Silicon-Containing Heterocyclic Polymers and Thin Films Made Therefrom

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ABSTRACT: Thin films, in the range of tens of micrometers thickness, have been prepared by casting onto glass plates the chloroform or *N*-methylpyrrolidone solutions of polyimides or poly(imide-amide)s containing silicon and phenylquinoxaline units in the main chain. The polymers have been synthesized by solution polycondensation reaction of aromatic diamines having preformed phenylquinoxaline rings with bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride or with a diacid chloride resulting from the reaction of this dianhydride with *p*-aminobenzoic acid. The polymers were easily soluble in polar aprotic solvents and showed high thermal stability. The free-standing films exhibited good mechanical properties with tensile strengths in the range of 48–86 MPa, tensile modulus in the range of 1.25–2.22 GPa and elongation at break in the range of 3–37%. Electrical insulating properties of some polymer films were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature. The values of the dielectric constant at 10 kHz were in the range of 2.94–3.08 for polyimides and 3.89–4.49 for poly(imide-amide)s. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3062–3068, 2006

Key words: polyimides; poly(imide-amide)s; thin films; high thermal stability; dielectric spectroscopy

INTRODUCTION

High-performance polymer films and coating materials are increasingly being required by the electronics industry for use as interlayer dielectrics and passivation coatings in integrated circuit fabrication. For optimum performance, the dielectrics used in these devices should display excellent thermal and chemical resistance, low moisture absorption, and a dielectric constant value as low as possible.[1] Aromatic polyimides are generally the polymers of choice for these applications because of their unique combination of chemical, physical, and mechanical properties.[2,3] However, these polymers are processed with great difficulty because many of them are insoluble and infusible. Knowing that the introduction of flexible groups such as dimethylsilane or ether linkages 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 way to easy processable compounds. On the other hand, it was shown that poly(phenylquinoxaline)s are a family of aromatic polymers known for their excellent thermal and chemical stability.[4,5] The pendent phenyl substituents improve the solubility and processing characteristics of these polymers as well as the thermooxidative stability over the unsubstituted polymers. Also, the bulky phenyl substituent of phenylquinoxaline units and dimethylsilane bridging groups limit chain packing of the polymer and increase the free volume of the polymers thus decreasing the dielectric constant. Therefore, we considered that by introducing silicon together with phenylquinoxaline rings into the repeating unit of aromatic polyimides, polymers with substantially improved solubility and processability could be obtained, having a better combination of properties. Thus, we have synthesized polyimides and poly(imide-amide)s by solution polycondensation of certain aromatic diamines containing preformed phenylquinoxaline rings with bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride, or with a diacid chloride resulting from the reaction of this dianhydride with p-aminobenzoic acid followed by treating with thionyl chloride. The electrical and mechanical characteristics of the polymer films made from these compounds have been evaluated with respect to their chemical structure and compared with those of related polymers previously reported.

EXPERIMENTAL

Synthesis of the monomers

The diaminophenylquinoxalines **I** were synthesized according to the literature.[6,7] Bis(3,4-dicarboxyphe-

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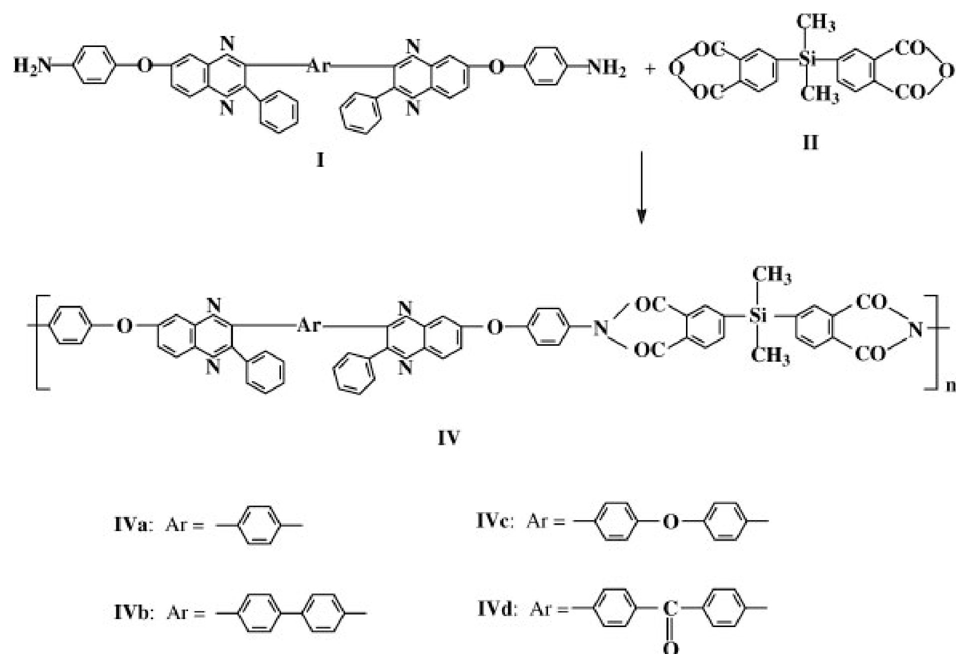


