Russian Chemical Bulletin, International Edition, Vol. 53, No. 9, pp. 2035—2040, September, 2004

Synthesis and characterization of new poly[phenylquinoxaline(ether)imides]*

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A series of new aromatic poly[phenylquinoxaline(ether)imides] were synthesized by solution polycondensation of aromatic diamines containing preformed phenylquinoxaline groups with dianhydrides having ether linkages and isopropylidene or hexafluoroisopropylidene units. All polymers are readily soluble in polar organic solvents (*N*-methylpyrrolidinone, DMF, dimethylacetamide) and in less polar liquids such as chloroform. Very thin coatings were deposited onto silicon wafers. According to atomic force microscopy, they had a smooth, pinhole-free surface. The polymers showed high thermal stability with decomposition temperatures above 470 °C and glass transition temperatures in the range of 210—238 °C, being thus characterized by a large gap between the glass transition and decomposition temperatures.

Key words: poly[phenylquinoxaline(ether)imides], diaminophenylquinoxalines, bis(ether anhydride)s, high thermal stability, thin films.

Aromatic polyimides represent a class of polymers known for their high thermal stability, excellent electrical and mechanical properties, and chemical resistance. These properties make them desirable for a variety of high-performance applications such as aerospace engineering, automobile production, microelectronics, optoelectronics, and so on.[1—4] However, most of polyimides are insoluble and infusible, which causes great processing difficulties. This is why a two-stage process is widely used for the manufacture of polyimides. In the first step, a soluble linear polyamic acid is obtained, which can be processed into thin materials such as films, coatings, or impregnated fabrics, while in the second step, these materials undergo a special high-temperature treatment (300 °C), resulting in polyheterocyclization along the macromolecular chain to give the fully imidized chemical structure of the polymer. However, even in this case, there are certain problems related to corrosion and short-term storage stability of polyamic acid solutions and to the evolution of water during imidization, which can give rise to microvoids or other defects in the final polyimide material. Numerous attempts have been made to improve the processing properties of heterocyclic thermally stable polymers, particularly, by improving their solubility and fusibility, while maintaining good thermal stability.[5—7] It is known that the introduction of flexible groups such as isopropylidene, hexafluoroisopropylidene, or ether groups into the backbone of a polyimide leads to soluble products having a high thermal stability. The synthesis of copolymers containing such groups is a promising route to easily processable compounds. In addition, poly(phenylquinoxalines) are aromatic polymers that have shown an excellent potential for high-temperature applications along with very good storageability at ambient temperature. They are known for their excellent thermal and chemical stabilities.[8,9] Thus, we assumed that the presence of isopropylidene or hexafluoroisopropylidene units together with phenylquinoxaline rings or ether linkages in a polyimide chain would give products with both excellent physical properties and good processability, in particular, appropriate for casting them into very thin films, which would be useful for high-performance applications.

In this paper, we report the synthesis of four aromatic poly[phenylquinoxaline(ether)imides] **1a—d** by solution polycondensation of aromatic diamines **2** containing preformed phenylquinoxaline rings with dianhydrides **3** having ether linkages and isopropylidene or hexafluoroisopropylidene groups (Scheme 1).

The solubility, inherent viscosity, molecular weight, thermal stability, and glass transition temperature were determined for copolymers **1**. The film forming ability and the quality of the thin films formed from these poly-

