Synthesis of High Performance Aromatic Polymers *via* Nucleophilic Nitro Displacement Reaction

T. TAKEKOSHI

General Electric Company, Research and Development Center, Schenectady, New York 12301, U.S.A.

ABSTRACT: Nucleophilic displacement reaction of activated aromatic nitro groups with various nucleophiles is a useful and versatile method for the synthesis of aromatic compounds such as ethers, thioethers and other functionalized intermediates and polymers. Various strong electron withdrawing groups can activate aromatic nitro groups. Effective activating groups include cyano, nitro, sulfone and carbonyl groups such as ester, ketone, anhydride, imide, etc. The reaction of activated nitro compounds with bisphenols and bisthiophenols yields bisethers and bisthioethers from which various aromatic polymers containing ether and sulfide groups can be derived. In many cases, nitro displacement reactions are essentially quantitative so that high molecular weight polymers are directly prepared by the displacement reaction of difunctional nitro compounds with bisphenols or bisthiophenols. Another type of unique nitro displacement occurs in the presence of catalytic amount of a nucleophile at higher temperatures resulting de-nitro coupling of two molecules of nitro compound to form substituted diarylethers.
   KEY WORDS   Nitro Displacement / Aromatic Ether / Dianhydride / Polyarylene Ether / Polyetherimide / Phthalonitrile Ether /

Intensive investigations on high temperature polymers in recent decades have lead to development of a large number of thermo-oxidatively stable polymers. Basic structures of these polymers are composed of difficult-to-oxidize "electron sink" such as aromatic rings with electron-withdrawing groups and heteroaromatic system. Polar and rigid structures of high symmetry associated with such aromatic ring systems are responsible for general lack of adequate processability of these polymers. More recently, greater efforts have been made by many researchers in improving processability of high temperature polymers. One of the effective approaches toward such goal is to insert aromatic ether linkages in the main chains of heteroaromatic systems. In general, such a structural modification lead to reduction of energy of internal rotation of the chains, resulting in lowering glass transition temperatures and crystalline melting temperatures. As a result the process characteristics of polymers are significantly improved without greatly sacrificing their thermal stability. However, few convenient synthetic methods have been available for the formation of aromatic ether bonds in high yields. Recently, it has been shown that certain activated aromatic nitro groups can be readily displaced by phenolate and thiophenolate anions to form various aromatic ethers and thioethers.[1,2] In this article we wish to review recent development of nitro displacement reaction in the synthesis of ether-containing aromatic monomers and polymers.

Nucleophilic displacement reactions of aromatic nitro groups have been known for many years.[3] Laubenheimer[4,5] described displacement of the nitro group of 3,4-dinitrochlorobenzene by aniline to form 2-nitro-5-

chlorodiphenylamine. The presence of co-product, nitrile ion was also confirmed by isolation of 4-aminoazobenzene which was the coupling product of aniline and benzenediazonium cation, the latter was in turn formed by the reaction of aniline and nitrous acid. Interestingly, very little had been described on the application of nitro displacement reaction unitl Gorvin[6] demonstrated the reaction of 2,2'-dibromo-4,4'-dinitrobenzophenone (I) and methoxide as shown in eq 1.

(1)
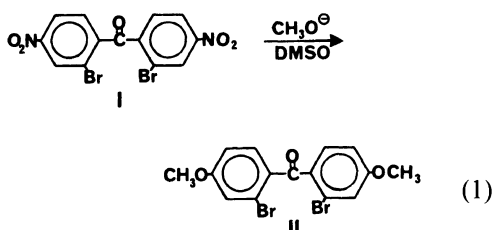
The reaction was nearly quantitative, indicating that the nitro groups were far more reactive than the bromo groups.

The successful result of Gorvin was attributed to the use of a dipolar aprotic solvent for the first time. In general, use of dipolar solvents is required in order to attain high yield of the product at moderate temperatures.

Caswell,[7] Beck,[8–10] Wirth,[11–13] Kornblum,[14] and Williams[15–17] have since shown that nitrobenzene derivatives with other strong electron-withdrawing groups undergo nitro displacement reactions. Among the acti-

vating groups, cyano group was the most effective followed by N-substituted imide, keto, and ester groups. Generally, phenolates used for nitro displacement reactions are required to be substantially anhydrous. In the presence of water, the ester and imide derivatives are readily deactivated by hydrolysis and ring-opening reaction, respectively. However, cyano and ketone derivatives are less sensitive to the presence of minor amount of water. In those cases, free phenols can be used in the presence of alkali carbonates or hydroxides. Under normal conditions, the coproduct, alkali nitrite does not undergo undesirable side reaction. However, during a prolonged reaction particularly at elevated temperatures, nitrite ions may attack other nucleophilic sites of the starting compounds or products.[17,18]
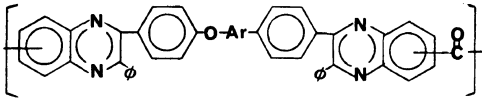
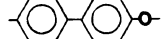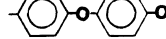## DISPLACEMENT ON NITRO DERIVATIVES OF AROMATIC KETONES

Radlmann[1] demonstrated for the first time that nitro displacement reactions were quantitative enough to form high molecular weight aromatic polyethers. Various polyetherketones were synthesized by the reaction of 4,4'-dinitrobenzophenone and bisphenols as shown in Table I.

