Synthesis and Properties of Silicon-Containing Polyamides

I. SAVA,[1] M. BRUMA,[1] B. SCHULZ,[2] F. MERCER,[3] V. N. REDDY,[3] N. BELOMOINA[4]

[1] Institute of Macromolecular Chemistry, Iasi, Romania

[2] University of Potsdam, Institute of Solid State Physics, Kantstrasse 55, 14513 Teltow, Germany

[3] Raychem Corporation, Menlo Park, California 94025

[4] Institute of Element Organic Compounds, Moscow, Russia

ABSTRACT: A series of aromatic polyamides incorporating silicon together with phenylquinoxaline or with hexafluoroisopropylidene groups has been synthesized by solution polycondensation of a silicon-containing diacid chloride with aromatic diamines having phenylquinoxaline rings or hexafluoroisopropylidene groups. These polymers are easily soluble in polar aprotic solvents, such as *N*-methylpyrrolidinone and dimethylformamide, and in tetrahydrofurane, and can be solution-cast into thin, transparent films having low dielectric constant, in the range of 3.26 to 3.68. These polymers show high thermal stability with decomposition temperature being above 400°C and glass transition temperature in the range of 236°C to 275°C. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1533–1538, 1997

Key words: silicon-containing polyamides; phenylquinoxaline; thermally stable polymers; dielectric properties

INTRODUCTION

Aromatic polyamides have received considerable attention because of their high thermal stability, chemical resistance, and good tensile properties. Numerous polyamides containing various substituents on the aromatic rings have been synthesized and studied for high-performance applications.[1,2] The polyamides containing all *para*-phenylene rings are the most interesting among these polymers, but they are neither soluble nor fusible and therefore they are processed with great difficulty. A major parameter that contributes to insolubility is the intermolecular bonding energy developed through hydrogen bridges and through dipole–dipole interactions. Much effort has been made to create structurally modified aromatic polymers having increased solubility and processability with retention of their good thermal stability. It was shown that the incorporation of the diphenylsilyl groups into the aromatic polymer backbone leads to soluble products having a remarkable thermal stability and good film-forming ability.[3] Also, being known that polyphenylquinoxalines have good solubility in organic solvents along with high temperature resistance,[4] the synthesis of copolymers containing phenylquinoxaline units is another promising way to easily processible compounds. Likewise, it was shown that the introduction of hexafluoroisopropylidene (6F) groups into the macromolecular chain increases the solubility, thermal stability, flame resistance, glass transition temperature (T_g), oxidation resistance, adhesion, optical transparency, and environmental stability, while decreasing the crys-
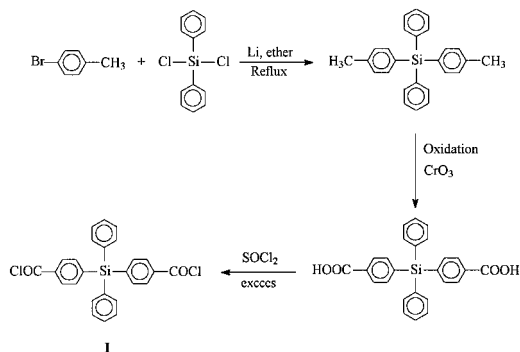
Scheme 1 Synthesis of bis(*p*-chlorocarbonylphenyl)-diphenylsilane **I**.

tallinity, dielectric constant, water absorption and color.[5]
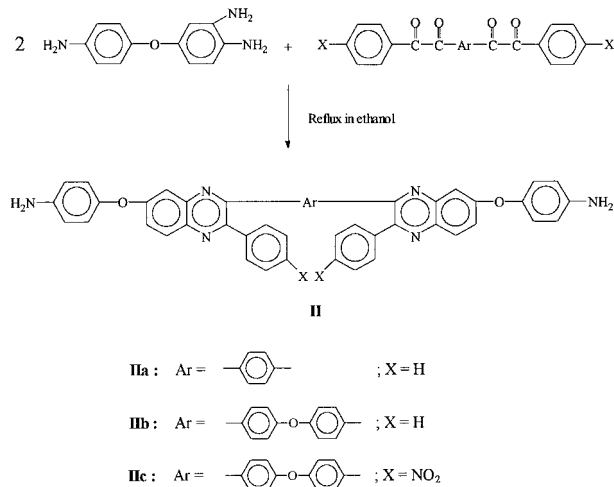
The presence of silicon together with phenyl-quinoxaline or with 6F groups into a single polymeric chain is expected to yield products having an even better combination of useful properties and processing capability. Therefore, we prepared a series of polymers containing these groups by low-temperature solution polycondensation reaction of a silicon-containing diacid chloride with aromatic diamines incorporating phenylquinoxaline rings or 6F groups, and we have studied their solubility, film-forming capability, thermal stability, and electroinsulating properties.

