Russian Chemical Bulletin, International Edition, Vol. 53, No. 9, pp. 1813—1823, September, 2004

Polymers containing phenylquinoxaline rings*

M. Bruma,[a]* ***E. Hamciuc,***[a] ***I. Sava,***[a] ***and N. M. Belomoina***[b]

[a]*Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41 A, Iasi 700487, Romania*
Fax: + 40 (232) 211299, E-mail: mbruma@icmpp.ro
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 6549. E-mail: bel@ineos.ac.ru

The synthesis and properties of poly(phenylquinoxalines) containing hexafluoroisopropylidene or silylene units in the backbone are described. The polymers have been prepared by polycondensation of aromatic diamines containing preformed phenylquinoxaline rings with a dianhydride or diacid chlorides containing hexafluoroisopropylidene groups, or with a dianhydride or diacid chlorides containing silylene units. The solubility, thermal stability, film forming ability, and electric insulating, mechanical, and electroluminescent properties of the thin films are discussed and compared with those of related heterocyclic polymers. Potential applications of poly(phenylquinoxalines) are outlined.

Key words: fluorine-containing poly[(phenylquinoxaline)amides], fluorine-containing poly[phenylquinoxaline(imide)amides], fluorine-containing poly[(phenylquinoxaline)imides], silicon-containing poly[(phenylquinoxaline)amides], silicon-containing poly[(phenylquinoxaline)imides], silicon-containing poly[phenylquinoxaline(imide)amides].

The ever increasing demand for heat resistant materials, particularly in the aerospace and microelectronic industries, has encouraged the search for heterocyclic polymers with targeted applications as dielectric films, interlayer dielectrics, or passivation coatings in integrated circuits. For spin-coating and casting processes, it is desirable to use fully cyclized heterocyclic polymers with a high thermal stability and ready solubility. Polyimides are generally the polymers of choice for these applications due to their good combination of chemical, physical, and mechanical properties.[1—3] However, fully aromatic polyimides are completely insoluble and infusible, and are obtained only from a linear intermediate (polyamidic acid). The two-stage process used for the synthesis of polyimides has some disadvantages related to the limited storage stability of the intermediate polyamidic acids and to the evolution of low-molecular weight volatile products during thermal polyheterocyclization, which can create voids in the final material.

Among the thermostable polymers widely studied for high-temperature applications, much attention has been given to polyphenylquinoxalines, which are soluble in organic solvents in the fully cyclized form and, therefore, the high-temperature curing, which is usually required for polyheterocyclization, can be avoided. Also, polyphenylquinoxalines show good storage properties at ambient temperature.[4,5.] In the past decades, extensive research into polyphenylquinoxalines has been carried out in order to obtain highly soluble and easily processable polymers, particularly capable to be cast into thin and very thin films. The incorporation of flexible groups such as hexafluoroisopropylidene or silylene groups, together with phenylquinoxaline rings into a single polymer chain was performed with the aim to attain an even better balance of useful properties. Thus, fluorinated and silicon-containing poly(phenylquinoxalines) have been intensively investigated in the last 10—15 years.

The fluorine atom, owing to its electronegativity and size and to the strength of the C—F bond, can be used to produce compounds with remarkable properties. The inclusion of hexafluoroisopropylidene groups into a polymer structure is expected to increase the thermal stability, flame retardancy, oxidation resistance, transparency, and environmental stability. However, this is often accompanied by a color change and lower crystallinity, surface energy, and water absorption. The bulky hexafluoroisopropylidene groups also serve to increase the free volume of the polymers, thus improving its electrical insulating characteristics.[6—8]

---

* Based on the report presented at the International Conference *"Modern Trends in Organoelement and Polymer Chemistry"* dedicated to the 50th 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. 1739—1748, September, 2004.

The introduction of Si—C bonds, *e.g.*, in diarylsilylene units, into aromatic polymers, can lead to substantially improved solubility, while maintaining a high thermal stability, and thus facilitate the processing of the resulting polymers from their solutions by common casting or spin-coating techniques. Although the C—C and Si—C bond energies are similar, the thermal stability is expected to increase because of the ionic character of the Si—C bond, as silicon is less electronegative than carbon.[9] Due to the ability of silicon to have, under favorable conditions, a coordination number greater than four, the silicon atom placed between aromatic neighbors provides σ—π-conjugation, which promotes the transport of electrons.[10,11] This fact has aroused more scientific and technological interest in silicon-containing aromatic polymers, because of their potential applications for the production of opto-electronic materials, such as photoresists or electroluminescent devices.

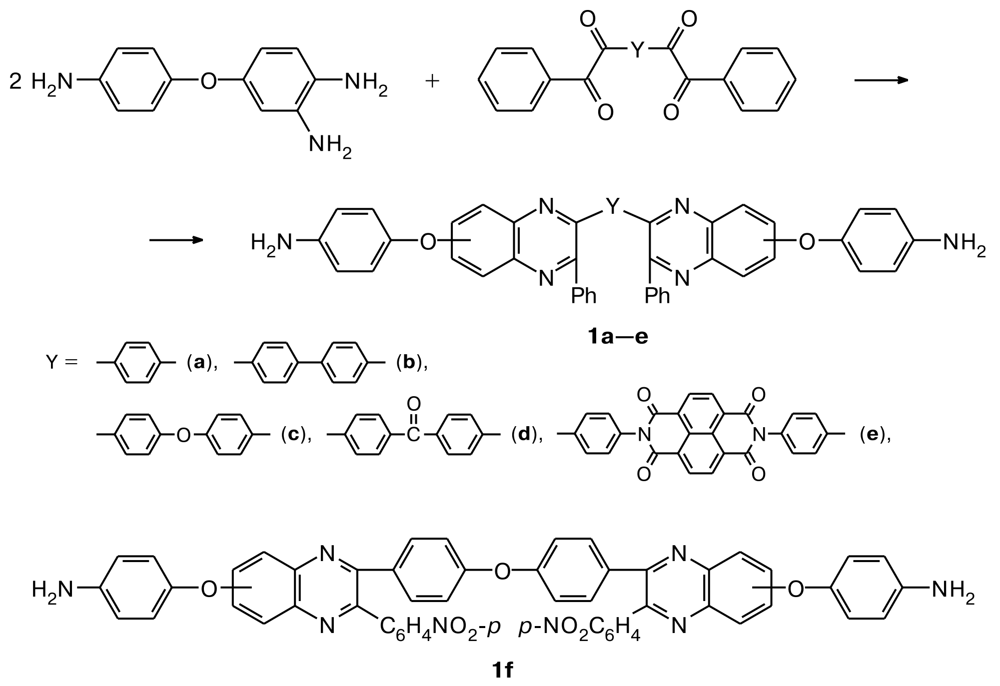
Here we present a review on poly(phenylquinoxalines) containing hexafluoroisopropylidene or silylene units in the backbone and discuss their properties and advantages for practical applications. These polymers have been mainly prepared by polycondensation of aromatic diamines containing phenylquinoxaline fragments with a dianhydride or diacid chlorides incorporating hexafluoroisopropylidene or silylene units.