α,β-Diketo groups can also activate aromatic nitro groups. Bis(bibenzyl)ethers (IV) were synthesized from 4-nitrobenzyl (III) and

Table I. Polyetherketones *via* nitro displacement[1]

HO–Ar–OH	Polym. temp	Polym. solvents	η_{rel} in NMP at 0.2%	Polymer melt temp
	°C			°C
Bisphenol A	65	DMSO/PhCl	1.32	195—220
4,4'-Dihydroxybiphenyl	145	DMSO	1.18	236—255
4,4'-Dihydroxydiphenylsulfone	140	DMSO	1.07	201—228

Table II. Polyetherquinoxalines[20]

–Ar–	Solvent	η_{rel}[a]	T_g[b]/°C
Nil	m-Cresol	0.77	285
	m-Cresol	0.56	264
	m-Cresol	0.62	278
	m-Cresol	0.52	248

[a] Measured in 0.5% solution in tetrachloroethane.
[b] Measured by thermomechanical analysis.

various bisphenols.[19]

$$(2)$$
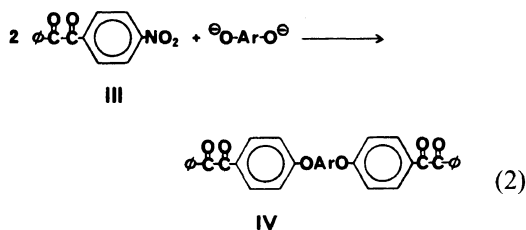
Reaction of (IV) and various tetraamines (V) afforded polyquinoxalines with improved processability,[19,20] Table II.

$$(3)$$
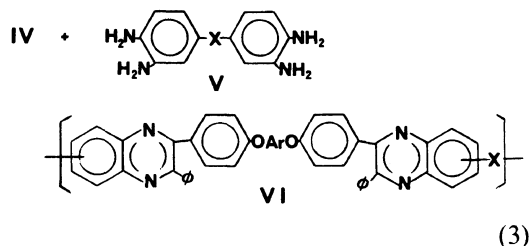
## DISPLACEMENT ON NITROBENZOIC AND NITROPHTHALIC ESTERS

Nucleophilic displacement of nitrobenzoic esters with phenoxides afforded various diphenylethercarboxylic esters in good yields.[2] Nitrophthalic esters are generally substantially more reactive than nitrobenzoic esters, except 3-nitrophthalic esters, for which the reaction

was sluggish pressumably because of the steric effect.[17] When difunctional phenolates were used, various di- and tetra-carboxyl esters of aromatic bisethers were obtained, as summarized in Table III.[2] Many of the products are useful intermediates for the synthesis of aromatic polyesters, polyamides and polyimides in which aromatic ether linkages are incorporated.

DISPLACEMENT ON NITROBEN-ZONITRILES AND NITRO-PHTHALONITRILES

The cyano activated nitro displacement reactions have been reported by Ringer,[21,22] Beck,[8,9] Snyder,[23] and Wirth.[11,12] The cyano group is one of the strongest activating groups in nucleophilic nitro displacement reactions. In particular, 3- and 4-nitrophthalonitriles reacted with phenolates at room temperature in DMSO as shown in Table IV.[11,12] The reaction proceeded reasonably well at room temperature even with poorly nucleophilic phenols such as salicylaldehyde, 2-cyanophenol, 2-nitrophenol and 4,4'-dihydroxydiphenylsulfone.

Bisphthalonitrile ethers (VII) could be hydrolyzed to the corresponding tetraacid which were in turn converted to bis(ether anhydride)s (VIII).[12,24]

$$(4)$$
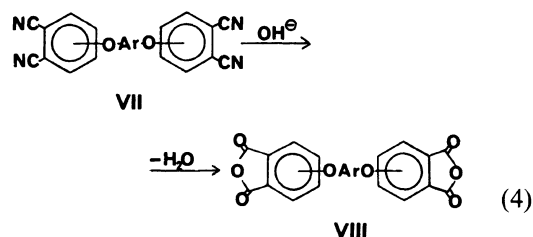
Because phenolate ions are more nucleophilic than amino or carboxylate groups, phenols containing the latter groups can displace activated nitro compounds without protecting these functional groups.[2,25] Various bisaminophenyl ethers (IX) were synthesized from aminophenols and dinitrobenzo-

