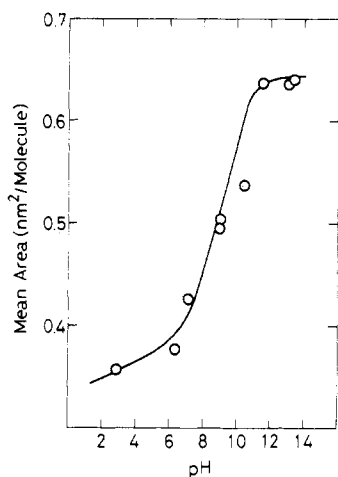**Figure 2.** π–A isotherms of 3 ($\bar{m}$ = 6.7) at different pH values at 20 °C. Inset shows a conformational model of PAA in subphase; —, PAA chain.


Figure 3. pH dependence of the mean area at zero pressure.

packed more tightly. Since the area did not change for several hours when we checked the time course of area at a constant pressure (20 mN/m), dissolution of amphiphilic molecules into the subphase might be negligible.

Figure 2 shows the π–A isotherms of **3** ($\bar{m}$ = 6.7), a typical polymer, at different pH values. The π–A curves have a tendency to expand with pH. Figure 3 shows the pH dependence of the area at zero pressure. The pK_a of the carboxylic acid group of a PAA chain is probably about 5.0, so the fraction of ionized carboxyl groups will vary considerably in the range of pH investigated. It is, in general, expected that ionization of the carboxyl groups will introduce ionic repulsion, which caused a conformational change of the PAA chain from a globular coil in acidic solution to an expanded conformation at high pH in the subphase. This probably explains the pH sensitivity of π–A curves as shown schematically in the Figure 2 inset.

Deposition of the surface monolayer of **3** ($\bar{m}$ = 6.7) was examined by using a quartz plate at 20 °C under a surface pressure of 20 mN/m. In the first downward stroke the monolayers could not be deposited, but in further strokes the monolayer was readily transferred in both the upward and downward strokes. The formation of the Y-type multilayer was assured, because decreases in the surface area were the same in the downward and upward strokes. The UV absorption spectra also supported the formation of a multilayer. Figure 4 shows the absorbance at 262 nm, which corresponds to PSt, plotted against the number of layers (N) deposited. The absorbance was proportional
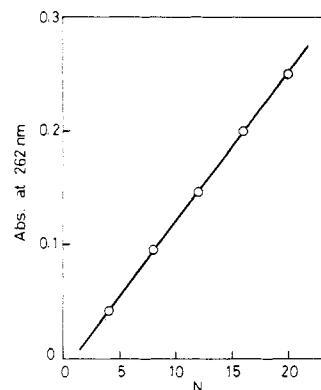
Figure 4. Absorbance at 262 nm of a built-up film as a function of the number of deposited layers (N).

to N at least up to 20 depositions.

We conclude that the monolayer properties of the well-defined amphiphilic block polymers are quite sensitive to the chain length of PSt as the hydrophobic segment and also to pH in the subphase resulting from the conformational change of PSt and/or PAA chains. The monolayers could be transferred on a quartz plate in the Y-type deposition. Attempts to reveal the structural characteristics of such multilayers are now in progress.