Scheme 1 Preparation of silicon-containing polyimides **IV**.

nyl)dimethylsilane dianhydride **II** was prepared by a multistep reaction, following a published method.[8] Bis[N-(chlorocarbonylphenyl)phthalimidyl]dimethylsilane **III** was synthesized following a procedure previously described.[9]

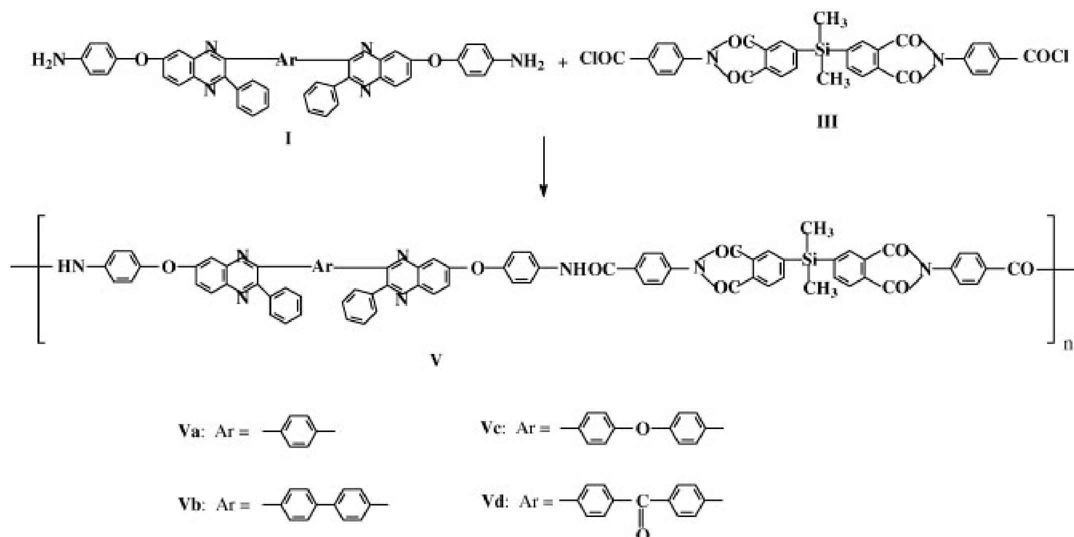
Synthesis of the polymers

Silicon-containing poly(phenylquinoxaline-imide)s[10] **IV** have been synthesized by solution polycondensation of equimolar amounts of aromatic diamines having preformed phenylquinoxaline rings **I** with bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride **II**, in N-methylpyrrolidone (NMP) as a solvent, under a nitrogen stream, as shown in Scheme 1.

Silicon-containing poly(phenylquinoxaline-imide-amide)s[11] **V** have been prepared by solution polycondensation of equimolar amounts of the same diamines **I** with a diacid chloride incorporating preformed imide rings and silicon **III**, in NMP as a solvent and with pyridine as an acid acceptor, as depicted in Scheme 2.

Preparation of polymer films

Films of silicon-containing poly(phenylquinoxaline-imide)s **IV** were prepared by casting a solution of



Scheme 2 Preparation of silicon-containing poly(imide-amide)s **V**.

TABLE I
Parameters Describing Mechanical Properties of Polymers IV and V

Polymer	E (GPa)	σ_y (MPa)	$\varepsilon_y = \lambda_y - 1$	σ_B (MPa)	λ_B
IVa	1.32	–	–	48.46	1.03
IVc	1.55	–	–	64.01	0.05
IVd	1.64	76.15	0.076	68.60	1.13
Vb	2.22	–	–	60.82	1.03
Vc	1.25	65.87	0.095	66.52	1.37
Vd	1.47	88.99	0.102	86.25	1.11

E, elastic modulus; σ_y, yield stress; ε_y, yield strain; σ_B, tensile strength; λ_B, draw ratio at break.

5% concentration of polymer in chloroform onto glass plates, followed by drying at room temperature for 24 h under a Petri dish and for another 2 h at 130°C.[12] Films of silicon-containing poly(phenylquinoxaline-imide-amide)s **V** were similarly prepared by using 10% polymer solution in NMP, which was cast onto glass plates and dried gradually at 100, 130, 160, 190, and 220°C, each for 30 min. The resulting flexible transparent films were stripped off the plates by immersion in hot water for 2 h.