EXPERIMENTAL

Synthesis of the Monomers

The silicon-containing monomer bis(*p*-chlorocarbonylphenyl)diphenylsilane **I** was synthesized starting from *p*-bromotoluene and diphenyldichlorosilane.[6] *p*-Bromotoluene was converted to *p*-tolyllithium and then reacted with diphenyldichlorosilane to produce the diphenyldi(*p*-tolyl)silane. The oxidation of the latter gave the corresponding bis(*p*-carboxyphenyl)diphenyl silane which, by treating with thionyl chloride, afforded the bis(*p*-chlorocarbonylphenyl)diphenylsilane **I**. These reactions are shown in Scheme 1.

Bis(aminophenylquinoxaline)s **II** were prepared by the reaction of 3,4,4′-triaminodiphenylether with bis(α-diketone)s such as 1,4-bis(phenylglioxalyl)benzene, 4,4′-bis(phenylglioxalyl)diphenylether, and 4,4′-bis(*p*-nitrophenylglioxalyl)diphenylether in ethanol at reflux temperature, according to a pub-
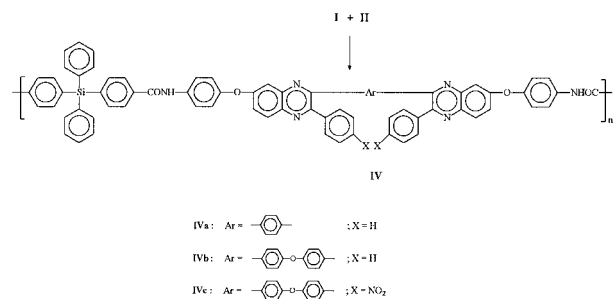
lished method,[7] as shown in Scheme 2. These diamines were purified by recrystallization from a mixture of dimethylformamide (DMF) and water. Melting points: IIa: 343–345°C; IIb: 159–160°C; IIc: 174–175°C.

The diamines containing 6F groups **III** such as 4,4′-(hexafluoroisopropylidene)-dianiline, 3,3′-(hexafluoroisopropylidene)dianiline, and 5,5′-(hexafluoroisopropylidene)di-*o*-toluidine were purchased from Aldrich (Germany) and used as received.

Synthesis of the Polymers

Silicon-containing polyamides with phenylquinoxaline units **IV** or hexafluoroisopropylidene groups **V** were prepared by low-temperature solution polycondensation of equimolar amounts of bis(*p*-chlorocarbonylphenyl)diphenylsilane **I** with diaminophenylquinoxalines **II** or with fluorinated diamines **III**, respectively, in *N*-methylpyrrolidinone (NMP) and in the presence of pyridine as acid acceptor, as shown in Schemes 3 and 4.

II

IIa : Ar = [ring] ; X = H

IIb : Ar = [ring]–O–[ring] ; X = H

IIc : Ar = [ring]–O–[ring] ; X = NO₂

Scheme 2 Synthesis of diaminophenylquinoxalines **II**.