References and Notes

(1) Langmuir, I. *J. Am. Chem. Soc.* **1917**, *39*, 1848.
(2) Blodgett, K. *J. Am. Chem. Soc.* **1935**, *57*, 1007.
(3) Mumby, S. J.; Swalen, J. D.; Rabolt, J. F. *Macromolecules* **1986**, *19*, 1054.
(4) Winter, C. S.; Tredgold, R. H.; Vickers, A. J. *Thin Solid Films* **1985**, *134*, 49.
(5) Laschewsky, A.; Ringsdorf, H.; Schmidt, G.; Schneider, J. *J. Am. Chem. Soc.* **1987**, *109*, 788.
(6) Watanabe, M.; Kosaka, Y.; Sanui, K.; Ogata, N. *Macromolecules* **1987**, *20*, 452.
(7) Christie, P.; Petty, M. C.; Roberts, G. G.; Richards, D. H.; Service, D.; Stewart, M. J. *Thin Solid Films* **1985**, *134*, 75.
(8) Ikada, Y.; Iwata, H.; Nagaoka, S.; Horii, F.; Hatada, M. *J. Macromol. Sci.—Phys.* **1980**, *B17*, (2), 191.
(9) Bamford, C.; Finch, C. *Trans. Faraday Soc.* **1963**, *59*, 540.
(10) Bamford, C.; Xiao-zu Han. *Polymer* **1981**, *22*, 1299.
(11) Niwa, M.; Katsurada, N.; Matsumoto, T.; Okamoto, M. submitted for publication in *J. Macromol. Sci.—Chem.*
(12) Niwa, M.; Hayashi, T.; Matsumoto, T. *J. Macromol. Sci.—Chem.* **1986**, *A23* (4), 433.
(13) Number-average molecular weights were measured by a Knauer vapor-pressure osmometer from acetone solutions at 37 °C.
(14) GPC curves were recorded on a Shimadzu high-performance liquid chromatograph (LC-3A) from THF solutions at 40 °C.
(15) ^{1}H NMR and ^{13}C NMR spectra were measured by a JOEL JNM-GX400 FT-NMR spectrometer with TMS as internal standard from CDCl$_3$ solutions at 400 and 100 MHz, respectively.

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Received January 4, 1988

Mechanisms of Ring-Opening Polymerization of 2-(Perfluoroalkyl)-2-oxazolines Initiated by Sulfonates: A Novel Covalent-Type Electrophilic Polymerization

The present paper describes the results of study on the ring-opening polymerization of 2-(perfluoroalkyl)-2-oxa-

Table I
Results of Polymerization of 1

run	1	2, mol %	solvent	temp, °C	time, h	yield, %	$M_n/10^{3a}$	$M_w/M_n{}^a$	$[\eta]$, dL/g^b
						polymer			
1	1a	2a, 5	CH_3NO_2	70	3	97	3.2	1.1	
2	1a	2a, 5	$PhNO_2$	70	3	95	2.8	1.1	
3	1a	2a, 5	CD_3CN	70	3	67	3.4	1.5	
4	1a	2a, 5	DMF	70	3	0			
5	1a	2a, 1	CH_3NO_2	70	9	57	>18		0.20
6	1a	2b, 25	CH_3NO_2	150	24	70	0.49	1.4	
7	1b	2a, 5	CH_3NO_2	70	3	71	c	c	0.040

^{a} Determined by GPC in DMF at 50 °C. The values are estimated from poly(2-methyl-2-oxazoline) standards. ^{b} In CF_3CO_2H, at 30 °C. ^{c} Insoluble in DMF.

Scheme I

1a, $R_f = C_2F_5$
b, $R_f = n-C_3F_7$

Scheme II
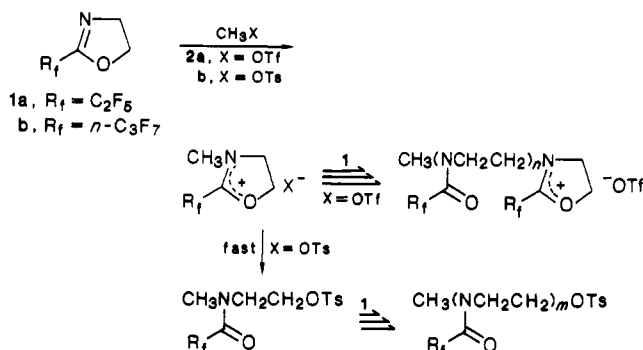
zolines (1) which proceeds via two different mechanisms of propagation depending upon the nature of the polymerization initiator. With methyl p-toluenesulfonate (tosylate) initiator, the propagating species of the polymerization of 1 is of the covalent tosylate ester type. With methyl trifluoromethanesulfonate (triflate) initiator, on the other hand, the propagating species is of the structure of oxazolinium cation (Scheme I).

