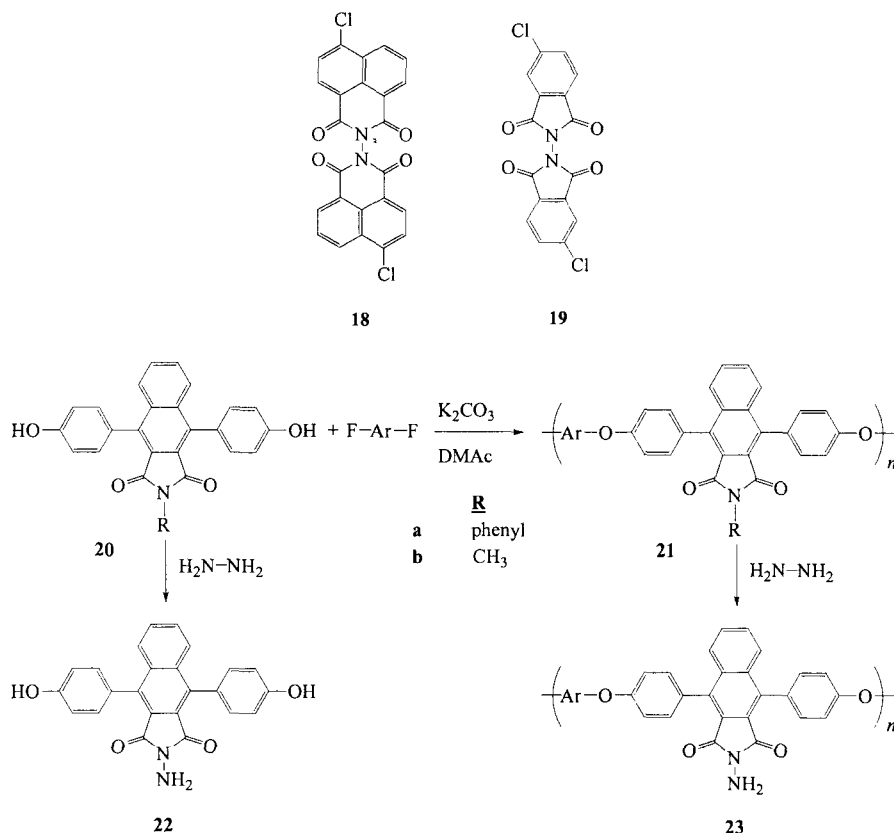
Polymer	η_{inh} (dL/g) ^a	Solubility	T_g (°C) ^b	TGA (°C) ^c
17a	0.85	<i>m</i> -Cresol, CHCl ₃	346	456
17b	1.13	<i>m</i> -Cresol, CHCl ₃	- ^d	500
17c	0.57	<i>m</i> -Cresol, CHCl ₃	322	434
17d	0.65	<i>m</i> -Cresol, CHCl ₃ , PhCl	319	494
17e	1.73	<i>m</i> -Cresol	353	467

^a 0.2 g/dL in *m*-cresol at 40°C; ^b Heating rate of 20 K/min under N₂ (160 mL/min);

^c 5% weight loss in N₂; ^d No T_g observed

Meng and coworkers^[14] prepared the *N*-aminoimidoaryl bisphenol **22** and by reaction with naphthalic anhydride or tetraphenylphthalic anhydride obtained bulky monomers **24a-b** that were converted into poly(aryl

ether)s **25** that had very high T_g s and were very stable thermoxidatively (Scheme 4; Table 5).