Synthesis of the monomers

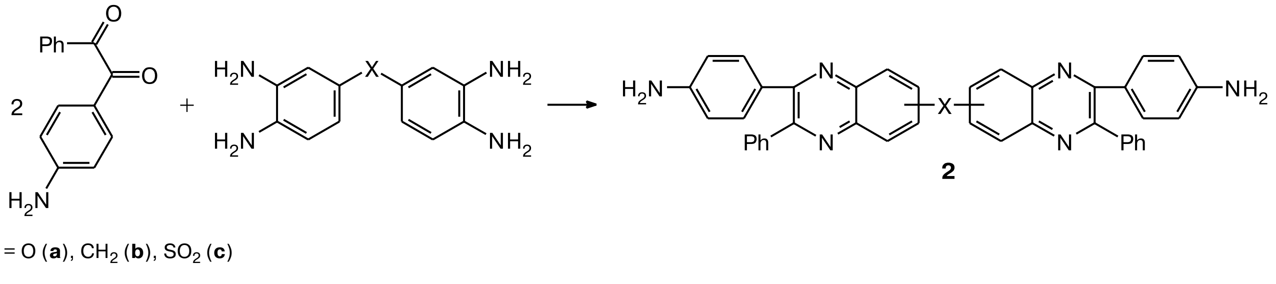
Di(aminophenyl)quinoxalines **1**, containing an aromatic fragment between the two phenylquinoxaline rings, have been prepared by a reported method[12] using the reaction of 3,4,4´-triaminodiphenyl ether with bis(α-diketones) (Scheme 1).

For the synthesis of di(aminophenyl)quinoxaline **1e**, containing a six-membered imide ring, the required α-di-

Scheme 1



Scheme 2

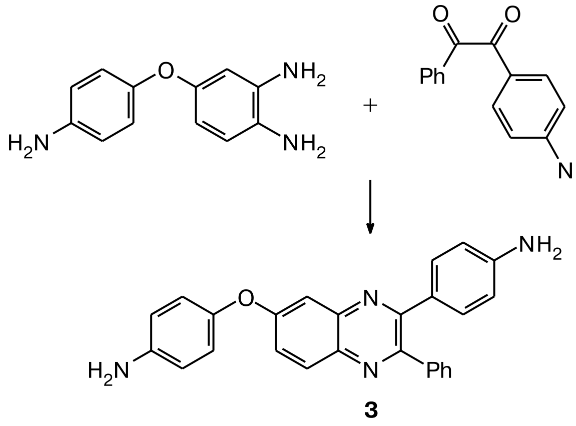


ketone was synthesized from 4-aminobenzil and naphthalenetetracarboxylic acid dianhydride.[13,14] Di(aminophenyl)quinoxaline **1f** containing a nitro group in the phenyl substituent was prepared by the reaction of 3,4,4′-triaminodiphenyl ether with 1,4-bis(*p*-nitrophenylglyoxalyl)diphenyl ether.[15]

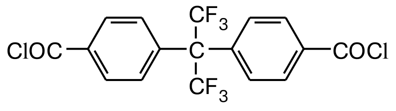
Di(aminophenyl)quinoxalines **2** containing an ether, methylene, or sulfone group between the two phenylquinoxaline rings were synthesized by the reactions of *p*-aminobenzil with 3,3′,4,4′-tetraaminodiphenyl ether, 3,3′,4,4′-tetraaminodiphenylmethane, or 3,3′,4,4″-tetraaminodiphenyl sulfone, respectively, on refluxing in ethanol[13] (Scheme 2).

Di(aminophenyl)quinoxaline **3** containing only one phenylquinoxaline fragment was synthesized by the reaction of 3,4,4′-triaminodiphenyl ether with *p*-aminobenzil[16,17] (Scheme 3).

Scheme 3



Hexafluoroisopropylidene-bis(4-benzoyl chloride) (**4**) was synthesized by treating the corresponding bis(benzoic acid) with excess thionyl chloride at reflux.[18]

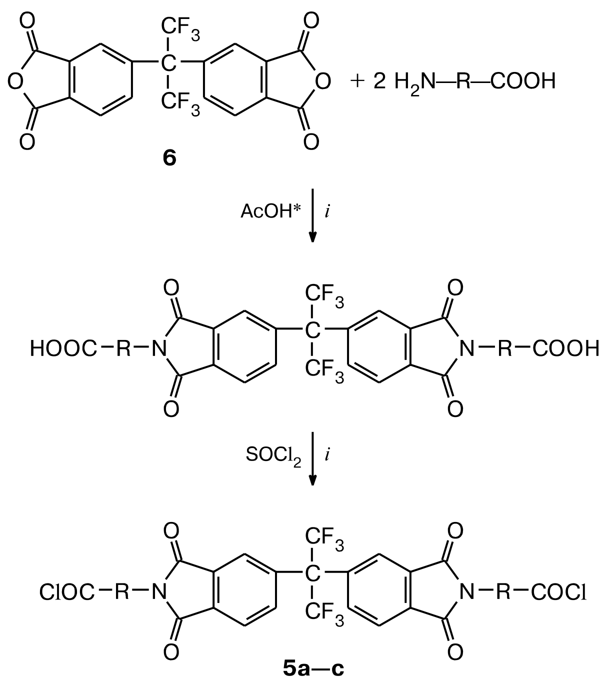


4

Diacid chlorides **5a—c** containing hexafluoroisopropylidene and imide groups were prepared by refluxing the corresponding dicarboxylic acids with excess thionyl chloride. The dicarboxylic acids had resulted from the reaction of hexafluoroisopropylidene-bis(phthalic anhydride) (**6**) with *p*- or *m*-aminobenzoic acid or with aminoacetic acid in boiling acetic acid (Scheme 4).[19—21]

Diacid chloride **7** was prepared from the corresponding dicarboxylic acid, resulting from the reaction of hexafluoroisopropylidene(dianiline) with trimellitic anhydride[22,23] (Scheme 5).

Scheme 4



R = p-C_6H_4 (**a**), m-C_6H_4 (**b**), CH_2 (**c**)

* Glacial. *i*. Refluxing.