The polymerization of 2-(perfluoroalkyl)-2-oxazolines has been described in a previous paper.[1] However, no mechanistic study has been reported. In the present study, an interesting and significant phenomena was disclosed, which was due to the unusual reactivity of 1, having a strong electron-withdrawing group at the 2-position.

Two 2-(perfluoroalkyl)-2-oxazolines (1), i.e., 2-(pentafluoroethyl)- (1a) and 2-(heptafluoro-n-propyl)-2-oxazolines (1b), were prepared as previously reported.[1] The polymerization of 1 was carried out in a sealed tube under nitrogen. White powdery polymers were obtained by reprecipitation from 50/50 diethyl ether and hexane.

The mechanism of the ring-opening polymerization of 1 was examined with methyl triflate (2a) and methyl tosylate (2b) initiators. As shown in Table I, the yield and the molecular weight distribution of the produced polymer with the initiator 2a were greatly affected by the solvent. Nitromethane was found most suitable for the polymerization of 1.

Conditions for a suitable rate of polymerization were very dependent on the initiator. The polymerization of 1a with 2a proceeded smoothly at 70 °C, but with 2b it required a higher temperature, e.g., 150 °C.

Our previous studies have clarified that the polymerizations of 2-alkyl-2-oxazolines with both 2a and 2b proceed exclusively via cationic onium type propagating species.[2] In these cases, the counteranion exerts no significant influence upon the propagation rate, i.e., the polymerization rates with these two initiators are almost the same. The difference in the required reaction conditions between the 1a/2a and 1a/2b systems in the present study suggests
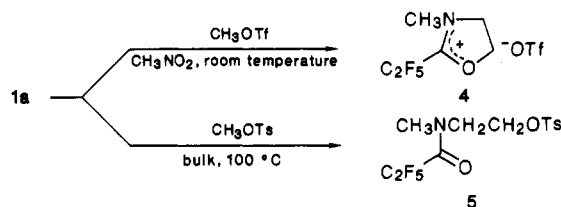
different mechanisms of propagation between the two systems.

The ring-opening polymerization of 1b successfully proceeded in a similar manner. However, the resulting polymer 3b showed poor solubility in the common solvent. Therefore, no detailed examinations concerning the polymer structure as well as the polymerization mechanism were performed.

In order to clarify mechanisms of the present polymerization, reactions of 1a with an excess amount of 2 were carried out, where the 1:1 adducts, model compounds of propagating species of the polymerization, were isolated (Scheme II).

The structures of adducts were determined by ^{1}H, ^{13}C, and ^{19}F NMR, IR, and mass spectra as well as elemental analyses. The 1:1 adduct of 1a with 2a was an ionic species, 4. The peaks due to oxazolinium ring protons of 4 appear at around δ 4.74 (NCH_2) and 5.48 (OCH_2) in the ^{1}H NMR spectrum. 4 is very reactive and is highly sensitive to moisture. But it is stable in dry nitromethane even at 70 °C for 3 h.

On the other hand, the 1:1 adduct of 1a with 2b is a covalent tosylate ester species, N-methyl-N-[2-(p-toluenesulfoxyl)ethyl]perfluoropropionamide (5). 5 had two isomeric forms, 5a (syn) and 5b (anti), because of restriction of free rotation around the amide C-N bond. The ratio 5a/5b was determined as 81/19 in $CDCl_3$ from its ^{1}H NMR spectrum. The peaks at around δ 3.68 (NCH_2 of 5a), 3.77 (NCH_2 of 5b), 4.19 (OCH_2 of 5b), and 4.21 (OCH_2 of 5a) in the ^{1}H NMR spectrum were reasonably ascribed to ester-type ethylene protons.