Table III. Nitro displacement reactions on nitrobenzoic and nitrophthalic esters

Phenols	Nitroesters	Solv./temp, °C	Products	
			Yield/%	mp/°C
Phenol	Phenyl 4-nitrobenzoate	DMF/100	81	94—95
Phenol	Phenyl 4-chlorobenzoate	DMF/100	<1	
Phenol	Phenyl 2-nitrobenzoate	DMF/95	42	109—110
Bisphenol A	2 × Ethyl 4-nitrobenzoate	DMSO/110	64	106—107
4,4′-Dihydroxybiphenyl	2 × Ethyl 4-nitrobenzoate	DMSO/130	70	157—158
Phenol	Diethyl 4-nitrophthalate	DMSO/100	95	bp 150—160 0.15 Torr
Phenol	Diethyl 2-nitroterephthalate	DMSO/100	86	bp 160 0.1 Torr
4-Aminophenol	Diethyl 4-nitrophthalate	DMSO/110	96	74—76
3-Aminophenol	Diethyl 4-nitrophthalate	DMSO/100	64	bp 220 0.15 Torr
Hydroquinone	2 × Diethyl 4-nitrophthalate	DMSO/100	53	48—50
Hydroquinone	2 × Diethyl 2-nitroisophthalate	DMSO/100	55	102—103
Hydroquinone	2 × Diethyl 2-nitroterephthalate	DMSO/100	27	124—125

Table IV. Nitro displacement reactions on nitrobenzonitriles and nitrophthalonitriles

Phenols	Nitro cpds.[a]	Solv./temp, °C	Products	
			Yield/%	mp/°C
Phenol	4-BN	DMSO/70	88.4	—
Phenol	2-BN	DMSO/70	98	—
4-Hydroxybenzoate	4-BN	DMSO/80	90	203.5—204.5
Hydroquinone	4-BN	DMF/120	93.4	212—213.5
Bisphenol A	4-BN	DMSO/70	93.2	106
Bisphenol A	2-BN	DMSO/70	96.2	127—127.5
Phenol·	4-PN	DMSO/RT	95.5	100—101
2-Cyanophenol	4-PN	DMSO/RT	69	134—136
2-Nitrophenol	4-PN	DMSO/RT	69	167—168
2-Hydroxybenzaldehyde	4-PN	DMSO/RT	60	144—146
Hydroquinone	4-PN	DMSO/RT	61	255—257
Resorcinol	4-PN	DMSO/RT	94.6	180—181
2-Chlorohydroquinone	4-PN	DMSO/RT	91	204—205.5
Bisphenol A	3-PN	DMSO/RT	100	179—180
Bisphenol A	4-PN	DMSO/RT	86	195—196
4,4′-Dihydroxybiphenyl	4-PN	DMSO/RT	96	233—233.5
4,4′-Dihydroxy-3,3′-dimethylbiphenyl	4-PN	DMSO/RT	97	238—241
4,4′-Dihydroxydiphenyl ether	4-PN	DMSO/RT	96.8	195—196
4,4′-Dihydroxydiphenyl sulfide	4-PN	DMSO/RT	75.1	175—177
4,4′-Dihydroxydiphenylsulfone	4-PN	DMSO/RT	60	229—230

[a] BN, nitrobenzonitrile; PN, nitrophthalonitrile.

nitriles as shown in Table V.

(5)
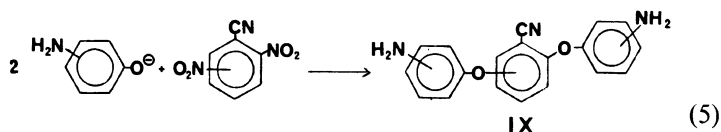
Table V. Nitro diplacement reaction on dinitrobenzonitriles with aminophenols

Reactants		Solv./temp, °C	Bis(aminophenoxy)benzonitriles	
Phenols	Benzonitriles		Yield/%	mp/°C
2-AP[a]	2,6-DBN[b]	DMSO/50	88	167—169
3-AP	2,6-DBN	DMSO/115	—	88—90
4-AP	2,4-DBN	DMSO/75	91.5	193—195
4-AP	2,6-DBN	DMSO/115	55	211—212
4-AP + 3-AP[d]	2,6-CNBN[c]	DMSO/50/120	76[e]	169—171

[a] AP, aminophenol.
[b] DBN, dinitrobenzonitrile.
[c] 2,6-CNBN, 2-chloro-6-nitrobenzonitrile.
[d] 4-AP (0.5 part) was added at 50°C and then 3-AP (0.5 part) at 120°C.
[e] The product was 2-(3-aminophenoxy)-6-(4-aminophenoxy)benzonitrile.

**Table VI.** Nitro displacement polymerization of dinitrobenzonitriles and bisphenol salts[40]

Dinitro[a] cpds.	Bisphenols[b]	React. condtn. Solv./temp, °C	Polymers				
			Yield %	$[\eta]$ dl g^{-1}	T_g[c] °C	TGA[d]/°C Air	N
2,4-DBN	BPA	DMSO/115	81	0.68	141	430	430
2,6-DBN	BPA	DMSO/145	75	0.51	173	385	420
2,4- and 2,6-DBN (1:1)	BPA	DMSO/140	89	0.60	160	420	425
2,4-DBN	4,4'-DDE	DMSO/140	79	0.24	136	360	380
2,6-DBN	4,4'-DDS	DMSO/115	77	0.40	147	450	450
2,4-DBN	4,4'-DDS	DMSO/115	85	0.32	134	450	450
2,6-DBN	Resorcinol + BPA (1:1)	DMSO/115	75	0.34	155	390	400
2,6-DBN	HQ + BPA (1:9)	DMSO/114	—	0.55	176	415	430
2,6-DBN	2-Cl-HQ + BPA (1:1)	DMSO/115	88	0.50	174	430	410
2,6-DBN + DDSO (1:1)	BPA	DMSO/150	91	0.38	178	430	420

[a] DBN, dinitrobenzonitrile; DDSO, 4,4-dichlorodiphenylsulfone.
[b] DDE, dihydroxydiphenyl ether; DDS, dihydroxydiphenylsulfide; HQ, hydroquinone.
[c] Measured by DSC.
[d] Temperature at which 1% of weight loss was observed.