Silicon-containing dianhydride **8** was prepared by a sequence of reactions in which 4-bromo-*o*-xylene reacted with dimethyldichlorosilane to produce bis(3,4-dimethylphenyl)dimethylsilane, which was oxidized with potassium permanganate, resulting in bis(3,4-dicarboxyphenyl)dimethylsilane (Scheme 6).[24,25]

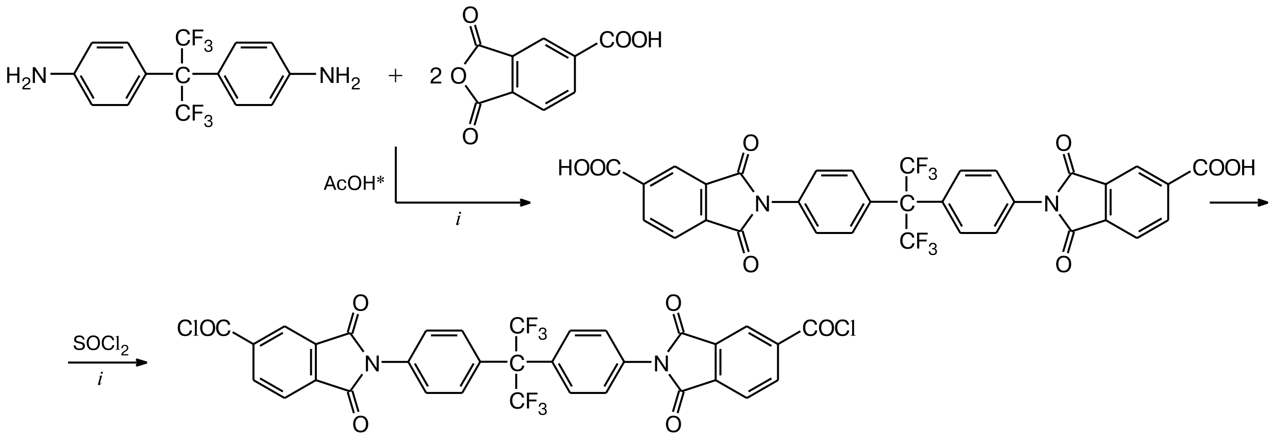
The syntheses of silicon-containing diacid chlorides **9**[26,27] and **10**[28] are shown in Schemes 7 and 8, respectively.

Synthesis of polymers

Polycondensation of di(aminophenyl)quinoxalines **1**, **2** or **3** with fluorinated monomers, dianhydride **6** or diacid chlorides **4**, **5**, or **7**, results in a series of fluorinated polymers: poly[(phenylquinoxaline)amides] **11**,[29] poly[phenylquinoxaline(imide)amides] **12** and **13**,[30—32] and poly[(phenylquinoxaline)imides] **14** and **15**.[33] Similarly, polycondensations with dianhydride **8** and diacid chlorides **9** and **10** has given silicon-containing polymers, poly[(phenylquinoxaline)amides] **16**,[34—36] **17**,[37] and **18**,[38] poly[(phenylquinoxaline)imides] **19**,[25,28] and poly[phenylquinoxaline(imide)amides] **20**.[28]

The polymers with amide groups **11—13**, **16—18**, and **20** were prepared by low-temperature polycondensation of di(aminophenyl)quinoxalines **1—3** with diacid chlorides **4, 5, 7, 9, 10**. A powdered diacid chloride was

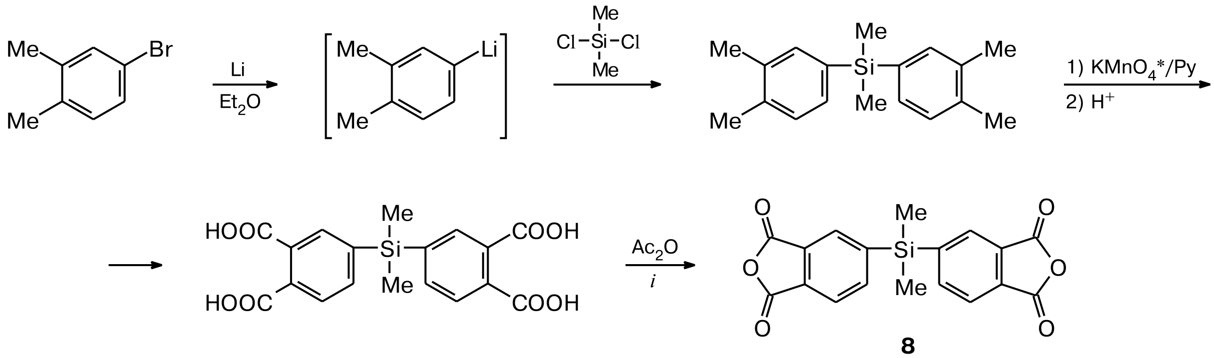
Scheme 5



7

i. Refluxing. * Glacial.

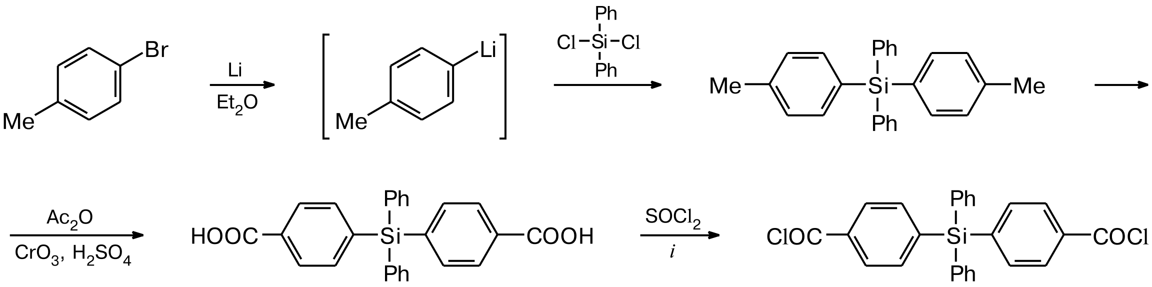
Scheme 6



8

i. Refluxing. * Aqueous.

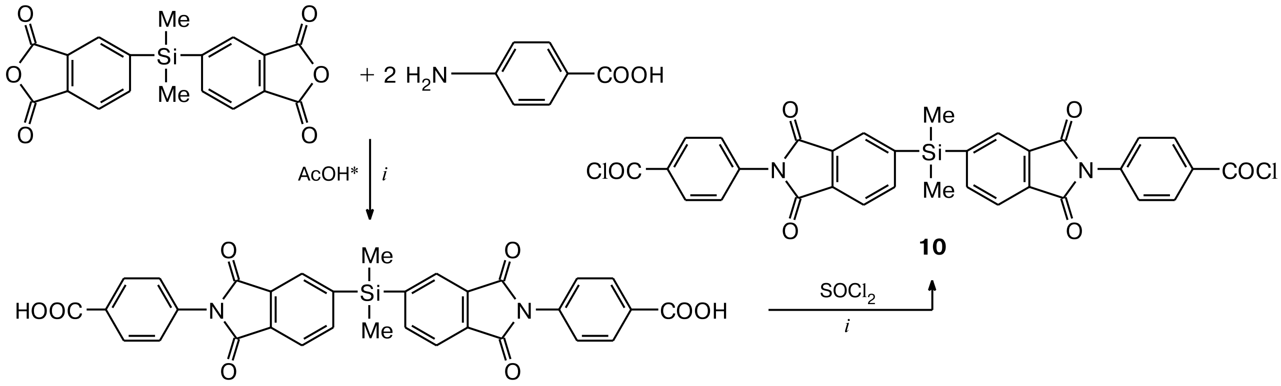
Scheme 7



9

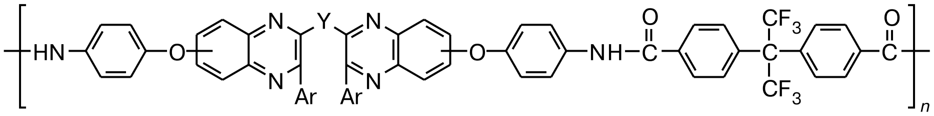
i. Refluxing.