Scheme 3

Table 5. Properties of polymers **25**

Polymers	T_g (°C)	TGA-5 (°C)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-6}$)	Color	Solubility
25ad	296	451	Insoluble	CHCl ₃	Brown	Hot DMSO
25ae	266	450	0.46	1.82	Yellow	CHCl ₃ , TCE, DMSO
25af	315	490	0.57	1.86	Yellow	CHCl ₃ , TCE, DMSO
25bd	308	466	Insoluble	CHCl ₃	Yellow	Hot DMSO
25be	301	477	0.43	1.53	Yellow	CHCl ₃ , TCE, DMSO
25bf	ND	450	4.6	0.46	Yellow	CHCl ₃ , TCE, DMSO

POLYMERS CONTAINING PENDENT STRUCTURES DERIVED FROM *N*-AMINOTRIAZOLES

The synthesis of 3,5-diphenyl-*N*-aminotriazole **26** can be readily carried out in high yield in a one-step process by the reaction of benzonitrile with hydrazine dihydrochloride^[15, 16]. By reaction of **26** with the imidobisphenol **27**^[14] previously prepared we synthesized the monomer **28** (Scheme 5). Poly(aryl ether)s **29a–d** were synthesized by reaction with activated fluorides and the properties of these polymers are given in Table 6^[17] (Scheme 6).

Alternatively we were able to synthesize the bis(hydroxyphenyl)triazole **30**. Reaction with phthalic anhydride **31a** or *t*-butylphthalic anhydride **31b** gave the imido-substituted biphenols **32a** and **32b** (Scheme 7). Poly(aryl ether)s **33a–e** and **34a–d** were synthesized and the properties of these polymers are shown in Table 7 (Scheme 8). All of the polymers synthesized were highly fluorescent materials with high T_g s as well as being

thermoxidatively stable as indicated by the TGA measurements.

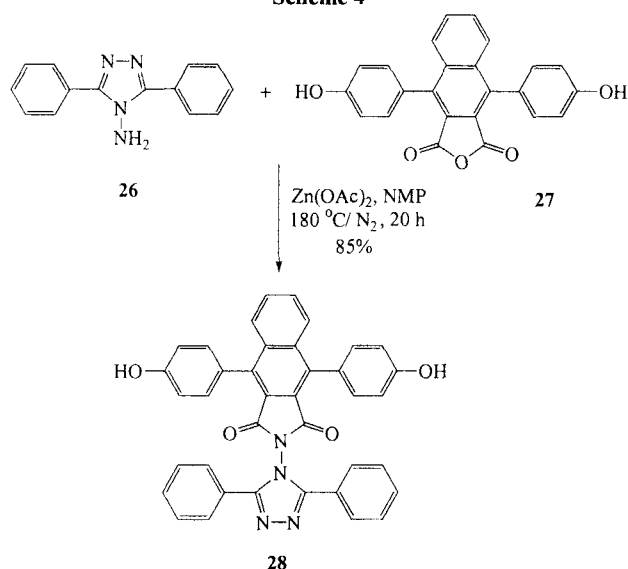
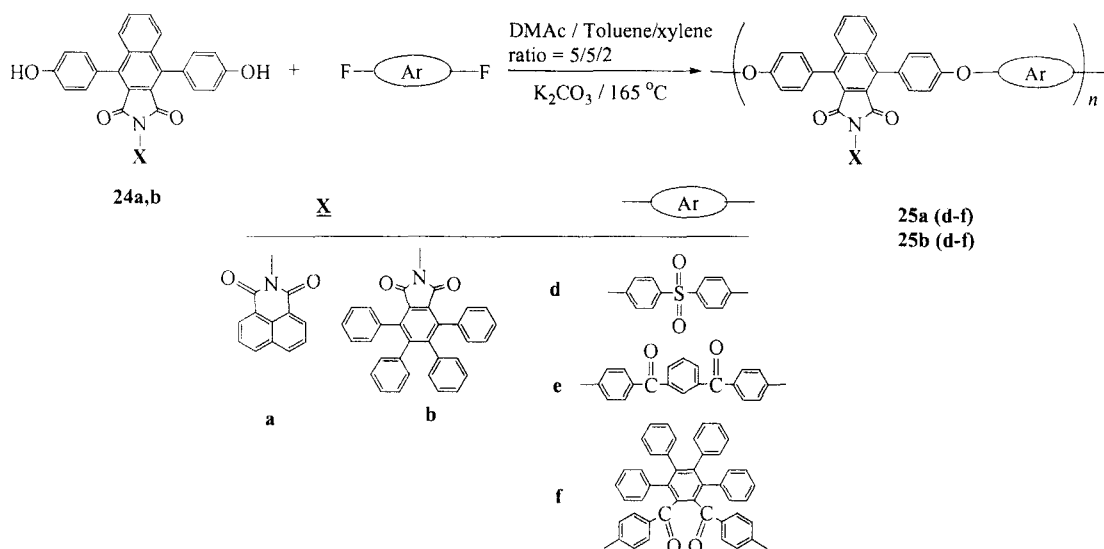