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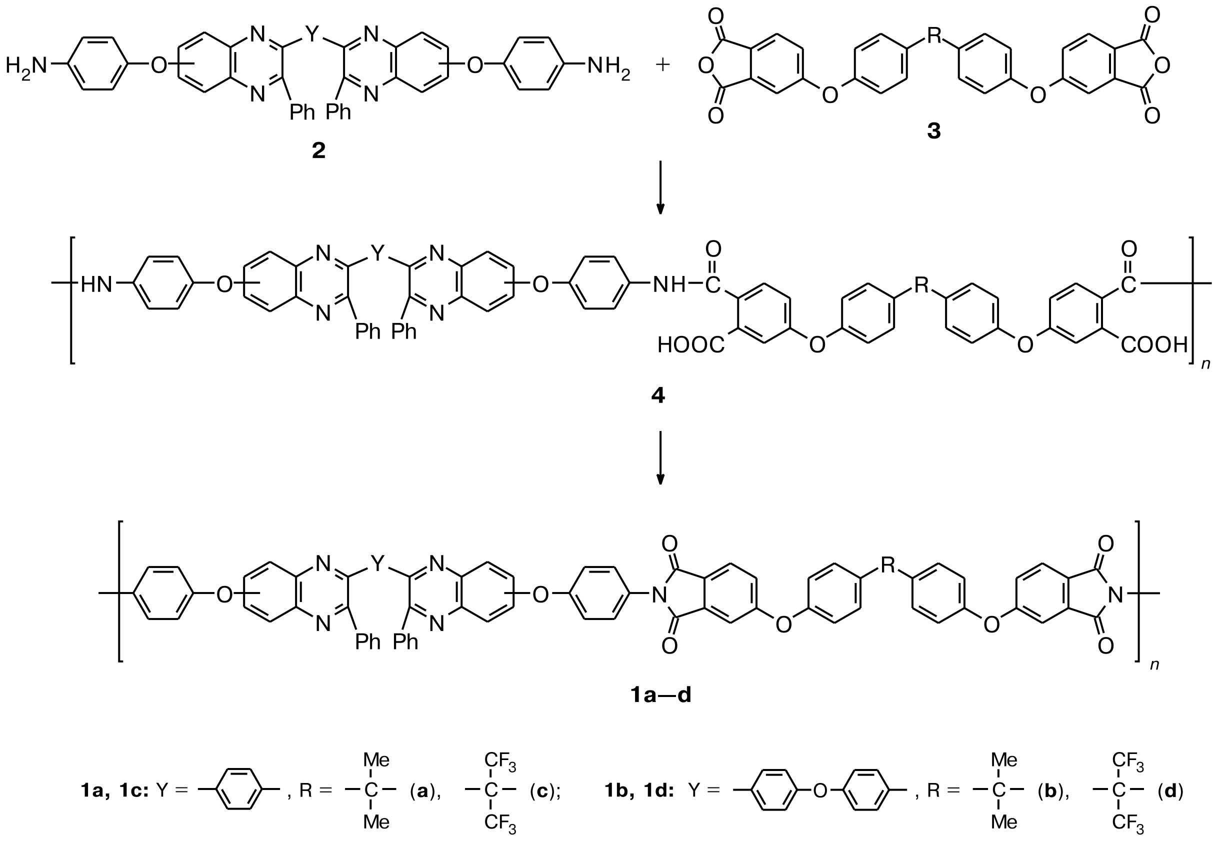
* Based on the report presented at the International Conference "Modern Trends in Organoelement and Polymer Chemistry" dedicated to the 50th year anniversary of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow, May 30—June 4, 2004).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1952—1957, September, 2004.