Scheme 8

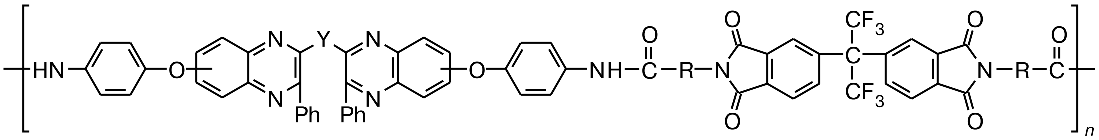


i. Refluxing. * Glacial.

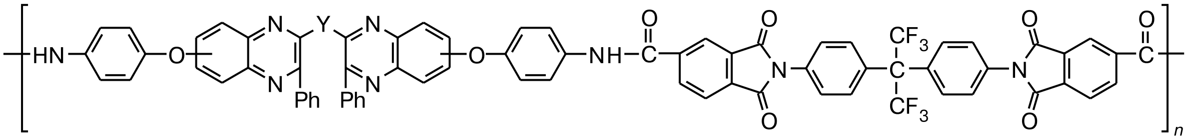
gradually added with stirring to a solution of diamine in *N*-methylpyrrolidone (NMP) cooled to –10 °C. The total monomer concentration in NMP was 10—15%. The reaction mixture was allowed to stand at –10 °C for 15 min. Then the temperature was raised to ~20 °C and stirring was continued for 2 h. The viscous polymer solution was treated with pyridine. A half of the solution was taken for film casting onto a glass plate (100 mm×100 mm). Then the solvent was removed by heating in the following mode: 100 °C, 30 min; 150 °C, 2 h; and 200 °C, 1 h. This gave flexible transparent films. The other half of the polymer solution was poured into water with vigorous stirring. The



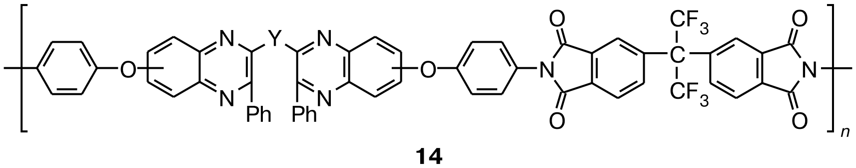
11



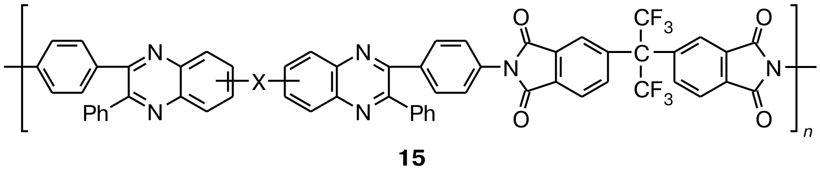
12



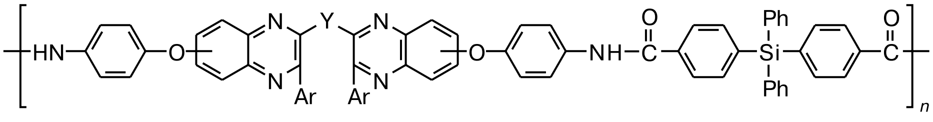
13



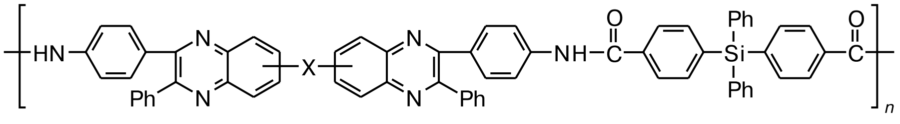
14



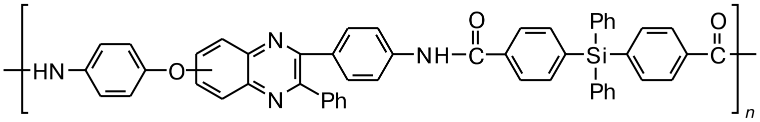
15



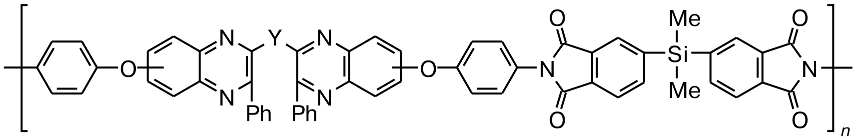
16



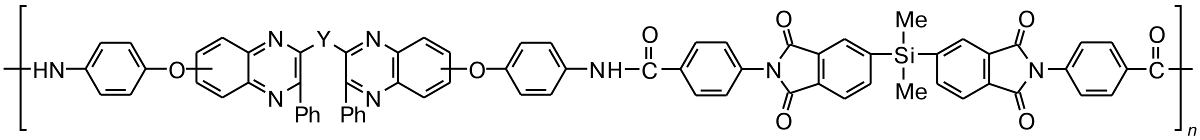
17



18



19



20

white fibers were filtered off, washed with water and ethanol, and dried at 150 °C for 24 h. The films were used to estimate the electrical and mechanical properties, while the precipitated polymer was used in other studies.

Poly[(phenylquinoxaline)imides] **14**, **15**, and **19** were prepared by high-temperature polycondensation in solution (without isolation of the intermediate polyamidic acid) of equimolar amounts of diamines **1**, **2**, or **3** with hexafluoroisopropylidene(diphthalic anhydride) or dimethylsilylene(diphthalic anhydride) in NMP under an inert atmosphere. The dianhydride powder was gradually added with stirring to a solution of diamine in NMP at ~20 °C. The reaction mixture was kept under these conditions for 1 h and then stirred for 2—3 h at 180—190 °C. The polymer solution was cooled to room temperature and partly used for film casting on glass plates or on silicon substrates. The rest was slowly poured into water to precipitate the polymers.