Polyetheramides with pendant cyano groups have been synthesized from IX.[25]

Similarly, 4-(3-aminophenoxy)phthalonitrile (X) have been obtained from 3-aminophenol and nitrophthalonitrile.[26] Recent literatures[27–30] indicated that 1,2-dicyano compounds such as succinonitrile, phthalonitrile and 1,2,4,5-tetracyanobenzene underwent cyclopolycondensation with various diamines to form thermally stable cross-linked polymers. We have shown that phthalonitrile moieties can be incorporated at the end groups of thermally stable and readily processable polyetherimides (XI) by using (X) as a chain capping agent.[26]

XI
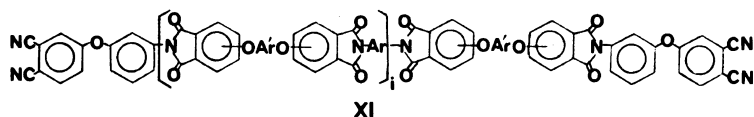
Similarly, phthalonitrile end groups have been also incorporated into polyethersulfones (XII).[26]

XII
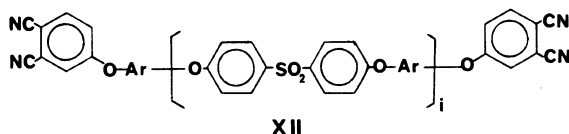
The above phthalonitrile terminated oligomers were cured effectively when they were heated at 200—250°C in the presence of tetraamines such as 3,3',4,4'-tetraaminobenzophenone. The crosslink density could be increased by addition of bisphthalonitrile ethers listed in Table IV. The crosslinking was found to be the result of the formation of 1,2-bisbenzimidazole (XIII) moiety as illustrated by the following model reaction of phthalonitrile and o-phenylenediamine.[26]
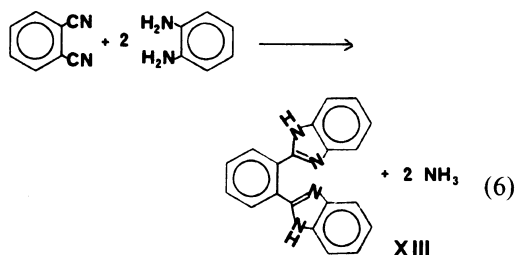

More recently, comparable phtharonitrile resin systems were also described by Keller et al.[31,32] Interestingly, 4,4'-bis(3,4-dicyanophenoxy)biphenyl was reported to give an electrically conductive substance when it was cured at 450°C under inert atmosphere.[33]

NITRO DISPLACEMENT POLYMERIZATION ON DINITROBENZONITRILES

Because of extremely strong activation by the cyano group, the two nitro groups of 2,4- and 2,6-dinitrobenzonitriles (XIV) were both readily displaced. High molecular weight aromatic polyethers containing pendant cyano groups were prepared by nitro displacement polymerization of XIV with various bisphenol salts as shown in Table VI.[11]
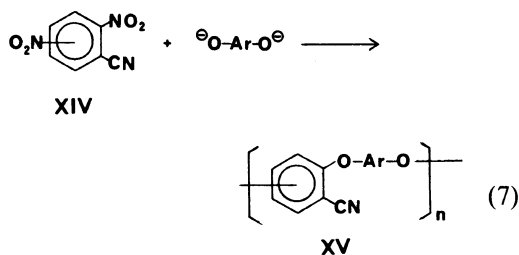
The majority of polyethernitriles were soluble in chlorinated hydrocarbons and tough flexible films were obtained from the solutions. High glass transition temperatures and excellent thermal stabilities of polyethernitriles were attributed to their aromatic structures and high polarity of cyano groups.
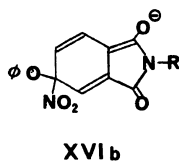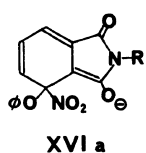
NITRO DISPLACEMENT ON NITROPHTHALIMIDES

Nitro groups activated by two carbonyl groups are very labile to nucleophilic displacement.[11,16,34-36] In particular, activation by cyclic imide groups is prominent. The high reactivity of N-substituted nitrophthalimides (XVI) is attributed to the "locked" conformation of two carbonyl groups in relation to the plane of the benzene ring as well as their strong electron-withdrawing effect. The neg-