The differences of structure between 4 and 5 are most clearly indicated by their ^{19}F NMR spectra. Parts a–d of Figures 1 show the peaks of CF_2 fluorine atoms in ^{19}F NMR spectra of the 1a/2a and 1a/2b polymerization systems ([M]/[I] = 3–4) and of 4 and 5, respectively. The intermediacy of 4 during the polymerization of 1a with 2a has been confirmed by the presence of the signal due to 4 at δ –40.2 in the 1a/2a polymerization system (Figure 1a). The peak at δ –38.5 in Figure 1a is ascribed to the CF_2 fluorine atoms of oxazolinium ring at the propagating ends (DP > 2).

On the other hand, the two peaks due to the 1:1 covalent species, 5a and 5b, were also observed at δ –38.6 (5a) and –36.4 (5b) in the 1a/2b polymerization system (Figure 1b). The peaks due to the covalent propagating species (DP >
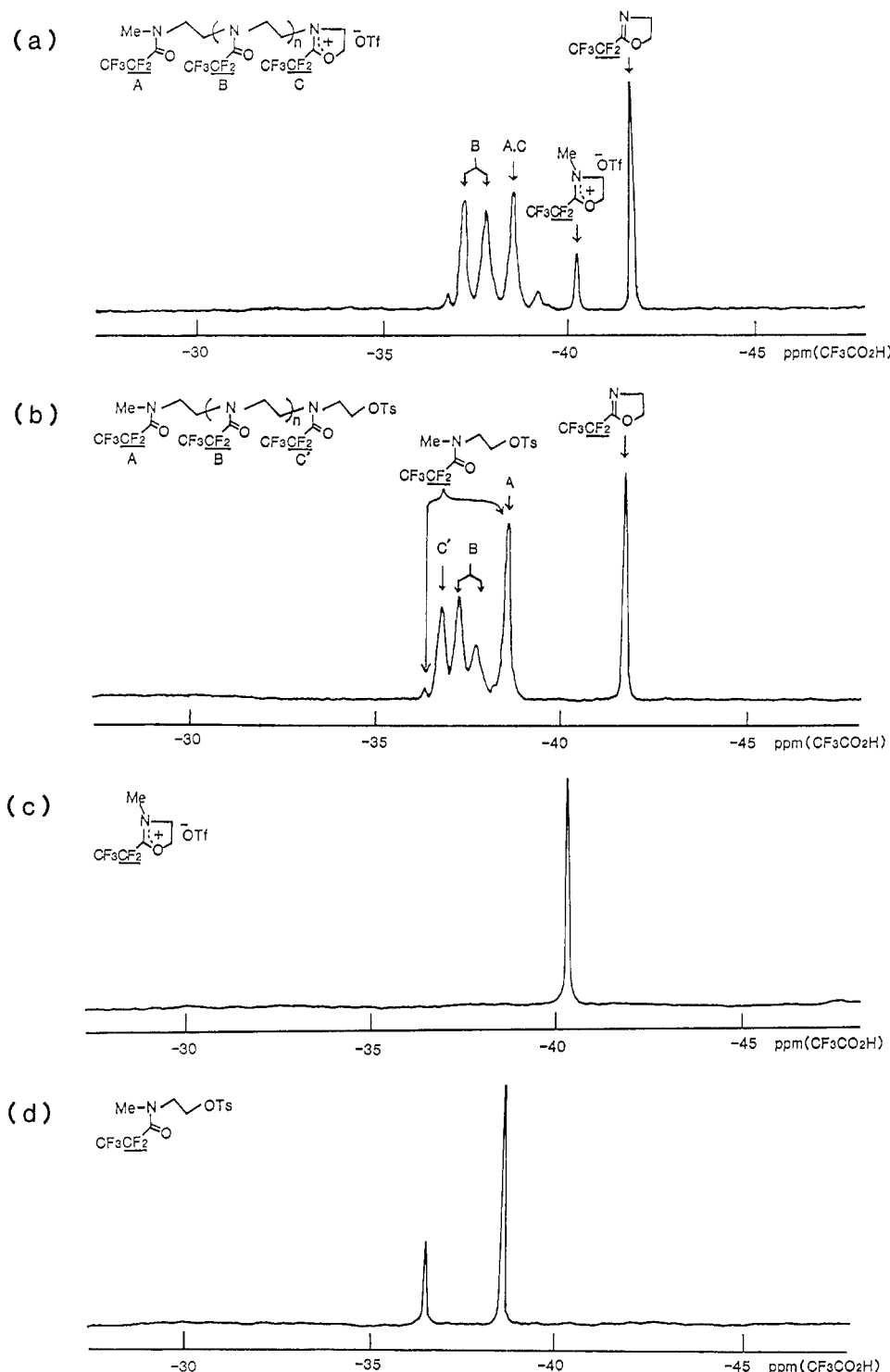
Figure 1. ^{19}F NMR spectra, 84.7 MHz, of the polymerization systems of (a) **1a/2a** ($[1a]_0 = 0.62$ mol/L, $[2a]_0 = 0.20$ mol/L, at 35 °C, after 400 min) and (b) **1a/2b** ($[1a]_0 = 1.61$ mol/L, $[2b]_0 = 0.41$ mol/L, at 150 °C, after 15 h) and 1:1 adducts (c) **4** and (d) **5** (in CD_3NO_2; external standard, CF_3CO_2H).