Properties of the polymers

The structures of polymers were identified by IR spectroscopy. The absorption peaks at 1350 and 1315 cm^{-1} present in all of the spectra were attributed to the quinoxaline rings The spectra of polymers **11—13**, **16—18**, and **20** containing amide groups exhibit a broad absorption band at 3450—3350 cm^{-1} and a band at 1680—1660 cm^{-1}, due to the N—H and C=O stretching vibrations, respectively. Polymers **11—15** containing hexafluoroisopropylidene groups are responsible for absorption maxima at 1180—1170 and 1220—1200 cm^{-1}, which were assigned to the C—F bonds. Polymers **16—18**, having silicon in the diphenylsilylene units, show absorption peaks at 1430, 1120, and 730—700 cm^{-1}, which are characteristic of phenylsilanes. Polymers **19** and **20**, containing silicon in dimethylsilane fragments, exhibited absorption bands at 1240 and 810 cm^{-1}, which is characteristic of the Me—Si bond.

Most of these polymers have relatively high molecular weights and narrow molecular-weight distributions with a very low amount of unreacted monomers and oligomers. For example, fluorine-containing poly[phenylquinoxaline(imide)amide] **13** has the molecular weight M_w ~250 000 g mol^{-1} and M_n ~145 000 g mol^{-1}, the oligomer content being below 4%. The UV spectra recorded for different molecular weights were closely similar, confirming the structure homogeneity of the polymers (Fig. 1).[31]

All these polymers are readily soluble in polar amidic solvents such as *N*-methylpyrrolidone, dimethylform-

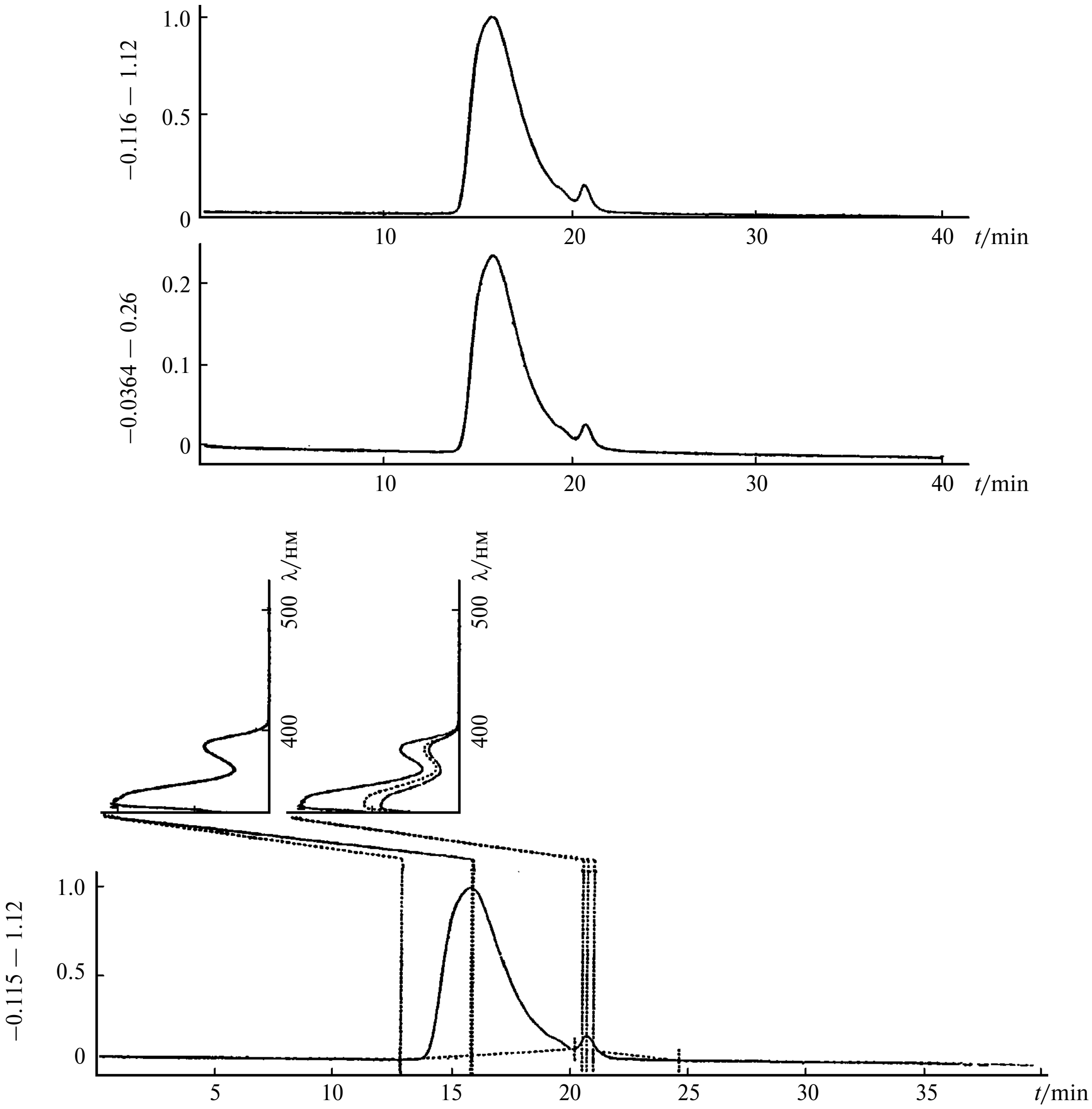


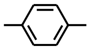
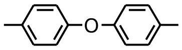
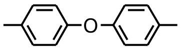
Fig. 1. GPC curve coupled with UV spectra of the high- and low-molecular-weight fractions of polymer **13a**.

amide, and dimethylacetamide. Some of them are soluble even in less polar solvents such as tetrahydrofuran or chloroform. The good solubility of these polymers is attributable to the presence of phenylquinoxaline rings, together with hexafluoroisopropylidene or dimethylsilane groups in the backbone. According to molecular modeling, the polymer macromolecules are far from being rigid linear chains, which is normally the case for wholly aromatic polyimides, polyoxadiazoles, or other heterocyclic polymers. Due to this molecular shape, the packing of the polymer chains is loose and the solvent can easily diffuse among the macromolecules, which facilitates solubilization. Typical model macromolecules are shown in Fig. 2.[25]

Fig. 2. Model molecule of the silicon-containing poly[(phenylquinoxaline)amide] **18**.

All of the polymers possess remarkable film forming properties. They were processed from solutions into flex-

Table 1. Mechanical properties of free-standing films of silicon-containing poly[(phenylquinoxaline)amides] **16a—c** (Ar = C_6H_4-X-*p*)

Polymer	Y	X	Elongation (%)	L*	M**
				MPa	
16a		H	37.70	100.74	386.17
16b		H	60.80	100.36	180.23
16c		NO_2	26.15	73.79	297.22

* Tensile strength.

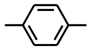
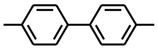
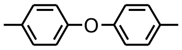
** Tensile modulus.

ible films by casting or spin-coating techniques. The free-standing films with a thickness in the micrometer range (5—30 μm) were flexible and creasable and maintained their integrity after repeated bending. The mechanical properties for a series of poly[(phenylquinoxaline)amides] **16a—c** containing silicon are given in Table 1.[35] These data are indicative of good mechanical properties, similar to those of related polyamides.