196

Table VII. Bis(ether anhydride)s[36]

| -Ar-	Isomer	Yield	mp
		%	°C
	3,3'-	100	228—229.5
	4,4'-	89.9	284.5—286
	3,3'-	98.0	306—307
	4,4'-	91.2	265—266
	3,3'-	88.9	280—281
	4,4'-	100	285—286.5
	3,3'-	97.0	186.5—187.5
	4,4'-	85.0	189—190
	3,3'-	98.9	254—255.5
	4,4'	100	238—239
	3,3'-	46.6	257—257.5
	4,4'-	97.0	189—190
	3,3'-	57.9	230.5—231.5
	4,4'-	99.6	251.5—252
	3,3'-	59.0	278—279
	4,4'-	70.5	215—216

ative charge on the expected Meisenheimer intermediate is, therefore, well delocalized by the contribution of the following resonance structures (XVIa and XVIb):


XVI a   **XVI b**

N-substituted 3- and 4-nitrophthalimides (XVI) were readily converted to bisetherimides (XVII) by nitro displacement reaction with various bisphenolate salts.
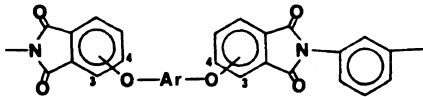
$$\textbf{XVI} \;+\; {}^{\ominus}\text{O--Ar--O}^{\ominus} \longrightarrow$$

$$(8)$$
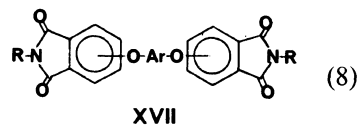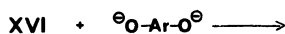
XVII

Hydrolysis of XVII, followed by cyclodehydration of the resulting tetraacids, afforded bisetheranhydrides (VIII), which are listed in Table VII.[35,36]
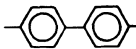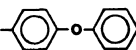
$$\textbf{XVII} \xrightarrow{\text{OH}^{\ominus}} \xrightarrow{-\text{H}_2\text{O}}$$
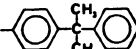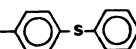

$$(9)$$

VIII
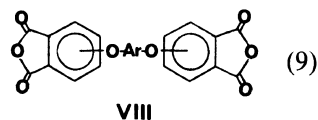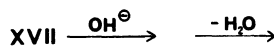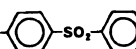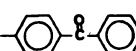
In contrast to dianhydrides presently available from commercial sources, bisetheranhydrides shown in Table VII were hydrolytically stable in the presence of atmospheric moisture and readily dissolved in conventional solvents. The moderate reactivity of the anhydride groups was attributed to the electro-donating effect of the aryloxy substitutions. A wide variety of polyetherimides (XVIII) were prepared by the reaction of bisetheranhydrides and various aromatic diamines.[37]

$$\textbf{VIII} \;+\; \text{H}_2\text{N--Ar'--NH}_2 \longrightarrow$$

$$(10)$$
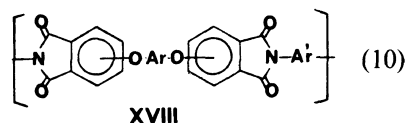
XVIII

Polyetherimides (XVIII) were thermally very stable as shown by the thermogravimetric results in Tables VIIIa and VIIIb. In addition, polyetherimides were soluble in completely imidized forms in various solvents such as chlorinated hydrocarbons, phenolic solvents and dipolar aprotic solvents. Because of flexible ether linkages, glass transition temperatures of polyetherimides were in a moderate range of 180 to 280°C which provided good thermal processing characteristics. The above unique combination of properties made it

Table VIIIa. Polyetherimides from *m*-phenylenediamine[37]

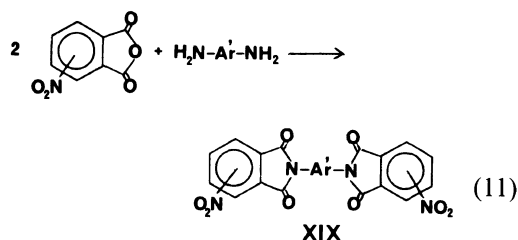| –Ar–	Isomer	$[\eta]^a$ dl g^{-1}	$T_g{}^b$ °C	TGA^c/°C Air	TGA^c/°C N$_2$	Solubility^d NMP	Solubility^d DMF	Solubility^d CHCl$_3$
(phenylene)	3,3′	0.57	241	460	500	s	s	i
	4,4′	0.70	224	500	515	s	i	i
(biphenyl)	3,3′	0.45	259	400	480	s	s	pi
	4,4′	0.96	255	485	490	s	i	i
(terphenyl)	3,3′	0.56	275	500	515	s	s	sw
	4,4′	0.51	247	480	535	s	i	pi
(diphenyl ether)	3,3′	0.53	238	480	480	s	s	s
	4,4′	1.04	227	500	490	s	i	pi
(isopropylidene)	3,3′	0.39	236	446	470	s	s	s
	4,4′	0.50	215	460	480	s	s	s
(sulfide)	3,3′	0.52	231	470	470	s	s	s
	4,4′	0.45	209	480	490	s	i	s
(sulfone)	3,3′	0.34	266	440	425	s	s	sw
	4,4′	0.70	265	460	500	s	s	sw
(carbonyl)	3,3′	0.27	248	490	485	s	s	s
	4,4′	1.35	239	480	510	s	i	i