2) appeared at δ −36.7, but no peak ascribable to ionic propagating species was observed.

From these observations it is concluded that the polymerizations of **1a** with **2a** and with **2b** proceed by two quite different mechanisms, i.e., via ionic-type and covalent-type propagating species, respectively. It is important to note that the polymerizations of unsubstituted 2-oxazoline and 2-alkyl-substituted derivatives with an initiator of methyl tosylate proceed via the oxazolinium propagating species.[2-4] Thus, the finding of the present study disclosing the propagation through the covalent tosylate ester constitutes a sharp contrast to the previous results with con-

ventional oxazoline monomers.

Since these 1:1 adducts are considered to be the models of propagating species in the polymerization of **1** with the two respective initiators, the equimolar reactions of these adducts with 2-oxazoline monomers were further examined in order to clarify the reactivity of the propagating species. The reaction of an ionic adduct **4** with **1a**, which corresponds to the polymerization of **1** with **2a**, proceeded smoothly at 35 °C in nitromethane. After 30 min, the extents of conversion of **4** and **1a** were 56 and 75%, respectively. A similar extent of conversion of **5** in its reaction with **1a** was attained at a much higher temperature

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,

$$Cl^- > CH_3 \!-\!\!\! \langle\!\!\!\!\!\!\rangle > Br^- > I^- > H \!-\!\!\!\langle\!\!\!\!\!\!\rangle > TsO^- > C_2F_5 \!-\!\!\!\langle\!\!\!\!\!\!\rangle > TfO^-$$
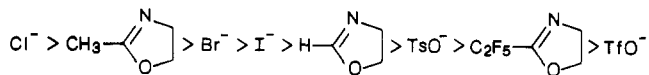
where the term of concentration is not considered.

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 ($\theta = 110°$).

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

References and Notes

(1) Bassiri, T. G.; Levy, A.; Litt, M. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 871.
(2) Kobayashi, S.; Saegusa, T. *Ring-Opening Polymerization*; Elsevier Applied Science Publishers: New York, 1985; Vol. 2, Chapter 11.
(3) Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules* **1972**, *5*, 359.
(4) Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules* **1973**, *6*, 315.
(5) Saegusa, T.; Ikeda, H. *Macromolecules* **1973**, *6*, 808.
(6) Saegusa, T.; Kobayashi, S.; Yamada, A. *Makromol. Chem.* **1976**, *177*, 2271.

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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, precluding 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