Table 6. Solution viscosities and thermal properties of polymers **29a–d**

Polymer	Yield (%)	η_{inh} (dL/g) ^a	T_g (°C)	T_d (°C) (–5 wt%)
29a	92	0.50	280	412
29b	90	0.37	258	426
29c	45	0.18	242	432
29d	89	0.37	222	415

^a Determined in DMF at 25 °C (0.2 g/dL)

POLYMERIC AROMATIC AZINES

Conjugated polyazine structures **35** have been synthesized by condensation of 1,2-diketones with the corresponding bishydrazones and their spectroscopy and conducting properties have been reviewed^[18]. All of the

polymers synthesized appear to be low molecular weight materials. Poly(aryl ether azines) have also been synthesized from the bisphenol derived from 4-hydroxybenzaldehyde and hydrazine followed by reaction with activated aromatic bishalides^[19]. High molecular weight polymers with T_g s in the range of 151–227°C were synthesized.

There are no reports of high molecular weight tetraaryl-substituted polyazine structures. We have explored three different routes for the synthesis of such structures. Our preliminary results are reported below.

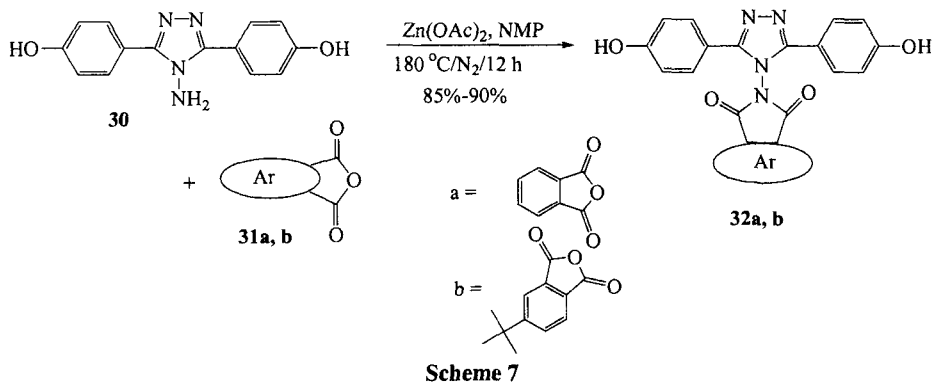
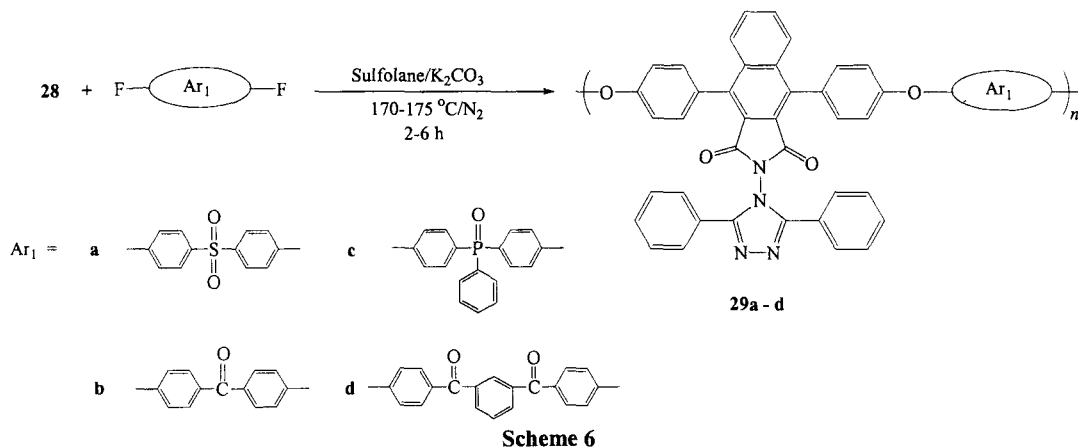