Measurements

Mechanical properties of the polymer films were analyzed by cold drawing of solution cast films and testing with an Instron 6000 Mechanical Testing Machine. The samples in the form of strips (thickness of 0.02 mm, width 2 mm) were drawn with a rate of 1 mm/min at room temperature. The stress dependencies versus draw ratio have been recorded. The initial length of deformed part of samples was 10 mm (the distance between clamp edges).

The dielectric measurements were carried out using a Novocontrol system composed from an Alpha frequency response analyzer and Quattro temperature controller. The samples were prepared in the form of films with thickness of about 20 μm with gold electrodes evaporated in vacuum. The samples were sandwiched between two copper electrodes of diameter 20 mm and placed inside temperature controlled sample cell. The complex permittivity: $\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ has been determined in the frequency range from 10^{-2} to 10^6 and at temperature range from −100 to 220°C. The AC voltage applied to the capacitor was equal to 1.5 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C.

RESULTS AND DISCUSSION

All polymers dissolved easily in polar amidic solvents such as NMP and dimethylacetamide. The polymers **IV** were also soluble in chloroform, which is very useful from a practical point of view. They exhibited high thermal stability with decomposition temperature being above 440°C and high transition temperature above 245°C.[10,11]

The present polymers possess remarkably film-forming ability. The films obtained by casting technique, having a thickness of tens of micrometers were used for mechanical and dielectric measurements.

Between the physical methods, which can be used to study polymers those involving the mechanical and dielectric properties are very important. The data on the mechanical properties are necessary since most applications of synthetic polymers require the materials to be strong, tough, and mechanically

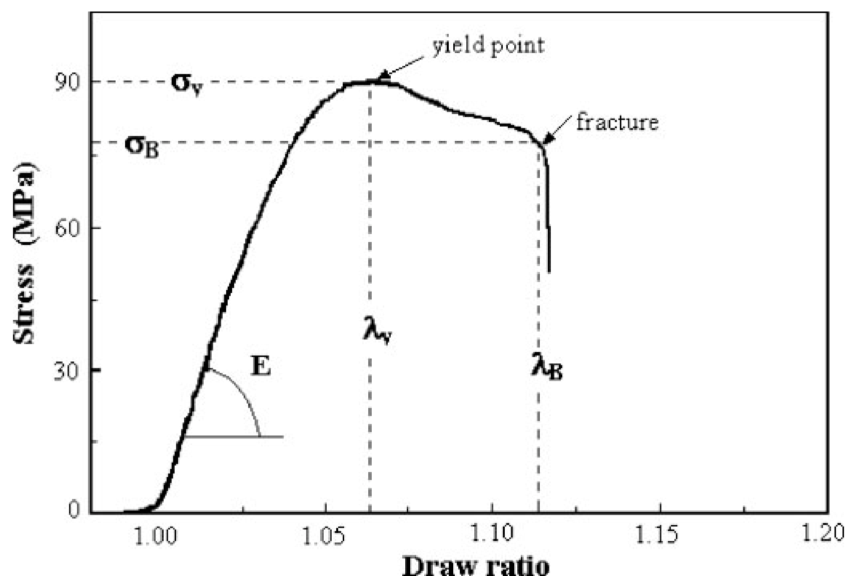


Figure 1 Schematic stress—strain dependence with the parameters characterizing the elasticity at small deformation as well as the yield and the break points.

stable. The electrical properties are required, when polymers are used for cable insulation, for capacitors, for insulation or packaging of electronic devices or as integral parts of electronic devices.

The mechanical properties of some silicon-containing polyimides **IV** and poly(imide-amide)s **V** films are summarized in Table I. The meaning of the parameters determined[13] is illustrated in Figure 1.

Elastic modulus (E) and the coordinates of the yield point (ε_y, σ_y), as well as of the point of fracture (λ_B, σ_B) have been determined as averages of 3–5 independent drawing experiments. The polymers showed similar type of behavior with respect to the elastic deformation range at small strains. The values of elastic modulus are in the range of 1.25–2.22 GPa, the values of tensile strength vary in the range of 48–86 MPa and elongation at break in the range of 3–37%, which shows that these polymers have good mechanical properties.