Scheme 1

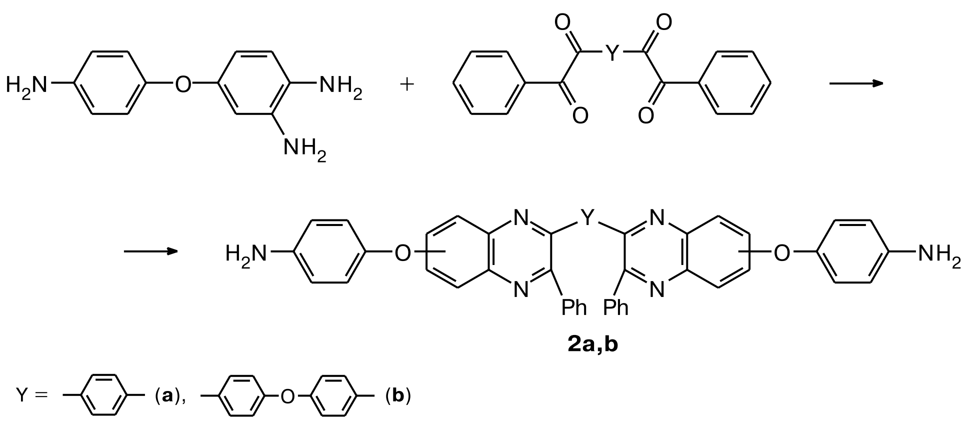


mers were investigated and compared with those of related polymers.

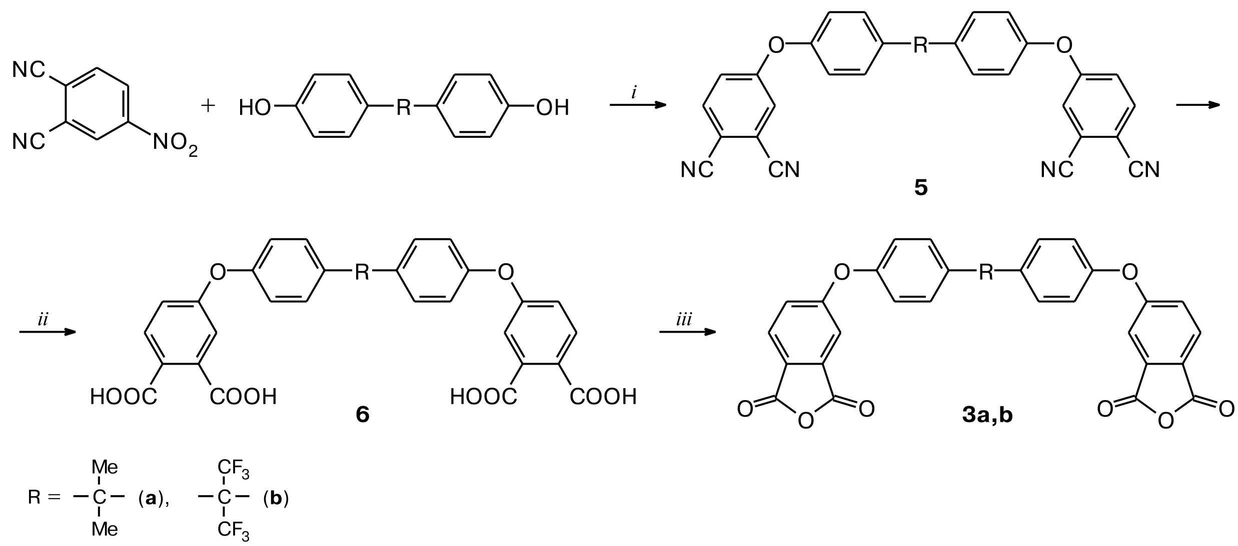
The diaminophenylquinoxalines **2a** and **2b** used for the polymer synthesis were prepared by the reaction of 3,4,4´-triaminodiphenyl ether with bis(α-diketones)[10] (Scheme 2).

The bis(ether anhydrides), **3a** and **3b**, were synthesized by a multistep procedure starting from the reaction of 4-nitrophthalodinitrile with isopropylidenebisphenol A or its fluorinated analog (Scheme 3).[11,12] This gave bis(ether dinitrile) **5**, which was subsequently hydrolyzed in an alkaline solution and acidified to yield tetracarboxylic acid **6**. Dehydration with acetic anhydride afforded bis(ether anhydride) **3**. The yield in each step was satisfactory, and the structures of the intermediate compounds **5** and **6** and final bis(ether anhydrides) **3a** and **3b** were confirmed by IR spectra and the melting points, which coincided with published data.[11,12]

Scheme 2



Scheme 3



Reagents and conditions: *i*. K_2CO_3, DMF, ~20 °C; *ii*. KOH, EtOH—H_2O, refluxing; *iii*. $(MeCO)_2CO$, refluxing.

