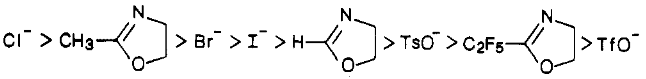
of 150 °C after 120 min. Thus the lower reactivity of covalent species was clearly demonstrated.

Decreased nucleophilic reactivity of **1a** in comparison with 2-methyl-2-oxazoline (**6**) was shown by the following results, i.e., the reaction of **4** with **6** was completed within 1 min at 35 °C, whereas the reaction of **4** with **1a** proceeded more slowly as described above. The lower nucleophilicity of **1a** is reasonably ascribed to the strong electron-withdrawing effect of the perfluoroalkyl substituent which decreases the electron density on the nitrogen atom. On the other hand, the introduction of the perfluoroalkyl group into the 2-oxazolinium ring enhances its ring-opening reactivity. Although **4** reacted with **1a** easily at 35 °C, its 2-alkyl analogue, 2,3-dimethyl-2-oxazolinium trifluoromethanesulfonate reacted with **1a** only at above 100 °C.

As described above, the introduction of the perfluoroalkyl group to the 2-position of oxazoline greatly affects both the nucleophilicity of the monomer and the ring-opening reactivity of the propagating onium ring. The nature of the propagating species in the oxazoline polymerization is controlled by the relative nucleophilicities of monomer and counteranion. When **1a** is reacted with **2b**, an oxazolinium salt is once generated as an intermediate species, which is very reactive and is immediately converted to the tosylate ester by reaction with the tosylate counteranion. In this case, the reaction between the oxazolinium intermediate and the monomer **1a** is much slower because of the decreased nucleophilicity of **1a**. Thus, the S_N2 dipole–dipole reaction between the tosylate ester at the growing end and the monomer **1a** is the rate-determining step of propagation. In the polymerization initiated by **2a**, on the other hand, triflate anion is much less nucleophilic than both tosylate and the monomer **1a**. Therefore, the S_N2 cation–dipole reaction between the oxazolinium and the monomer **1a** is the rate-determining step of propagation.

In the case of **6**, its polymerization initiated by **2a**, **2b**, or methyl iodide proceeds exclusively via an ionic mechanism, since the monomer is more nucleophilic than triflate, tosylate, and iodide anions.[3,5] The polymerization of **6** initiated by benzyl chloride, however, was found to proceed selectively via a covalent mechanism.[6]

Together with the results concerning the nature of propagating species in the polymerizations of 2-oxazoline and its 2-substituted derivatives with several initiators,[2–6] a few 2-oxazoline monomers and counteranions derived from initiators are arranged in the following order of relative nucleophilicity,



where the term of concentration is not considered.

In general, polymers having perfluoroalkyl chains possess specific characteristics such as high repellencies against water and oil, chemical stability, and heat stability. The film of polymer **3b** showed a high contact angle against water (θ = 110°).

Further studies on the kinetic measurements as well as the properties of the resulting polymers are in progress.

Registry No. **1a**, 7024-92-2; **1a** (homopolymer), 114505-58-7; **1b**, 2499-91-4; **1b** (homopolymer), 114505-59-8; **4**, 114532-36-4; **5**, 114505-29-2; **2a**, 80-48-8; **2b**, 333-27-7.

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Synthesis of Poly(aryl ether–phenylquinoxalines)

Poly(phenylquinoxaline) (PPQ, 1) and related structures comprise a class of high-temperature polymers exhibiting many desirable characteristics including excellent thermooxidative stability, high glass transition temperature (T_g) and modulus, and low dielectric constant.[1] In addition, PPQ is soluble in selected organic solvents (e.g., chloroform and *m*-cresol) in a fully cyclized form, preculding the need for high-temperature curing reactions. PPQ is generally synthesized through the condensation of an aromatic bis(*o*-diamine) with a bis(phenyl-α-dicarbonyl) compound.[2,3] Both homopolymers and statistically random copolymers have been prepared with glass transition temperatures ranging from 284 to 420 °C, depending on the monomers used in the synthesis. Structures with lower T_gs generally contain ether linkages introduced through the bis(dicarbonyl) monomer.[4] High elongations and tough ductile mechanical properties are typical characteristics of these materials. Furthermore, it has generally been recognized that aromatic ether linkages in the polymer backbone provide improved solubility and processibility as well as a lower T_g.[5]

An example of a high-temperature polymer which has been favorably modified by the introduction of arylene ether linkages is poly(ether–imide).[6] In contrast to many other high-temperature polyimides, the fully cyclized poly(ether–imide) structure has excellent solution and melt properties and may be processed as an engineering thermoplastic (i.e., injection molding etc.). Although the synthesis of poly(ether–imides) is best achieved via the conventional poly(amic acid) route, these polymers may also be prepared by a nitro displacement polymerization where generation of the ether linkage is the polymer-forming reaction. The nitro group in the bisimide monomer is activated toward nucleophilic aromatic substitution by the presence of two carbonyl substituents associated with the adjacent imide ring. A detracting feature of the nitro displacement polymerization method is the side reaction between the imide ring and the sodium nitrite generated in the polymerization.[7] Mild conditions must be employed to obtain high polymer by this route.