[a] Measured in *m*-cresol at 25°C.
[b] Measured by DSC.
[c] Temperature at which 1% weight loss occurred.
[d] s, soluble; i, insoluble; pi, partially insoluble; sw, swelled.

possible to polymerize these polymers under unconventional conditions such as high temperature homogeneous solution polymerizations in nonpolar organic solvents[38] or in phenolic solvents[37] as well as solventless melt polymerization.[39]

Polyetherimides could also be prepared by the following alternate process. The reaction of 3- or 4-nitrophthalic anhydride with various diamines provided intermediates bisnitroimides (XIX) in high yields.

$$2 \quad \text{(anhydride)} + H_2N\text{-}Ar'\text{-}NH_2 \longrightarrow$$

$$\text{(bisnitroimide)} \quad (11)$$

XIX

Bisnitroimides were subsequently subjected to nitro displacement polymerization with various bisphenol salts in dipolar aprotic solvents.[40,41]

Table VIIIb. Polyetherimides from oxydianiline[37]

-Ar-	Isomer	$[\eta]^a$ dl g^{-1}	T_g^b °C	TGA^c/°C Air	TGA^c/°C N$_2$	Solubility^d NMP	Solubility^d DMF	Solubility^d CHCl$_3$
(phenyl)	3,3′	0.44	226	490	480	s	s	s
	4,4′	0.67	209	480	520	sw	i	i
(p-phenylene)	3,3′	2.25	263	475	505	s	i	i
	4,4′	1.71	237	486	553	s	i	sw
(biphenyl)	3,3′	1.70	277	485	510	s	s	s
	4,4′	0.83	229	490	540	s	i	i
(-O-)	3,3′	1.92	239	470	503	s	s	s
	4,4′	0.97	215	480	510	s	i	s
(-C(CH$_3$)$_2$-)	3,3′	0.66	235	470	490	s	s	s
	4,4′	1.09	223	480	520	s	pi	pi
(-S-)	3,3′	1.15	234	477	477	s	i	s
	4,4′	1.02	212	480	485	s	i	i
(-SO$_2$-)	3,3′	0.76	267	455	458	s	s	sw
	4,4′	1.13	260	470	470	s	s	sw
(-CO-)	3,3′	2.00	252	480	500	s	s	s
	4,4′	0.33	210	455	510	s	i	s

^{a} Measured in *m*-cresol at 25°C.
^{b} Measured by DSC.
^{c} Temperature at which 1% weight loss occurred.
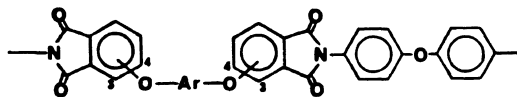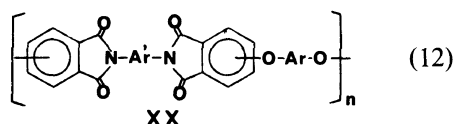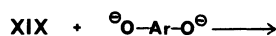^{d} s, soluble; i, insoluble; pi, partially insoluble; sw, swelled.

$$\text{XIX} + {}^{\ominus}\text{O-Ar-O}^{\ominus} \longrightarrow$$

$$\qquad (12)$$

XX

The resulting polyetherimides had repeating units identical with the structure (XVIII) although their end groups may be different.

Similarly, various thioether analogs, *i.e.*, bis(thioetheranhydride)s[42] and polythioetherimides[43] have been also synthesized by nitro displacement reaction. Polyetherimides with a wide range of properties can be prepared by selecting various combinations of diamines and bisphenols. The properties of these homopolymers can be further modified readily by copolymerization with different monomers in order to meet market needs. Polyetherimides described above are generally amorphous and suitable as injection molding resins.

ULTEM®* resin manufactured by General Electric Company is a polyetherimide based on bisphenol A and *m*-phenylenediamine. The polymer is characterized by high strength, high rigidity and good ductility as shown in Table

IX. The thermal properties of ULTEM® resin are also listed in Table IX. High heat distortion temperature, excellent flame resistance and nonsmoking property are some of the important characteristics of this resin.

COUPLING REACTION OF ACTIVATED AROMATIC NITRO COMPOUNDS

When solutions of N-methyl-4-nitro-phthalimide in dipolar aprotic solvents were heated above 140°C in the presence of potassium nitrite or fluoride, bis(phthalimido)-ether (XXI) was obtained in good yield.[44]