IV

IVa : Ar = [ring] ; X = H

IVb : Ar = [ring]–o–[ring] ; X = H

IVc : Ar = [ring]–o–[ring] ; X = NO₂

Scheme 3 Synthesis of silicon-containing polyamides with phenylquinoxaline units **III**.
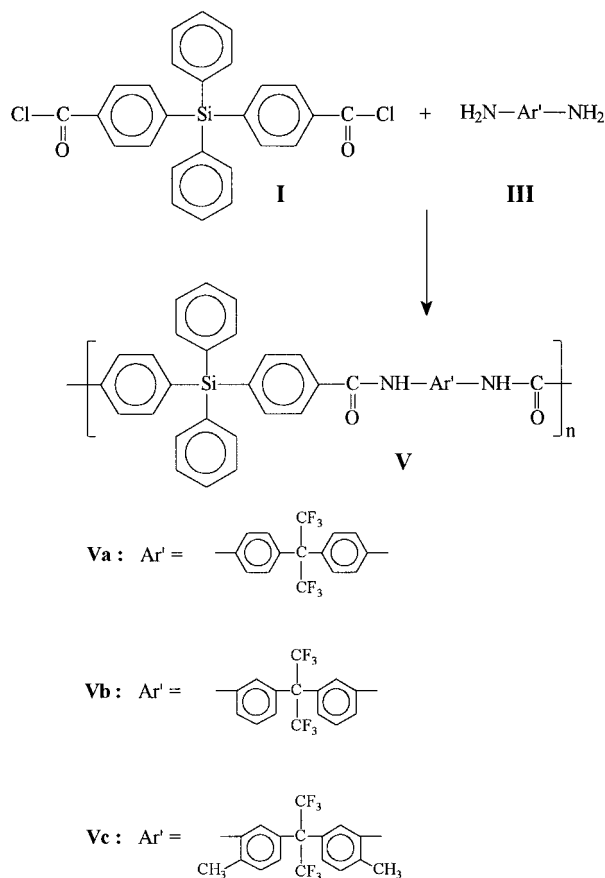
Scheme 4 Synthesis of silicon-containing polyamides with hexafluoroisopropylidene units **IV.**

The following example illustrates the general procedure: In a 100-mL three-necked flask equipped with mechanical stirrer and nitrogen inlet and outlet we placed 2.808 g (0.004 mol) diamine **IIa,** 40 mL NMP, and 1 mL pyridine, and the mixture was stirred until complete dissolution. The solution was cooled to −10°C and 1.844 g (0.004 mol) diacid chloride **I** was added with rapid stirring. The flask contents were kept below 0°C for 10 min. The cooling bath was removed and the reaction mixture was allowed to reach room temperature, after which it was stirred for a further 2 h. Half of the resulting solution was cast onto glass plates and after evaporating the solvent at 100, 130, 160, and 200°C for periods of 30 min each, transparent films were obtained. These were stripped off the plates by immersion in water and then were used for recording infrared (IR) spectra and for dielectric constant measurements. The other half of the polymer solution was poured into water and the precipitated polymer was filtered, washed with water under stirring, and

dried in vacuum at 100°C for 1 h. The precipitated polymers were used for thermal analyses.

Measurements

The inherent viscosities (η_{inh}) were determined at 20°C for polymer solutions (5 g/L) in NMP by using an Ubbelohde viscometer.

The IR spectra of the polymers were obtained with a Specord M-80 spectrophotometer by using polymer films of 4−7-μm thickness.

The thermogravimetric analysis (TGA) of the precipitated polymers was performed with a Seiko-Robotic TG/DTA 320 equipment, operating at a heating rate of 10°C/min, in air, under a purge rate of 300 mL/min. Weight loss at 400 and 500°C was reported as calculated from the resulting thermograms. Also, temperature of 5% weight loss was recorded for each polymer and was regarded as initial decomposition temperature (IDT).

The T_gs of the precipitated polymers were determined with a Seiko DSC 220C differential scanning calorimeter. Samples of 5−7 mg of each polymer were weighed in an aluminium pan, heated from room temperature to above 300°C, held for 3 min, cooled to room temperature, and reheated to above 300°C. All heating and cooling ramps were at 10°C/min, under nitrogen, at a purge rate of 50 mL/min. Heat flow-versus-temperature plots from the second scan were used for reporting the T_g. The midpoint of the inflection curve resulting from the typical second transition was assigned as the T_g temperature of the respective polymers.

The dielectric constants of the polymer films having a thickness of 20−30 μm were determined by using the previously described fluid displacement method.[8] The capacitance of the films was measured using circular gold electrodes (diameter 2.54 cm) mounted in a brass dielectric cell held at a constant temperature (25°C), and a Gen Rad
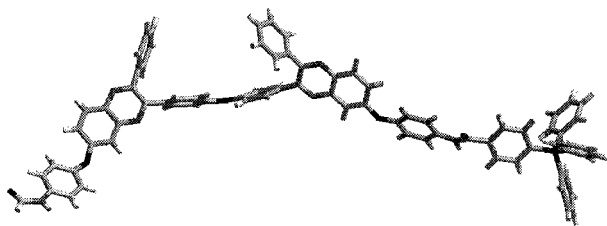

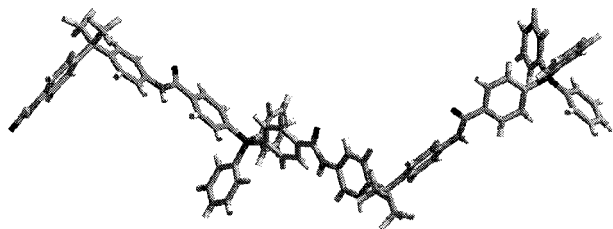**Figure 1** Model molecule for a repeating unit of the polymer **IVb.**

Figure 2 Model molecule of two repeating units of the polymer **Va.**

Precision LC Digibridge (Model 1688) operating at 10 kHz.