As a means of preparing the quinoxaline-based analogue of the poly(ether–imides), we have investigated PPQ synthesis through a halo displacement approach. We surmised the electron-deficient pyrazine component of the quinoxaline ring system would activate 6- or 7-halo substituents toward nucleophilic aromatic substitution. Facile displacement should occur at these positions since the pyrazine ring can stabilize the negative charge developed in the transition state through a Meisenheimer-like complex (I), analogous to conventional activating groups (e.g., sulfone, carbonyl)[8,9] (Scheme I). In our approach to poly(aryl ether–phenylquinoxalines), the quinoxaline ring is formed in the monomer synthesis, rather than in the polymerization, and the appropriately halo-substituted

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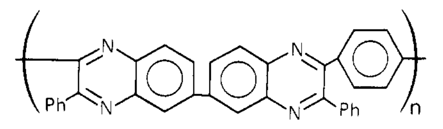


I

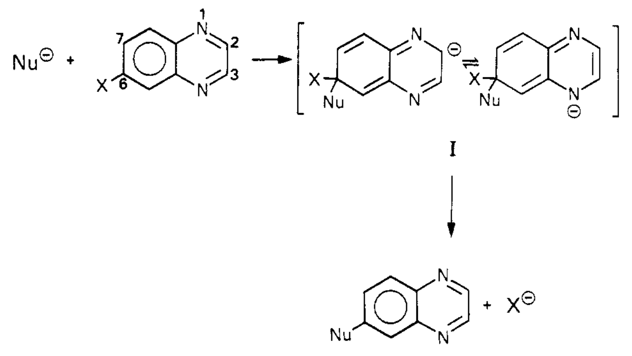
bisquinoxaline is subjected to an aromatic displacement polymerization with various bisphenates.

A model reaction between 2,3-diphenyl-6-fluoroquinoxaline (**2**)[10] and sodium *m*-cresolate was carried out in *N*-methyl-2-pyrrolidone (NMP) (Scheme II). After addition of **2** to the anhydrous sodium cresolate solution at room temperature, the reaction mixture was heated to 160 °C for 1 h. Analysis of the reaction mixture by HPLC (85:15 acetonitrile/water, μ-Bondapak-C18 column) showed quantitative conversion of **2** and the formation of a single product peak. The product was isolated by flash chromatography (5% ethyl acetate/hexane) as a white crystalline solid (97% yield) with spectral properties and C, H, and N analysis characteristic of the expected 6-(3-methylphenoxy)-2,3-diphenylquinoxaline (**3**) (mp = 132–133 °C). The model reaction demonstrated that the 6-fluoro group is readily displaced by phenates, as a result of activation by the adjacent pyrazine ring. Although nucleophilic displacement is known to occur at the 2- and 3-positions of quinoxalines (i.e., positions adjacent to nitrogen),[11] this represents the first example of nucleophilic aromatic substitution at positions in the fused benzene ring of these ring systems. The transformation occurred with high selectivity and was clearly suitable as a polymer-forming reaction.

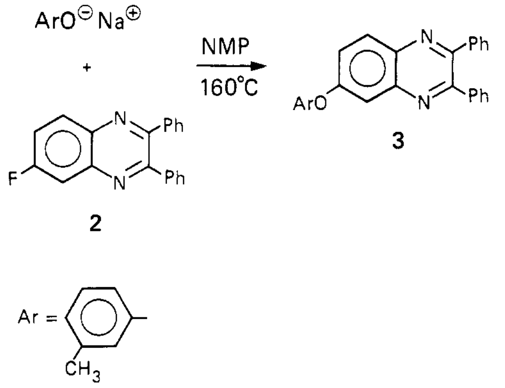
To demonstrate the feasibility of the quinoxaline-activated poly(aryl ether) synthesis, the appropriate bis(6-fluoroquinoxalinyl)-based monomer had to be prepared. This was carried out by the reaction of 1,4-bis(phenylglyoxalyl)benzene with 4-fluoro-1,2-phenylenediamine in refluxing chloroform with trifluoroacetic acid as the catalyst. The resulting 1,4-bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene (**4**) was isolated in 90% yield, and was recrystallized (ethyl acetate) to afford polymer grade monomer.[12] Due to the nonselectivity of the quinoxaline formation, three isomers are possible (i.e., 6,6′-, 6,7′-, 7,7′-difluoro), analogous to the multiple isomeric phenylquinoxaline moieties formed in PPQ syntheses.[13]