(13)
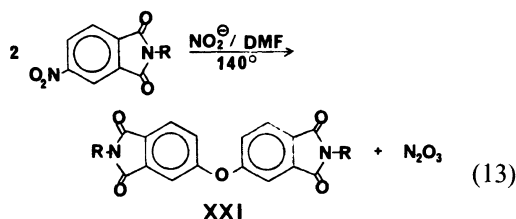
Similar reaction has been reported in which p-nitrobenzonitrile and p-chlorobenzonitrile were converted to 4,4′-dicyanodiphenylether by the action of stoichiometric amount of sodium nitrite in N-methylpyrrolidone.[45] The initial displacement of nitro group by an initiating nucleophile (nitrite or fluoride) produces unstable nitrite ester of 4-hydroxy-phthalimide (XXII) which reacts with the co-product nitrite ion to produce phthalimido-xylate (XXIII) and nitrous anhydride. The latter presumably decomposes to nitrogen oxides.
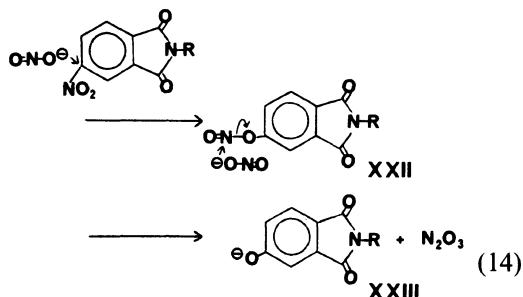
(14)

Table IX. Properties of ULTEM® polyetherimide

Mechanical properties	
Tensile strength at yield	$105 \, N \, mm^{-2}$
Tensile modulus	$3,000 \, N \, mm^{-2}$
Tensile elongation, ultimate	60—80%
Flexural strength	$145 \, N \, mm^{-2}$
Flexural modulus	$3,300 \, N \, mm^{-2}$
Compressive strength	$140 \, N \, mm^{-2}$
Compressive modulus	$2,900 \, N \, mm^{-2}$
Gardner impact strength	$36 \, N \cdot m$
Izod impact strength	
Notched	$50 \, J \, m^{-1}$
Unnotched	$1,300 \, J \, m^{-1}$
Thermal properties	
Glass transition	217°C
Heat deflection temp	
at 264 psi	200°C
at 66 psi	210°C
Flammability	
Limited oxygen index	47
UL 94 vertical burn	V-0 at 0.64 mm
NBS smoke density	
D_s at 4 min	0.7
D_{max} at 20 min	30

The phthalimidoxylate then undergoes nitro displacement to form the ether XXI and regenerates new nitrite ion. Therefore, entire cycle is repeated with nitrite ion as a catalyst.

(15)
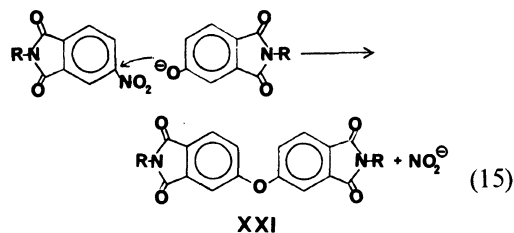
4,4′-Bis(phthalimido)ether can be converted to diphenylether-3,3′,4,4′-tetracarboxylic dianhydride by hydrolysis followed by cyclodehydration. The dianhydride has been synthesized by Kolesnikov et al.[46] by oxidation of tetramethyldiphenylether. Polyimides have been also prepared from the dianhydride and various diamines.[46]

---

* ULTEM® is a registered trademark of General Electric Co.

Similar coupling reactions were observed when molten 3-nitrophthalic anhydride was reacted with a catalytic quantity of alkali nitrites. 2,2′,3,3′-Tetracarboxydiphenylether dianhydride was formed in good yields at moderate conversion rates.[47]

$$ 2 \quad \text{XXIV} \xrightarrow{\text{KNO}_2} \text{XXV} + N_2O_3 \qquad (16) $$
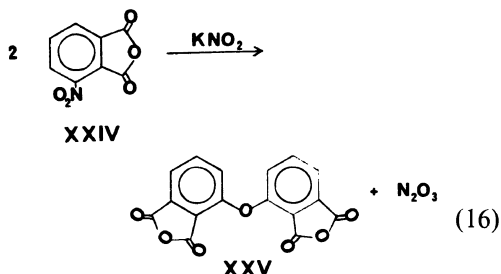
The major side reaction was catalyst deactivation by the following ring-opening reaction with the nitrite.

$$ \text{XXIV} + 2\,KNO_2 \longrightarrow + N_2O_3 \qquad (17) $$
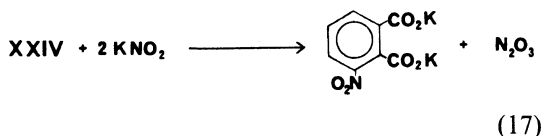
Unlike the coupling reaction of 4-nitrophthalimide, the use of dipolar solvents was detrimental, presumably the ring-opening reaction predominated. On the other hand the use of nonpolar inert solvents such as trichlorobenzene was beneficial to moderate otherwise potentially dangerous exotherm.