Results and Discussion

The structure of polymers **1** was identified by IR spectra and elemental analysis. The presence of strong bands at 1780, 1725, 1375, and 740 cm^{-1} confirms the formation of the imide ring. The absorption band at 1240 cm^{-1}, present in all the spectra, is due to the ether bond. The aromatic C—H fragments absorb at 3070 cm^{-1}. The bands due to the aromatic C=C bonds occur at 1600 and 1500 cm^{-1}. The characteristics of polymers **1a—d** are summarized in Table 1.

All these polymers are readily soluble in organic solvents, *N*-methylpyrrolidinone (NMP), DMF, dimethylacetamide (DMAA), and $CHCl_3$, which allows the final polyimides to be obtained directly in the reaction solution. This is more convenient than the synthesis and isolation of the intermediate polyamic acids. The improved solubility of these polymers is due to the relatively high flexibility of the macromolecular chains, caused by the presence of ether groups in the repeating unit. The hexafluoroisopropylidene or isopropylidene groups, which introduce asymmetry and steric hindrance, prevent a close packing of the chains. The same effect is brought about by the bulky phenylquinoxaline rings. This arrangement of the phenylquinoxaline and hexafluoroisopropylidene or isopropylidene groups, responsible for a greater distance between the chains, is confirmed by molecular modeling (Fig. 1). The shape of the macromolecular fragments dif-

Table 1. Characteristics of polymers **1**

Polymer	Found / Calculated (%)			Molecular formula	$T_{g.t}^a$	$T_{in.d}^b$	T_{10}^c	M_w	M_n	M_w/M_n	η_{lg}^d /dl g^{-1}
	C	H	N		°C			g mol^{-1}			
1a	77.50	4.17	7.05	$C_{77}H_{48}N_6O_8$	221	490	525	38600	26600	1.45	0.43
	78.04	4.05	7.09								
1b	77.70	4.72	6.49	$C_{83}H_{52}N_6O_9$	210	502	520	45100	26400	1.71	0.43
	78.05	4.07	6.58								
1c	70.80	3.85	6.37	$C_{77}H_{42}F_6N_6O_8$	238	470	516	72000	39900	1.81	0.49
	71.50	3.25	6.50								
1d	71.80	3.81	5.73	$C_{83}H_{46}F_6N_6O_9$	213	506	520	58300	34600	1.69	0.46
	71.90	3.32	6.07								

[a] Glass transition temperature.

[b] Initial decomposition temperature: the temperature of 5% weight loss.

[c] Temperature of 10% weight loss.

[d] Inherent viscosity was measured at the concentration of 0.5 g of the polymer in 100 mL of NMP at 20 °C.

Table 2. Conditions of synthesis of polymers **1**

Polymer	Amine	Anhydride	NMP /mL	*C* (%)
	g			
1a	0.700	0.520	11	9.98
1b	0.792	0.520	12	9.85
1c	0.700	0.628	13	9.26
1d	0.792	0.628	14	9.21

Note. Reaction duration at ~20 °C was 3 h; that at 180—190 °C was 4 h.

fers appreciably from the linear rigid-rod shape of traditional aromatic polyimides (see Fig. 1). The disturbed packing of macromolecular chains facilitates the diffusion of small solvent molecules between the polymer chains, resulting in a better solubility. The higher solubility makes these polymers potential candidates for practical applications in spin coating and casting processes

The inherent viscosity of the polymers was in the range of 0.4—0.5 dl g^{-1} (see Table 1).

The molecular weight of the polymers was determined by gel permeation chromatography. The weight-average molecular weights M_w are in the range of 39000—72000 g mol^{-1}, the number-average molecular weights M_n are in the 26000—40000 g mol^{-1} range, and the polydispersity M_w/M_n is 1.45 to 1.81 (see Table 1). The molecular weight distributions were essentially unimodal without evidence of significant oligomeric or unreacted species.