Polymerization of **4** with bisphenol AF (**5a**) was carried out in the presence of potassium carbonate (excess) in NMP/toluene (2/1) by the standard procedure[14] (Scheme III). During the initial stages of the polymerization, the water generated by the bisphenate formation was removed as an azeotrope with toluene. Upon completion of bisphenate formation and dehydration, the polymerization mixture was heated to 180–190 °C to effect the displacement reaction. High polymer was attained within 24 h as judged by a dramatic increase in viscosity. Notably, high molecular weight poly(aryl ether–phenylquinoxalines) were formed by using conventional polymerization conditions, whereas poly(ether–imide) synthesis requires milder conditions to avoid side reactions associated with the nitrite ion generated in the polymerization. The resulting polymer **6a** was coagulated in excess methanol, subjected to the appropriate solvent rinses, and dried in a vacuum oven (80 °C) for 24 h. This general procedure was applied to several bisphenols (**5a–c**) affording high molecular weight materials (**6a–c**), as indicated by the intrinsic viscosity measurements (Table I). In addition, each of the polymers gave tough fingernail-creasable films, indicative of high molecular weight material. In contrast to conventional PPQ, the poly(aryl ether–phenylquinoxalines) were soluble in NMP, a solvent commonly used for polymer processing in the microelectronics industry.

Scheme I



Scheme II



Scheme III

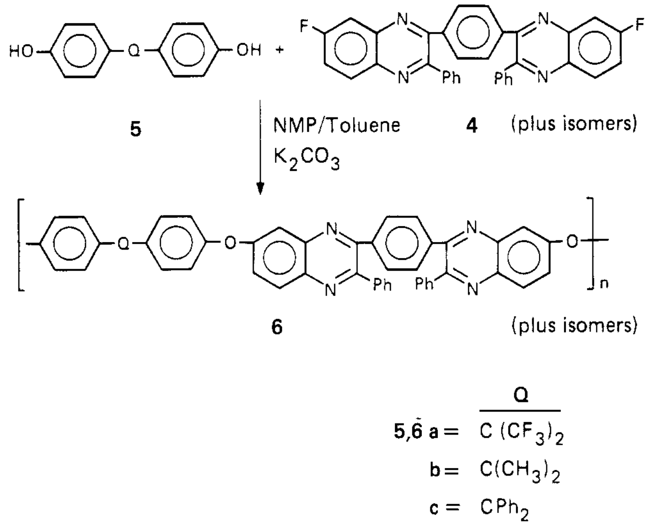
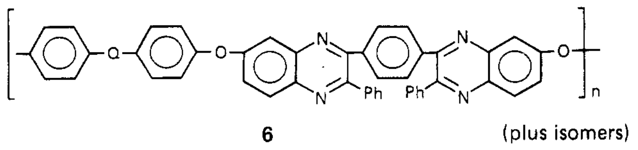


Table I
Characteristics of Poly(aryl ether–phenylquinoxaline)



6 (plus isomers)

sample	Q	$[\eta]$,[a] dL/g	T_g,[b] °C
6a	$C(CF_3)_2$	1.20	275
6b	$C(CH_3)_2$	1.20	255
6c	$C(Ph)_2$	1.45	270

[a] NMP, 25 °C. [b] Heating rate = 10 °C/min.

The glass transition temperatures of **6a–c** ranged from 255 to 275 °C, depending on the bisphenol utilized (Table I). Interestingly, these values are 20–40 °C higher than those of the poly(ether–imide) analogue, consistent with the expected affect of pendent phenyl groups.[15] In addition, **6a** showed a decomposition temperature of 520 °C (5 °C/min heating rate, nitrogen atmosphere), comparable to **1** (PDT = 540 °C).[16] Isothermal aging of **6a** at 400 °C (nitrogen atmosphere) resulted in a weight loss rate of 0.05 wt %/h, slightly higher than that of **1** (0.02 wt %/h), yet comparable to that of PMDA-ODA polyimide (0.04 wt %/h). Thus, these materials represent a class of high-T_g thermoplastics with excellent thermal stability.