Thermally stable polyimides have been also prepared from 2,2′,3,3′-tetracarboxydiphenylether dianhydride with various diamines.[48]

REFERENCES

1. E. Radlmann, W. Schmidt, and G. E. Nischk, *Maklomol. Chem.*, **130**, 45 (1969).
2. D. R. Heath and J. G. Wirth, U. S. Patent 3,763,210 (1973).
3. J. F. Bennett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).
4. A. Laubenheimer, *Chem. Ber.*, **9**, 768 (1876).
5. A. Laubenheimer, *Chem. Ber.*, **9**, 1826 (1876).
6. J. H. Gorvin, *Chem. Ind.* (*London*), **36**, 1525 (1969).
7. L. Caswell and T. Kao, *J. Heterocycl. Chem.*, **3**, 333 (1966).
8. J. R. Beck, *J. Org. Chem.*, **37**, 3224 (1972).
9. J. R. Beck, *J. Org. Chem.*, **38**, 4086 (1973).
10. J. R. Beck, R. L. Sobczak, R. G. Suhr, and J. A. Yahner, *J. Org. Chem.*, **39**, 1839 (1974).
11. D. R. Heath and J. G. Wirth, U. S. Patent 3,730,946 (1973).
12. D. R. Heath and J. G. Wirth, U. S. Patent 3,787,475 (1974).
13. J. G. Wirth and D. R. Heath, U. S. Patent 3,838,097 (1974).
14. N. Kornblum, L. Cheng, R. C. Kerber, M. M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith, and P. A. Wade, *J. Org. Chem.*, **41**, 1560 (1976).
15. F. J. Williams, U. S. Patent 3,933,862 (1976).
16. F. J. Williams and P. E. Donahue, *J. Org. Chem.*, **42**, 3414 (1977).
17. F. J. Williams, H. M. Relles, J. S. Manello, and P. E. Donahue, *J. Org. Chem.*, **42**, 3419 (1977).
18. R. L. Markezich, O. S. Zamek, P. E. Donahue, and F. J. Williams, *J. Org. Chem.*, **42**, 3435 (1977).
19. H. M. Relles, C. M. Orlando, D. R. Heath, R. W. Schluenz, J. S. Manello, and S. Hoff, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2441 (1977).
20. A. K. St. Clair and N. J. Johnston, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 3009 (1977).
21. W. Reinders and W. E. Ringer, *Rec. Trav. Chim.*, **18**, 326 (1899).
22. W. E. Ringer, *Rec. Trav. Chim.*, **18**, 330 (1899).
23. R. D. Knudsen and H. R. Snyder, *J. Org. Chem.*, **39**, 3343 (1974).
24. D. R. Heath and J. G. Wirth, U. S. Patent 3,869,499 (1975).
25. D. R. Heath and J. G. Wirth, U. S. Patent 3,763,211 (1973).
26. T. Takekoshi, W. B. Hillig, G. A. Mellinger, J. E. Kochanowski, J. S. Manello, M. J. Webber, R. W. Bulson, and J. W. Nehrich, NASA Contract Report, NASA CR-145007 (1975).
27. D. I. Packham and F. A. Rackley, *Polymer*, **10**, 559 (1969).
28. D. I. Packham and J. C. Haydon, *Polymer*, **11**, 385 (1970).
29. R. J. Gaymans, K. A. Hodd, and W. A. Holmes-Walker, *Polymer*, **12**, 400 (1971).
30. E. Woehrle, *Makromol. Chem.*, **160**, 83 (1972); *ibid.*, **160**, 99 (1972).
31. T. M. Keller and J. R. Griffith, "Resins for Aerospace," *Am. Chem. Soc. Symp. Ser.*, **132**, 25 (1980).
32. T. M. Keller and T. R. Price, *J. Macromol. Sci., Chem.*, **A18**, 931 (1982).
33. T. M. Keller, *Polym. Mater. Sci. Eng.*, **52**, 192 (1985).
34. J. G. Wirth and D. R. Heath, U. S. Patent 3,838,097 (1974).
35. D. R. Heath and T. Takekoshi, U. S. Patent 3,879,428 (1975).
36. T. Takekoshi, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1759 (1985).

37. T. Takekoshi, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *J. Polym. Sci., Polym. Symp.*, **74**, 93 (1986).

38. T. Takekoshi and J. E. Kochanowski, U. S. Patent 3,991,004 (1976).

39. T. Takekoshi and J. E. Kochanowski, U. S. Patent 3,803,085 (1974).

40. T. Takekoshi, J. G. Wirth, D. R. Heath, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3069 (1980).

41. D. M. White, T. Takekoshi, F. J. Williams, H. M. Relles, P. E. Donahue, H. J. Klopfer, G. R. Louks, J. S. Manello, R. O. Matthews, and R. W. Schluenz, *J.* *Polym. Sci., Polym. Chem. Ed.*, **19**, 1635 (1981).

42. F. J. Williams, U. S. Patent 3,933,862 (1976).

43. F. J. Williams, U. S. Patent 3,933,749 (1976).

44. R. L. Markezich and O. S. Zamek, *J. Org. Chem.*, **42**, 3431 (1977).

45. H. Eilingsfeld and E. Schaffner, Ger. Patent 2,037,781 (1972).

46. G. S. Kolesnikov, O. Ya. Fedotova, E. I. Hofbauer, and V. G. Shelgayeva, *Vysokomol. Soyed., Ser. A*, **9**, 612 (1967).

47. A. S. Hay and T. Takekoshi, Br. Patent 1,467,275 (1977).

48. T. Takekoshi, U. S. Patent 4,048,142 (1977).