All of the polymers exhibit good film-forming properties. Their solutions in NMP with a concentration of about 10% were cast onto glass substrates and dried to yield thin transparent films with a thickness of 10 μm. The films were tough, flexible, and transparent. Very thin coatings with a thickness of about ~10 nm were prepared from dilute (2 %) solutions in NMP by spin-coating onto silicon wafers. These coatings showed a very strong adhesion to silicon. The quality of the films (as-deposited on the substrates) was studied by atomic force microscopy (AFM). The films exhibited very smooth surfaces over a large scanning range (1—100 μm). Their root-mean-square (rms) roughness calculated from the AFM data is of the same order of magnitude as that for highly polished silicon wafers used as substrates. This means that the deposited films are very smooth and homogeneous. They do not show any pinholes or cracks and are practically defectless. These features are highly demanded and necessary for using films of this type in microelectronic devices.[13] A typical AFM image is shown in Fig. 2.

The thermal stability was studied by thermogravimetric analysis (TGA). The TGA curves show that the polymers start to decompose in the range of 470—506 °C and show a 10% weight loss at 516—525 °C (see Table 1). These values illustrate the high thermal stability of the polymers. Comparison of polymers **1** under study with related poly[(ether)imides],[14,15] synthesized recently by condens-

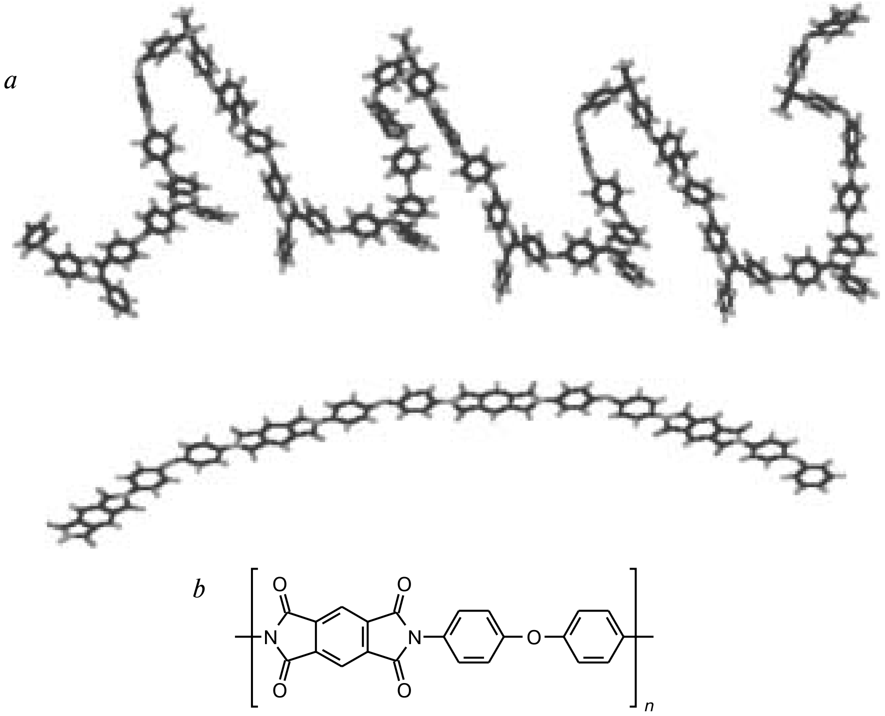


Fig. 1. Model molecules of polymer **1b** (four repeating units)(*a*) and a traditional aromatic polyimide (*b*).