The electrical insulating properties of free-standing polymer films were estimated based on the dielectric constant at different relative humidity values. Most of the polymers had low dielectric constants, namely, 2.9—3.6 at 0% relative humidity (RH). These values are similar to the dielectric constants of related fluorinated polyimides, and they are often lower than this value (3.5) for the polyimide obtained from pyromellitic dianhydride and 4,4′-diaminodiphenyl ether (H-film), which is a promising dielectric for high-performance applications. The dependence of the dielectric constant on the relative humidity is linear for some of the polymers (Table 2), which makes them attractive for the manufacture of high-performance humidity sensors.[33]

When comparing fluorine-containing poly(phenylquinoxalines) with silicon-containing poly(phenylquinoxalines), it can be seen that their dielectric constants are very similar, although the hexafluoroisopropylidene group was expected to decrease the dielectric constant. As a matter of fact, the polar amide and/or imide groups, which are also present in the macromolecule, also influence significantly the dielectric constant. Very thin films (with a thickness in the nanometer range) of some polymers were deposited onto silicon wafers. According to atomic force microscopy (AFM) data, the films display very smooth surfaces.[10] The root-mean-square roughness of the films was about 5—15 Å, being in the same range as that of the highly polished silicon wafers used as the substrates. This implies that the films are compact, homogeneous and contain no cracks or pinholes and almost no defects. The films, particularly those made of silicon-containing poly[(phenylquinoxaline)amides] and poly[(phenylquinoxaline)imides], had a strong adhesion to the silicon wafers. This feature may be useful for potential applications in advanced microelectronics. Typical AFM images are shown in Fig. 3.

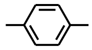
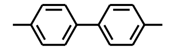
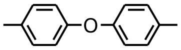
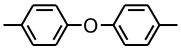
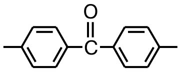
Table 2. Dielectric constants of fluorinated poly(phenylquinoxalineimides) **14a—c**

Polymer	Y	Dielectric constant (relative humidity (%))
14a		2.920 (0.00), 3.160 (25.40), 3.420 (54.00), 3.610 (71.60)
14b		3.150 (0.00), 3.360 (26.00), 3.650 (50.90), 3.910 (72.50)
14c		3.050 (0.00), 3.260 (26.20), 3.510 (54.60), 3.630 (71.20)
Polyimide H-film		2.850 (0.00), 3.055 (18.80), 3.160 (31.30), 3.350 (56.10)

The thermal stability of the polymers was estimated by thermogravimetric analysis. All poly(phenylquinoxalines) containing either hexafluoroisopropylidene or silicon in the backbone exhibited a high thermal stability, with initial decomposition temperatures (the temperature of 5% weight loss) for most of them being above 400 °C and even above 450 °C. The decomposition temperatures of polymers incorporating methylene bridges were in the range of 350—450 °C. As an example, Table 3 presents the thermal data for a series of poly[(phenylquinoxaline)amides] **11a—e**, containing hexafluoroisopropylidene fragments.

When considering these poly(phenylquinoxaline)-type polymers, one can conclude that their thermal behavior is very similar to that of related wholly aromatic/heteroaromatic polymers that do not contain any flexible groups,

Table 3. Thermal properties of fluorinated poly[(phenylquinoxaline)amides] **11a—e** (Ar = C_6H_4-X-*p*)

Polymer	Y	X	η_{lg} /dl g^{-1}	*IDT*	T_{10}	T_g
					°C	
11a		H	0.7	415	504	289
11b		H	0.55	450	505	292
11c		H	0.8	461	516	264
11d		NO_2	0.75	380	450	291
11e		H	0.7	417	524	285

Note. η_{lg} is the inherent viscosity, *IDT* is the initial decomposition temperature (5% weigh loss), T_{10} is the temperature of 10% weight loss, T_g is the glass transition temperature.

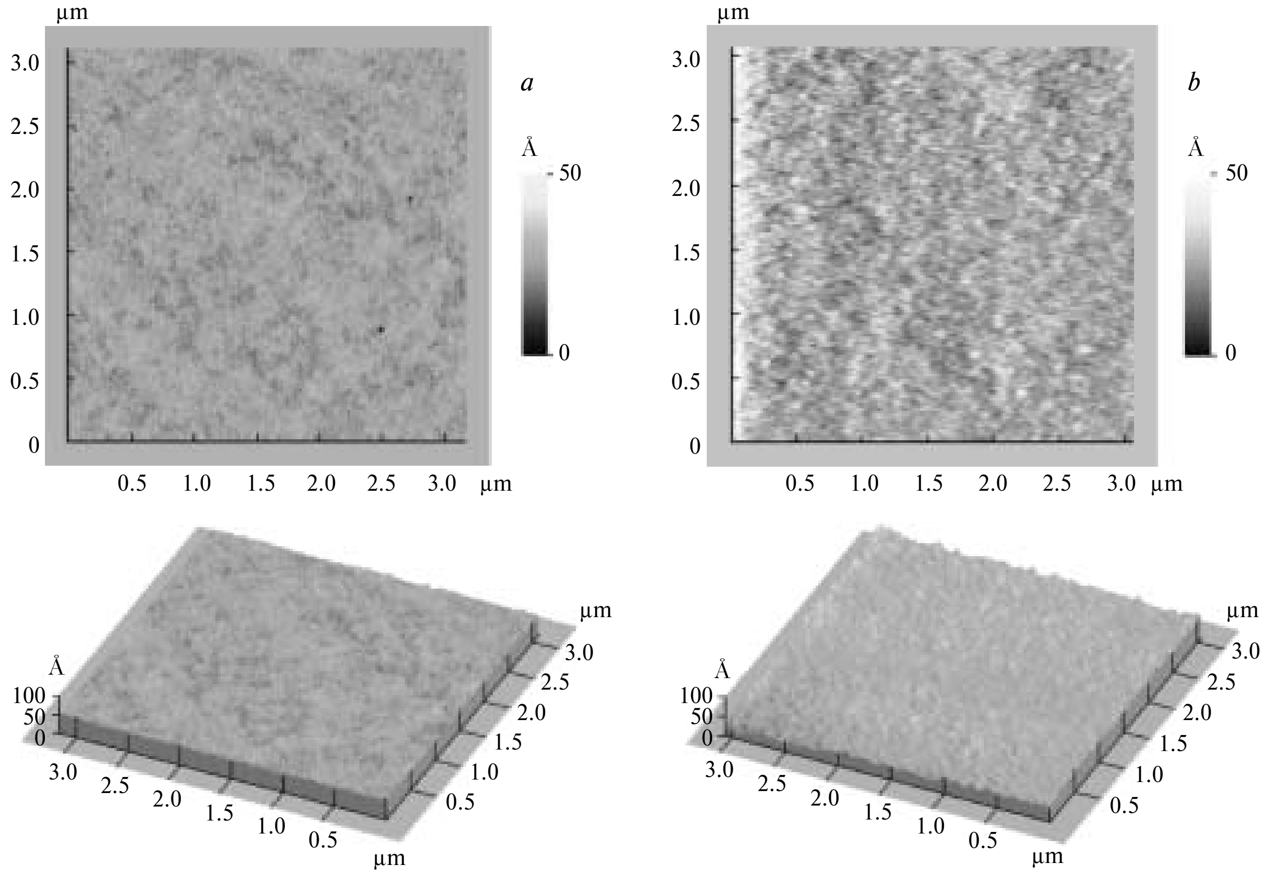


Fig. 3. Top-view and side-view AFM images of very thin films made of silicon-containing poly[(phenylquinoxaline)amides] **16a** (*a*) and **16b** (*b*).