Model molecules for a polymer fragment were obtained by means of the Hyperchem program Version 4.0.[9]

RESULTS AND DISCUSSION

The structure of silicon-containing polyamides with phenylquinoxaline units **IV** or with 6F groups **V** was identified by IR spectra. All IR spectra showed wide absorption band at 3450 cm^{-1} characteristic of NH, and one at 1670 cm^{-1} due to C=O in amide groups. Absorption bands at 1430, 1110, and 700 cm^{-1} are characteristic of phenylsilane bonds and are present in all the spectra. Absorption peaks in the spectra of polymers **V** at 1180 and 1220 cm^{-1} were attributed to the 6F groups.

All these polymers are soluble in polar aprotic solvents such NMP and DMF and even in less-polar liquids such as tetrahydrofurane, which is a convenient and easily accessible solvent. The improved solubility compared with that of aromatic polyamides or polyimides, or even with that of related poly(phenylquinoxaline–amide)s,[7,10]

and fluorinated polyamides[11] which do not contain silicon could be due to the bending of the chain at the silicone atoms and to the voluminous phenyl substituents attached to silicone. Also, the phenyl substituents at the quinoxaline ring in the case of polymers **IV** and the flexible 6F groups in the case of polymers **V** do not allow the macromolecules to pack through hydrogen bonds between amide groups; thus they facilitate the penetration of the small molecules of solvent between the polymer chains. The disturbed packing of the macromolecular chains can be visualized by molecular modeling (Figs. 1 and 2).

The inherent viscosities are in the range 0.25–0.54 dL/g (Table I). Thin, transparent, free-standing films were obtained by casting the NMP–polymer solutions onto glass plates. The films resulting from polymers **IV** and **Va** were flexible, whereas those prepared from polymers **Vb** and **Vc** were brittle, probably because of the lower molecular weight of those polymers determined by the reduced reactivity of the corresponding fluorinated diamines containing the amine functions in *meta*-position. Repeated purifications of these two diamines did not lead to significant increase in film flexibility. Very thin coatings having a thickness below 10 nm were prepared from all these polymers by spin-coating technique onto silicon wafers by using 0.1–0.2% polymer solutions in NMP + xylene. These coatings showed a smooth surface with no defects, as shown by atom force microscopy (AFM) examination.

The thermal stability of the polymers was studied by TGA. All the polymers except **IVc** are thermally stable up to about 400°C, as indicated by the insignificant weight loss (less than 3.5%) in TGA thermograms (Table I). The polymer **IVc** shows a weight loss in slight excess of 5% at 400°C

Table I Properties of the Silicon-containing Polyamides

Polymer	Inherent Viscosity (dL/g)	T_g[a] (°C)	IDT[b] (°C)	Weight Loss at 400°C (%)	Weight Loss at 500°C (%)	Dielectric Constant[c]
IVa	0.54	253	455	3.3	8.5	3.48
IVb	0.51	255	460	2.8	8.3	3.49
IVc	0.46	275	390	5.4	20.7	3.68
Va	0.38	270	453	3.0	6.9	3.63
Vb	0.27	236	460	2.8	6.7	3.53
Vc	0.25	238	427	2.8	12.3	3.26

[a] Determined from DSC curves, on the second heating run, at a heating rate of 20°C/min.
[b] IDT: Initial decomposition temperature (temperature of 5% weight loss of the polymers).
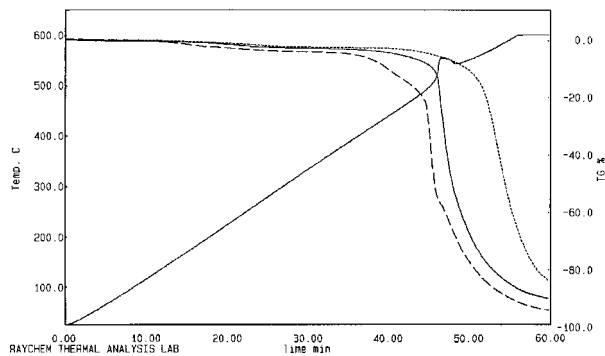[c] Measured on polymer films at 0% relative humidity and 10 kHz.