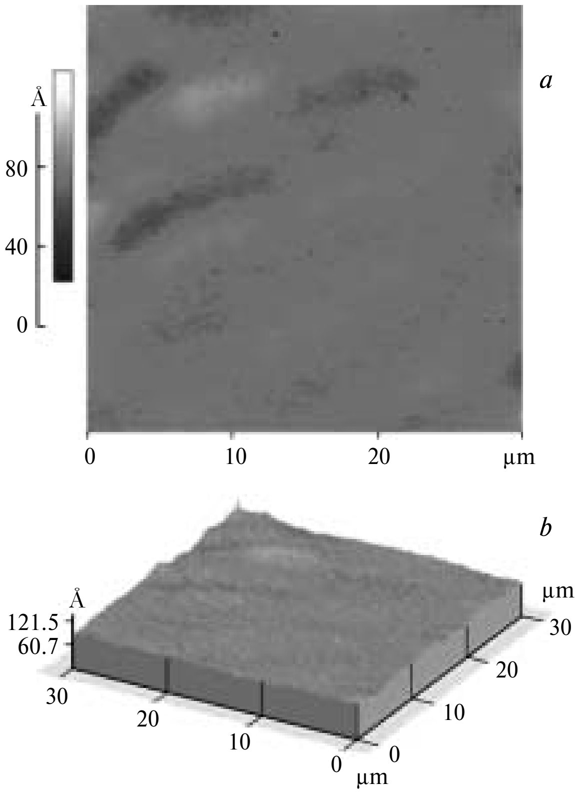


Fig. 2. AFM images of a film made of polymer **1a** (*a*, top view; *b*, side view).

ing the same dianhydrides with *p*-phenylenediamine or 2,2-di(4-aminophenyl)hexafluoropropane, shows that their decomposition temperatures are in the same range. This implies similar thermal stabilities of the phenylquinoxaline and imide fragments. Also, comparison of polymers **1** with related fluorinated poly[imide(phenylquinoxalines)],[16] obtained earlier from hexafluoroisopropylidene-diphthalic anhydride and the same diamines containing preformed phenylquinoxaline rings, indicates that their thermal stabilities are similar. This means that the presence of ether linkages preserves the high thermal stability while improving the solubility.

The glass transition temperatures ($T_{g.t}$) of the polymers estimated from the DSC curves were in the range of 210—238 °C (see Table 1 and Fig. 3). The DSC measurements showed no evidence of crystallization or melting, which proves an amorphous morphology. It can be noted that polymers **1b** and **1d**, which contain diphenyl oxide fragments between the phenylquinoxaline groups in the segment coming from the diamine monomer, have slightly lower $T_{g.t}$ values than their counterparts **1a** and **1c** (210, 213 *vs.* 221, 238 °C, respectively). This decrease in $T_{g.t}$ is due to the increase in the flexibility of the polymer backbone determined by the ether bridges present in both monomer segments. One may also note the large interval between $T_{g.t}$ and the decomposition temperature, which could be advantageous in the processing of these polymers by the thermoforming technique.

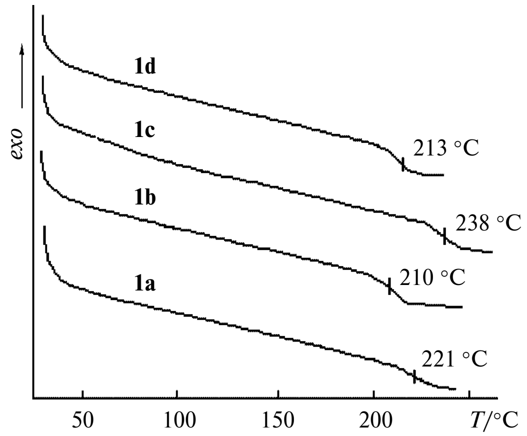


Fig. 3. DSC curves of polymer **1**.

Thus, the incorporation of phenylquinoxaline units and ether linkages, together with isopropylidene or hexafluoroisopropylidene groups into the backbone of aromatic polyimides affords polymers with substantially improved solubilities in polar aprotic solvents and even in less polar liquids such as chloroform. These polymers maintain high thermal stability, with the decomposition temperature being above 470 °C and $T_{g.t}$ being 210—238 °C. The large interval between the glass transition temperature and decomposition temperature may be advantageous for the thermoforming processing of the polymers. The polymers can be processed from NMP solutions into thin and ultrathin pinhole-free films. All these properties associated with easy processability make these polymers potential candidates for high-performance applications.