Table 7. Solution viscosities and thermal properties of polymers 33a–e, 34a–d

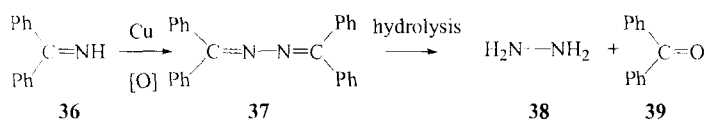
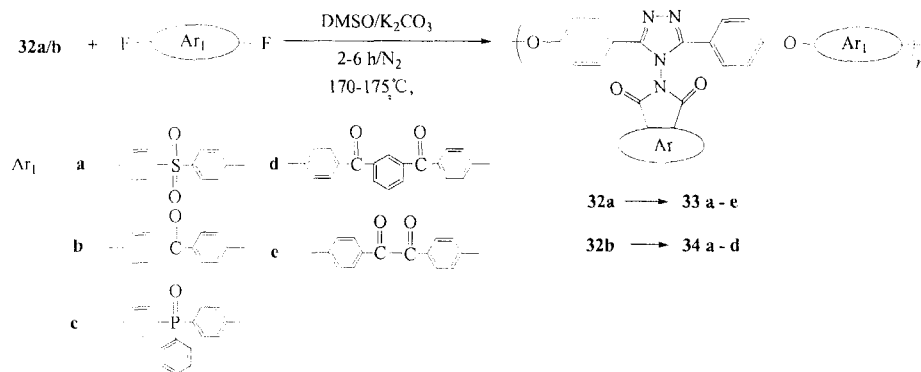
Polymer	Polymerization T (°C)/ t (h)	Yield (%)	η_{inh} (dL/g) ^a	T_g (°C)	T_d (°C) (–5 wt%)
33a	170/ 2	95	0.64	266	437
33b	175/2.5	97	0.88	245	419
33c	175 / 6	90	0.42	283	433
33d	175 / 2	93	0.38	201	437
33e	130 - 40/2	83	0.28	208	361
	150 / 5				
34a	170/2	91	0.65	250	411
34b	175/2	94	1.09	237	404
34c	175/6	94	0.34	270	423
34d	175/1	93	0.45	220	424

^a In DMF at 25 °C (0.2 g/dL)

Oxidative Coupling of Bisimino Compounds

The oxidative coupling of benzophenone imine **36** to the azine **37** followed by hydrolysis to hydrazine **38** and benzophenone **39** has been studied as a commercial route for the synthesis of hydrazine^[20] (Scheme 9). The

conversion to azine proceeds in high yield; however, the starting imine utilized is a mixture of the imine with benzophenone.



We have synthesized the bisimino monomers **40a-f**. Utilizing a copper/amine complex as catalyst derived from copper (I) chloride and *N,N,N',N'*-tetramethylethylenediamine that is an effective catalyst for oxidative coupling of phenols^[21] and acetylenes^[22] (Scheme 10) we were only able to synthesize relatively low molecular weight polymers (Table 8). The monomers are difficult to purify and hydrolysis of the imino groups during the polymerization reaction probably takes place.