Figure 3   TGA curves of polymers **IV.** (——) **IVa;** (· · · ·) **IVb;** (----) **IVc.**

but most of the initial weight loss is above 100°C, which could be associated with moisture loss (Fig. 3). The IDT of the polymers, except **IVc** and **Vc,** is in the range of 450–460°C. The IDT of the polymer **IVc** is 390°C and the largest weight change between 400 and 500°C observed in this polymer could be due to the presence of the NO_2 group, which is more sensitive to degradation. Indeed the weight loss of polymer **IVc** at 500°C is 20.7%, whereas the related compounds **IVa** and **IVb** show only 8.5% and 8.3%, respectively. Similar thermal behavior was shown by previously reported poly(amide–imide)s containing p-nitrophenyl-substituted quinoxaline rings which were prepared by using the same diamine (**IIc**) but with other diacid chlorides.[12] Those polymers, too, had IDTs slightly below 400°C, in the range of 370–390°C, being lower that of related polymers without NO_2 on the phenyl substituents. The IDT of the polymer **Vc** is 427°C and the larger weight loss between 400 and 500°C compared with polymers **Va** and **Vb** is probably associated with the decomposition of CH_3 groups (Fig. 4). Thus the total weight loss of polymer **Vc** at 500°C is 12.3%,
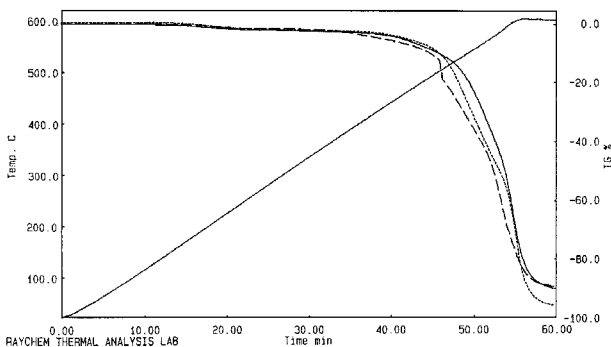

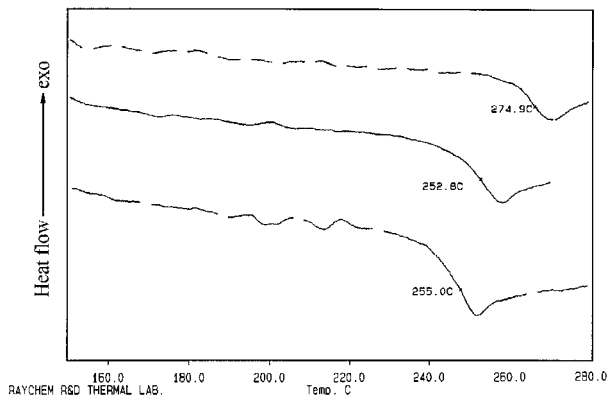**Figure 4**   TGA curves of the polymers **V.** (——) **Va;** (· · · ·) **Vb;** (----) **Vc.**

Figure 5   DSC curves of polymers **IV.** (——) **IVa;** (· · · ·) **IVb;** (----) **IVc.**

whereas related products **Va** and **Vb** show only 6.7% and 6.9%, respectively, weight loss at 500°C.

The decomposition of polymers **IV** results in an exothermic reaction ("flame out") between 520 and 580°C, as shown by the nonlinear excursion in the temperature curve as plotted in real time. In the case of polymers **V** the temperature scan shows no exothermic flame out during their burning/pyrolysis.

T_gs of these polymers as shown by differential scanning calorimetry (DSC) analysis are in the range of 236–275°C (Figs. 5 and 6). The polymers **Vb** and **Vc** show lower T_g values, being 236 and 238°C, respectively, which could be explained by the *meta*-catenation of the diamine segment in these two polymers. It can be seen that there is a large interval between glass transition and decomposition temperatures of all these polymers, which can be advantageous for their processing.