Experimental

The melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices) apparatus.

The IR spectra were recorded on a Specord M 80 spectrometer in the transmission mode at 4 $\mathrm{cm^{-1}}$ resolution for KBr pellets with applied monomers or precipitated polymers.

The inherent viscosities of the polymers were determined in NMP at 20 °C and at a concentration of 0.5 $\mathrm{g\,dL^{-1}}$ using an Ubbelohde viscometer.

The weight average (M_w) and number-average molecular weights (M_n) were determined by gel permeation chromatography (GPC) on a Waters GPC apparatus provided with refraction and UV detectors and a PL Mixed C column. The measurements were carried out with 2% solutions of the polymers, DMF containing 0.1 *M* $NaNO_3$ being used as both the solvent and the eluent. Polystyrene standards with known molecular weights were used for calibration.

The thermogravimetric analysis (TGA) of the precipitated polymers was done on a MOM derivatograph (Hungary) at a heating rate of 12 °C $\mathrm{min^{-1}}$ in air. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded in the TGA curves.

The glass transition temperatures ($T_{\mathrm{g.t}}$) of the precipitated polymers were determined on a DSC 12 E Mettler differential scanning calorimeter at a heating rate of 10 °C min^{-1} under nitrogen. The samples were heated from 20 °C to >300 °C at a rate of 10 °C min^{-1} under nitrogen.

The model molecules for a polymer fragment were obtained by molecular mechanics (MM+) using the Hyperchem program, version 4.0.[17]

The surfaces of the thin films on silicon wafers were studied by atomic force microscopy (AFM) using a SA1/BD2 apparatus (Park Scientific Instruments) with a Si_3N_4 pyramidal type tip in the contact mode under a constant force.

Di(aminophenyl)-substituted quinoxalines (2a,b) (general procedure). Bis(α-diketone) (0.001 mol) was added to a suspension of 3,4,4′-triaminodiphenyl ether (0.02 mol) in 20 mL of a $CHCl_3$—MeOH mixture (10 : 1). After 24 h, the solution was precipitated in 200 mL of MeOH. The resulting precipitate was filtered and dried. The yield of quinoxaline **2** was 80%. The physicochemical characteristics coincided with those described previously.[10]

Bis[(ether)anhydrides] 3a,b were prepared by published procedures. The physicochemical characteristics coincided with those obtained previously.[11,12]

Poly[phenylquinoxaline(ether)imides] (1a—d). Diamine **2a** (0.7 g, 0.01 mol) and NMP (11 mL) were introduced into a 100-mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet and outlet. The mixture was stirred under nitrogen to complete dissolution. Then dianhydride **3a** (0.52 g, 0.001 mol) was added to the resulting solution and stirring was continued for 3 h at room temperature under N_2. The solution became viscous. The solution was heated at 185—190 °C for 4 h under a nitrogen stream to perform the cyclization of the polyamidic acid **4a** to the corresponding polyimide **1a**, and the flask was cooled down to ~20 °C. The resulting polymer solution was slowly poured into water to precipitate polymer **1a** as a fibrous material. The precipitate was filtered, washed three times with water with stirring, and dried at 120 °C. The inherent viscosity of a 0.5% NMP solution at 20 °C was 0.5 dL g^{-1}. The IR spectrum showed absorption peaks at 1725, 1780, 1375 and 740 cm^{-1} due to the imide ring. Polymers **1b—d** were prepared in a similar way. The reactant ratios and synthetic details are given in Table 2.

The authors are grateful to Dr. T. Kopnick (Institute of Thin Film Technology and Microsensors, Teltow, Germany) for AFM measurements and for GPC analyses.

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Received June 7, 2004