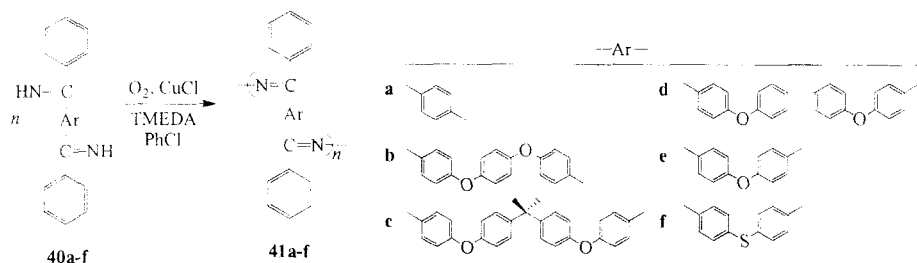
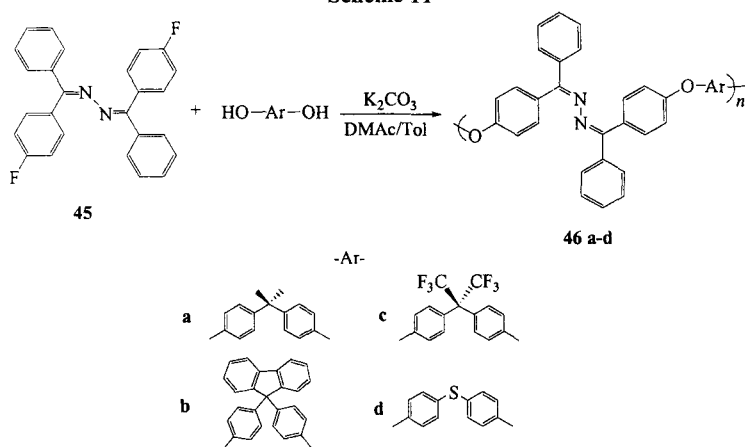
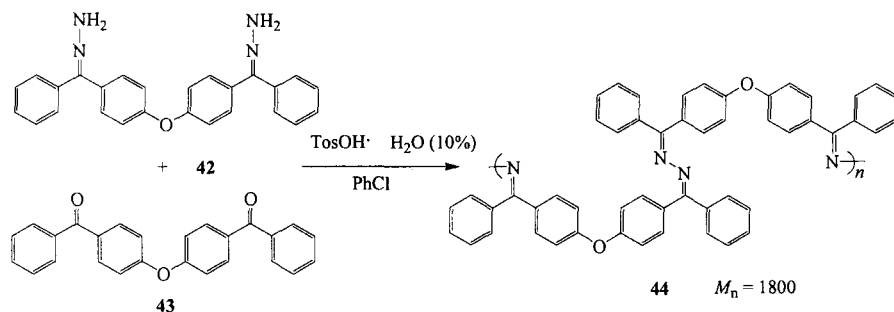


Table 8. Polyazines **40a-f**

Polymer	Yield (%)	M_n	M_w
40a	80	Insoluble	-
40b	82	6200	10100
40c	78	2400	3200
40d	74	2200	2900
40e	26	2300	2700
40f	76	2400	3100

Condensation of Diketones with Bishydrazones

Preliminary studies on the condensation of bishydrazones **42** with diketones **43** in the presence of *p*-toluene sulfonic acid as catalyst gave only very low molecular weight polymers (Scheme 11).

**Table 9.** Properties of aromatic poly(ether azines) **46a–d**

Polymer	$M_n (\times 10^3)$	$M_w (\times 10^3)$	PDI	T_g (°C)	TGA -5%	Yield (%)
46a	30.4	45.5	1.49	154	383	91
46b	35.1	57.5	1.64	215	392	94
46c	71	103	1.45	168	387	96
46d	15	27	1.79	136		84

Poly(aryl ether azines)

High molecular weight poly(aryl ether azines) **46a–d** were synthesized by a nucleophilic substitution reaction between the difluorotetraphenyl azine **45** and various phenols (Scheme 12). The properties of these polymers are given in Table 9. The T_g s of the polymers are in the same range as the poly(ether azines) prepared from the azines of dialdehydes previously reported^[19].

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