Electroinsulating properties of these polymers have been evaluated on the basis of dielectric con-
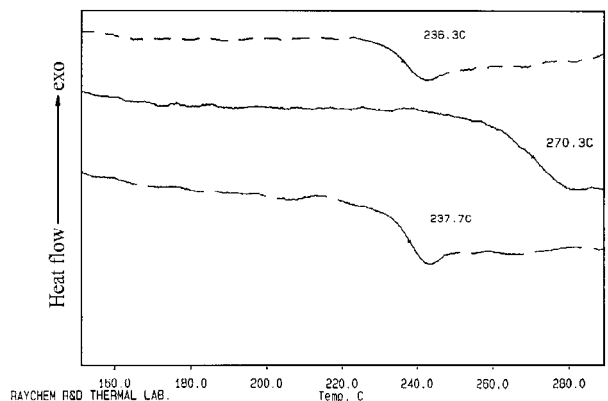

Figure 6   DSC curves of the polymers **V.** (——) **Va;** (· · · ·) **Vb;** (----) **Vc.**

stant values. The dielectric constant of polymer films is in the range of 3.26–3.68, being comparable with that of polyimide "H" film (3.5), which is one of the most common high-performance dielectrics used in microelectronics.[13] Also, by comparing these polymers with fluorine-containing poly(phenylquinoxaline–imide–amide)s previously reported[14]—which were prepared by using the same diaminophenylquinoxalines but with other diacid chlorides, and whose dielectric constant is in the range of 3.53–3.71—it can be seen that the values of their dielectric constants are very similar. Also, comparison of the present polyamides with earlier reported fluorinated polyamides—which were prepared by using the same fluorinated diamines but with different diacid chlorides—shows that their dielectric constants are very close to each other, the values of the latter being in the range of 3.44–3.97.[15] These facts show that the dielectric constants are influenced mainly by the highly polarized carbonyl in amide groups in all these types of polymers. The present polymers, having low dielectric constant and a remarkable capability to be solution-processed into very thin defectless coatings, show promise for future use in microelectronics. Detailed investigation is under way on the specific properties of ultrathin films; those results will be published separately.

CONCLUSIONS

By introducing silicon together with phenylquinoxaline or with hexafluoroisopropylidene groups into the chain of aromatic polyamides, polymers with improved solubility and processability were obtained. They were cast from solutions into thin and ultrathin films having low dielectric constant. These polymers show high thermal stability and a large window between glass transition and decomposition, which may be advantageous for their processing. Potential applications as insulating layers in microelectronics are foreseen.

REFERENCES

1. J. Preston, in *Encyclopedia of Polymer Science and Engineering,* 2nd ed., Vol. 4, H. Mark, Ed., Wiley & Sons, New York, 1988, p. 381.
2. J. Lin and D. C. Sherrington, *Adv. Polym. Sci.,* **111,** 179 (1994).
3. I. Sava, B. Schulz, S. Zhu, and M. Bruma, *High Perform. Polym.,* **7,** 493 (1995).
4. M. Bruma, in *Handbook of Thermoplastics,* O. Olabisi, Ed., Marcel Dekker, New York, 1966, Chap. 31.
5. M. Bruma, J. Fitch, and P. Cassidy, *J. Macromol. Sci., Rev. Macromol. Chem. Phys., C,* **36,** 119 (1996).
6. H. Nagy-Kovacs, A. D. Delman, and B. Simms, *J. Polym. Sci., A-1,* **8,** 869 (1970).
7. V. V. Korshak, E. S. Krongauz, N. M. Belomoina, H. Raubach, and D. Hein, *Acta Polym.,* **34,** 213 (1983).
8. F. W. Mercer and T. D. Goodman, *High Perform. Polym.,* **3,** 297 (1991).
9. Hyperchem Version 4.0, Hypercube Inc., Ontario (1994).
10. J. M. Augl and J. V. Duffy, *J. Polym. Sci., A-1,* **10,** 1123 (1972).
11. R. H. Vora, U.S. Pat. 4914180 (1990); *Chem. Abst.,* **114,** 7455h (1991); and U.S. Pat. 4962181 (1990); *Chem. Abst.,* **114,** 63467a (1991).
12. M. Bruma, I. Sava, E. Hamciuc, N. M. Belomoina, and E. S. Krongauz, *Angew. Makromol. Chem.,* **193,** 113 (1991).
13. C. E. Sroog, *Prog. Polym. Sci.,* **16,** 561 (1991).
14. E. Hamciuc, M. Bruma, F. W. Mercer, N. M. Belomoina, and C. I. Simionescu, *Angew. Makromol. Chem.,* **227,** 19 (1995).
15. M. Bruma, F. Mercer, S. Gronewald, J. Arbaugh, J. Fitch, and P. Cassidy, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.,* **36,** 727 (1995).