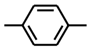
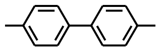
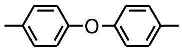
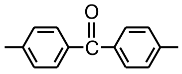
while their processability is significantly improved due to the presence of these flexible units.

Most of the polymers in question containing hexafluoroisopropylidene groups usually have a glass transition temperature (T_g) in the range of 225—305 °C, while silicon-containing polymers are characterized by T_g of 245—305 °C. All of these polymers show a large gap between the glass transition and decomposition temperatures, which may be advantageous for their processing by a thermoforming technique.

The thin films of silicon-containing poly[(phenylquinoxaline)amides] deposited on silicon wafers were kept at 250, 300, 350, and 400 °C for 15 min[36] and their reflectance IR spectra were recorded. The spectra remained unchanged (Fig. 4), indicating a high thermal stability of the films. However, after this thermal treatment, the polymer films become completely insoluble and lose the thermoplastic properties. This behavior is very important from a practical standpoint, as the polymer films would maintain their shape at high temperature and would be completely resistant to organic solvents. It is believed that during thermal treatment up to 400 °C, some cross-linking is induced through the quinoxaline rings.[39]

The light-emitting ability of poly(phenylquinoxalines) **19a—d** containing silicon and imide rings was estimated on the basis of photoluminescence spectra recorded for polymer solutions in *N*-methylpyrrolidone or for spin-coated films after irradiation with UV light.[25,28] The UV absorption spectra of these polymers in solutions showed maxima in the range of 363—374 nm, their behaviors being rather similar, although an aromatic radical (Ar)

Table 4. UV absorption and fluorescence (Fl) spectra of silicon-containing poly[(phenylquinoxaline)imides] **19a—d**

Polymer	Y	UV/nm		Fl/nm	
		Solution	Film	Solution	Film
19a		374	374	415	425
19b		374	380	420	425
19c		369	374	420	425
19d		363	372	420	425

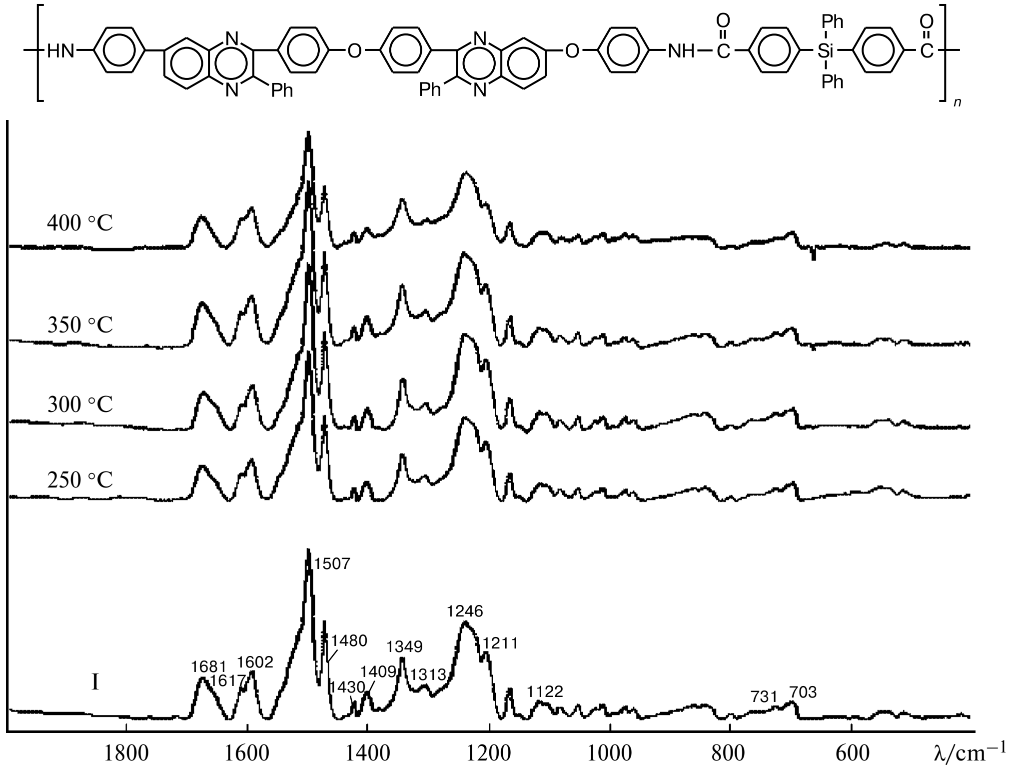


Fig. 4. Fourier Transform IR spectra of very thin films made of silicon-containing poly[(phenylquinoxaline)amides] **16b** (I is before thermal treatment).

with a different extent of conjugation had been introduced between the two phenylquinoxaline units (Table 4). Therefore, the absorption properties of the polymers are mainly determined by the phenylquinoxaline rings. The polymer films showed absorption maxima in the range of 372—380 nm, being slightly red-shifted compared to those for solutions, which indicates a negligible intermolecular interaction of the conjugated fragments of the polymer chain.

All the silicon-containing poly(phenylquinoxaline-imides) showed blue fluorescence both in solutions and in the films with a maximum in the range of 415—425 nm (see Table 4). The fluorescence intensities of polymers **19a—c** are comparable with each other, being in the range of 4000 s^{-1}, while the fluorescence intensity of the polymer **19d** is about an order of magnitude lower. This may be due to some fluorescence quenching by the carbonyl groups in the phenylquinoxaline moiety. A typical example of absorption and fluorescence spectra of a polymer in solution and as spin-coated film is presented in Fig. 5. This type of behavior of silicon-containing poly(phenylquinoxaline-imides) can enable the use of some of these compounds in the design of blue light-emitting devices.

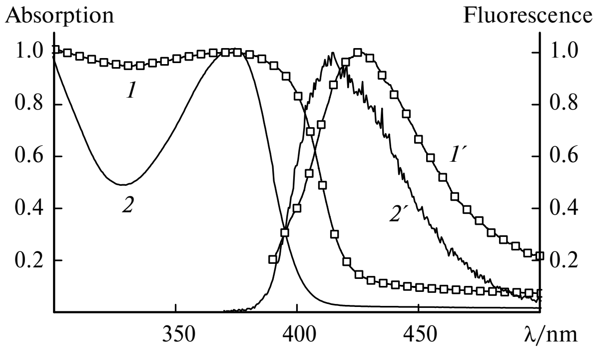


Fig. 5. Absorption (*1*, *2*) and fluorescence (*1′*, *2′*) spectra of polymer **19a**.