The results demonstrate that quinoxaline-based poly(aryl ethers) can be synthesized via a halo displacement polymerization, where the fused pyrazine ring is the activating group. The polymerization provides a general method for the preparation of aryl ether based PPQs, where the structure of the aryl ether moiety is readily controlled by varying the bisphenol used. The materials obtained by this method are the PPQ analogue of the poly(ether–imides) and should show many of the same desirable properties including good melt and solution processability. Moreover, heterocyclic activated nucleophilic displacement chemistry should prove effective with monomers derived from other ring systems, providing a general synthetic methodology to high-temperature, high-T_g aryl ether–heterocyclic polymers.

Future work on poly(aryl ether–phenylquinoxalines) will focus on demonstrating the scope of materials possible by utilizing bisquinoxaline monomers derived from other bis(α-diketones) as well as other bisphenols. Further studies on the polymerization process will entail leaving group effects (i.e., chloro, nitro), ether interchange, and molecular weight control. In addition, the mechanical and thermal properties will be investigated together with both the solution and melt viscosities.

Registry No. **2**, 114583-79-8; **3**, 114583-80-1; **4**, 114583-85-6; **6a** (copolymer), 114583-86-7; **6a** (SRU), 114633-53-3; **6b** (copolymer), 114613-38-6; **6b** (SRU), 114633-54-4; **6c** (copolymer), 114613-39-7; **6c** (SRU), 114633-55-5; sodium *m*-cresolate, 3019-89-4; 1,1-bis(phenyl glyoxalyl)benzene, 3363-97-1; 4-fluoro-1,2-phenylenediamine, 367-31-7.

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(13) The ^{19}F NMR showed resonances at 108.56 and 108.70 ppm (relative to phosphoric acid), which we assigned as fluorine in the 6- and 7-positions of **4**. The intensities of the resonances were similar, indicating all three isomers were probably present in a statistical distribution. Attempts to separate the possible isomers by HPLC were not successful.

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Preparation of Polyacetylene Chains in Low-Polydispersity Diblock and Triblock Copolymers

Studies of polyacetylene have been hampered by its intractability and (especially when doped) its sensitivity to air.[1] It would be desirable to prepare well-defined solubilized polyacetylene samples in order to more fully understand interchain and intrachain phenomena (especially those relevant to electrical conduction) and polymer morphology. Many grafts,[2] blends,[3] and blocks[4] containing polyacetylene have been made by classical techniques, and considerable control over polymer purity and morphology is now possible through the Feast (ring opening) method of preparing polyacetylene.[5] However, there is still a need for absolute control over polymer preparation, ideally to give soluble, block copolymers with as narrow a molecular weight distribution as is possible.[6] We report such a method here.

Tungsten[7a] or molybdenum[7b] catalysts of the type M(CHR)(NAr)(OCMe$_3$)$_2$ (R = alkyl or polymer chain; Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$) have been shown to polymerize norbornene to give essentially monodisperse polynorbene and (when M = Mo) poly-*endo*-5,6-dicarbomethoxynorbornene, as well as block copolymers.[8] 7,8-Bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**1**; Scheme I) is also smoothly polymerized by these catalysts.[9,10] Similarly, block copolymers ($\mathbf{3}^{A-B}$ and $\mathbf{3}^{A-B-A}$ in Scheme I) can be synthesized by the sequential addition of **1** and norbornene (**2**) to Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$[11] followed by cleavage with benzaldehyde or pivaldehyde. The order of addition of **1** or **2** can be reversed with similar results. GPC analyses of representative polymers are shown in Table I.

Upon heating **3**,[12] *o*-C$_6$H$_4$(CF$_3$)$_2$ is eliminated to generate a polyene chain containing $2B + 1$ double bonds attached to one polynorbornene chain ($\mathbf{4}^{A-B}$) or two polynorbornene chains ($\mathbf{4}^{A-B-A}$) (Scheme I). The results of GPC studies (in dichloromethane) on these orange to deep red, toluene-soluble, block copolymers **4** are analogous; those for $\mathbf{4}^{A-B-A}$ are listed in Table II. When $B = 5$ the polymer has a molecular weight and low polydispersity characteristic of a well-behaved system. When $B = 10$, 15, or 20, a new, relatively high molecular peak is observed that dominates when $B = 20$ (an average of 41 double bonds). We hypothesize that the high molecular weight fraction results from aggregation or cross-linking of the polyene chains in the expected macromolecule. Note that the number of macromolecules that make up the "aggregate" (N = high M_n/low M_n) increases with B; for $A = 100$, $N = 8.4$, 10.0, and 12.6 for $B = 10$, 15, and 20, respectively. Also note the N decreases as A increases; for $B = 15$, $N = 13.4$ and 10.0 for $A = 50$ and 100, respectively; for $B = 20$, $N = 15.2$ and 12.6 for $A = 50$ and 100, respectively. The polynorbornene both solubilizes the aggregated or cross-linked