References

1. J. W. Bureau, F. Bernard, and D. Broussoux, *Rev. Tech. Thomson CSF*, 1989, **20—21**, 689.
2. C. E. Sroog, *Prog. Polym. Sci.*, 1991, **16**, 561.
3. P. M. Hergenrother, *High Perform. Polym.*, 2003, **15**, 3.
4. E. S. Krongauz, *Vysokomolekulyar. Soedinen., Ser. A*, 1984, **26**, 227 [*Polym. Sci. USSR, Ser. A*, 1984, **26** (Engl. Transl.)].
5. M. Bruma, in *Handbook of Thermoplastics*, Ed. O. Olabisi, Dekker, New York,1997, p. 771.
6. F. W. Mercer and M. T. McKenzie, *High Perform. Polym.*, 1993, **5**, 97.
7. M. Bruma, J. W. Fitch, and P. E. Cassidy, *J. Macromol. Sci., Rev. Macromol. Chem. Phys., C*, 1996, **36**, 119.

8. P. E. Cassidy and J. W. Fitch, in *Modern Fluoropolymers*, Ed. J. Scheirs, Wiley, NewYork, 1997, p. 173.
9. D. A. Armitage, in *Comprehensive Heterocyclic Chemistry*, Ed. A. R. Katritzky, Pergamon Press, Oxford, 1984, **1**, p. 573.
10. M. Bruma and B. Schulz, *J. Macromol. Sci., Polym. Rev., C*, 2001, **41**, 1.
11. M. Bruma, A. L. Rusonov, and N. M. Belomoina, *Vysokomolekulyar. Soedinen., Ser. A*, 2004, **46**, 1 [*Polym. Sci., Ser. A*, 2004, **26** (Engl. Transl.)].
12. V. V. Korshak, E. S. Krongauz, A. P. Travnikova, N. M. Belomoina, H. Raubach, and D. Hein, *Acta Polym.*, 1983, **34**, 213.
13. USSR Pat. 540461, 1977; *Byul. izobret.*, 1977, No. 37; *Chem. Abstr.*, 1978, **88**, 153223s.
14. V. V. Korshak, E. S. Krongauz, N. M. Belomoina, S. A. Babich, M. Bruma, I. Sava, and E. Hamciuc, *Acta Polym.*, 1988, **39**, 409.
15. M. Bruma, I. Sava, E. Hamciuc, N. M. Belomoina, and E. S. Krongauz, *Angew. Makromol. Chem.*, 1991, **193**, 113.
16. Ger. (East) Pat. 138015, 1979; *Chem. Abstr.*, 1980, **92**, 128960e.
17. M. Bruma, I. Sava, W. H. Daly, F. W. Mercer, N. M. Belomoina, and I. I. Negulescu, *J. Macromol. Sci., Pure Appl. Chem., A*, 1993, **30**, 789.
18. C. J. Thaemlitz and P. E. Cassidy, *Polymer*, 1992, **32**, 206.
19. E. Hamciuc, M. Bruma, F. W. Mercer, and C. I. Simionescu, *Angew. Makromol. Chem.*, 1993, **210**, 143.
20. M. Bruma, F. Mercer, B. Schulz, R. Dietel, J. Fitch, and P. Cassidy, *High Perform. Polym.*, 1994, **6**, 183.
21. C. Hamciuc, E. Hamciuc, I. Sava, I. Diaconu, and M. Bruma, *High Perform. Polym.*, 2000, **12**, 265.
22. C. J. Thaemlitz, W. J. Weikel, and P. E. Cassidy, *Polymer*, 1992, **33**, 3278.
23. C. Hamciuc, E. Hamciuc, F. W. Mercer, N. M. Belomoina, and M. Bruma, *High Perform. Polym.*, 1996, **8**, 445.
24. J. R. Pratt and S. F. Thames, *J. Org. Chem.*, 1973, **38**, 4271.
25. E. Hamciuc, B. Schulz, T. Kopnick, Y. Kaminorz, and M. Bruma, *High Perform. Polym.*, 2002, **14**, 63.
26. N. D. Ghatge and J. Y. Jadhav, *Synt. React. Inorg. Met. — Org. Chem.*, 1984, **14**, 83.
27. M. Bruma, B. Schulz, T. Kopnick, and J. Robison, *High Perform. Polym.*, 2000, **12**, 429.
28. B. Schulz, E. Hamciuc, T. Kopnick, Y. Kaminorz, and M. Bruma, *Macromol. Symp.*, 2003, **199**, 391.
29. M. Bruma, E. Hamciuc, B. Schulz, T. Kopnick, B. Stiller, and F. Mercer, *Polymer*, 1999, **40**, 6865.
30. E. Hamciuc, M. Bruma, F. W. Mercer, N. M. Belomoina, and C. I. Simionescu, *Angew. Makromol. Chem.*, 1995, **227**, 19.
31. M. Bruma, C. Hamciuc, E. Hamciuc, F. Mercer, N. Belomoina, and B. Schulz, *Macromol. Symp.*, 1997, **122**, 303.
32. E. Hamciuc, C. Hamciuc, I. Sava, and M. Bruma, *Eur. Polym. J.*, 2001, **37**, 287.
33. I. Sava, M. Bruma, N. M. Belomoina, and F. W. Mercer, *Angew. Makromol. Chem.*, 1993, **211**, 113.
34. I. Sava, M. Bruma, B. Schulz, F. Mercer, V. N. Reddy, and N. M. Belomoina, *J. Appl. Polym. Sci.*, 1997, **65**, 1533.
35. I. Sava, M. Szesztay, M. Bruma, F. Mercer, and B. Schulz, *Angew. Makromol. Chem.*, 1997, **253**, 169.
36. M. Bruma, B. Schulz, T. Kopnick, R. Dietel, B. Stiller, F. Mercer, and V. N. Reddy, *High Perform. Polym.*, 1998, **10**, 207.
37. M. Bruma, B. Schulz, T. Kopnick, B. Stiller, N. Belomoina, and F. Mercer, *Eur. Polym. J.*, 1999, **35**, 1253.
38. M. Bruma, B. Schulz, T. Kopnick, B. Stiller, and F. Mercer, *Mater. Sci. Eng. C*, 1999, **8—9**, 361.
39. K. A. Voloshchuk, G. M. Tseitlin, A. B. Blyumenfeld, N. S. Zabelnikov, and A. A. Atrushkevich, *Vysokomolekulyar. Soedineniya, Ser. A*, 1989, **31**, 295 [*Polym. Sci. USSR, Ser. A*, 1989, **31** (Engl. Transl.)].

Received June 7, 2004;
in revised form, 2004