Electrical insulating properties of some polymer films were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and

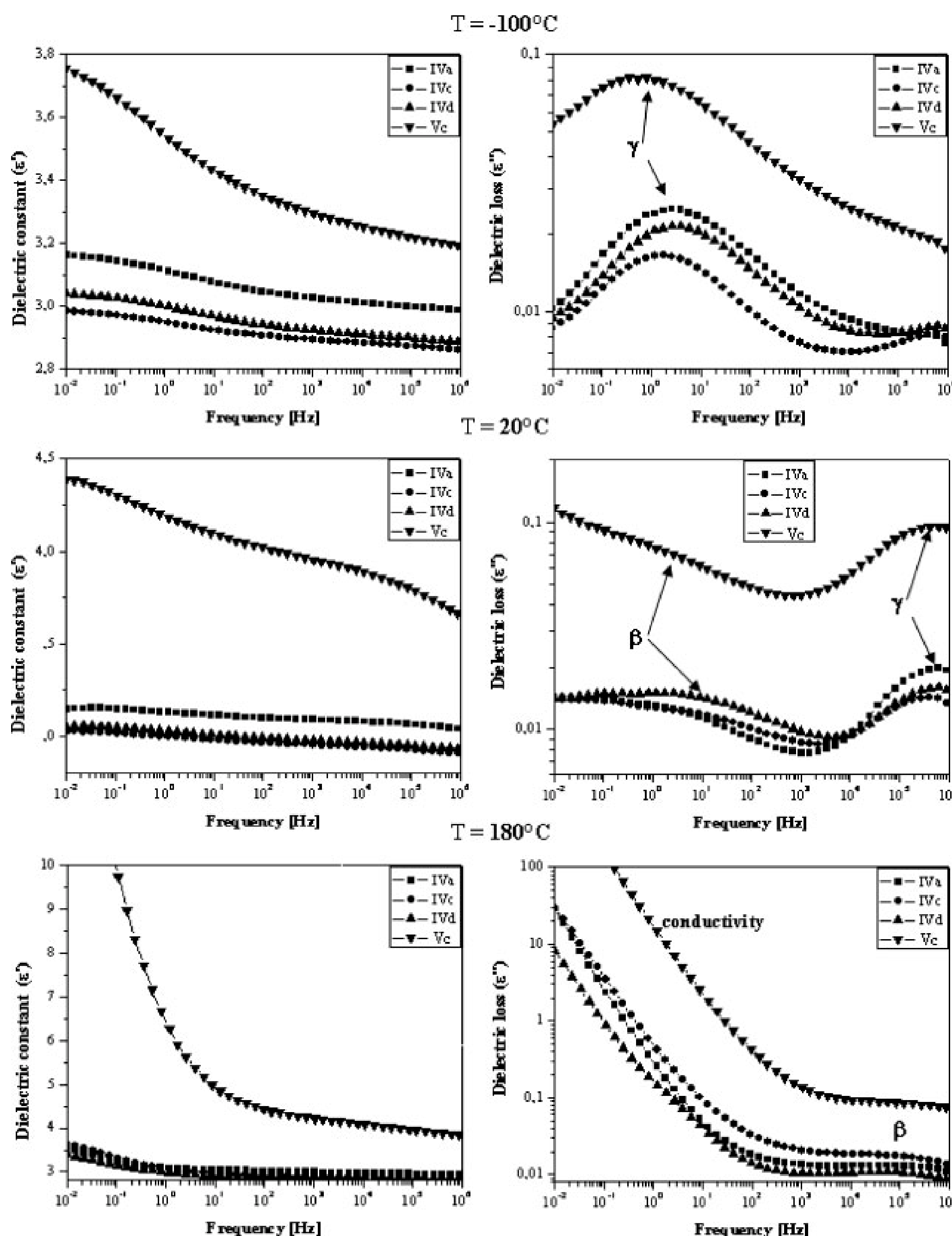


Figure 2 Dependences of dielectric constant (ε') and dielectric loss (ε'') versus frequency at different temperatures for polymers **IV** and **V**.

TABLE II
Dielectric Constant at Selected Frequencies, at 20°C, for Polymers IV and V

Polymer	Dielectric constant at		
	100 Hz	10 kHz	1 MHz
IVa	3.10	3.08	3.04
IVc	2.97	2.94	2.91
IVd	2.99	2.97	2.93
Vb	4.88	4.49	4.06
Vc	4.02	3.89	3.66

temperature. The dielectric permittivity of a material is, in general, a complex quantity, when measured in the frequency domain. Its real part (ε′) is called the ''dielectric constant'' and decreases with increase in frequency with characteristic steps. Its imaginary part (ε″) is usually called the ''dielectric loss'' and may show the maxima on the diagrams versus frequency (or versus temperature). The maxima on dielectric loss diagrams and ''steps'' on dielectric constant diagrams correspond to different molecular relaxation phenomena. They could be caused by the local orientational change of small part of side groups or main chain (secondary relaxations) or by cooperative movements of longer chain fragments, allowing global mobility corresponding to the glass transition phenomenon (primary relaxation).

Figure 2 presents the dependence of real and imaginary parts of complex permittivity on frequency, for some polymers **IV** and **V** at three chosen temperatures.

The dielectric constant increased with decrease in frequency as well as with increase in temperature. In the case of poly(imide-amide)s **V**, at high temperature and low frequency this parameter increased sharply because of the mobility of charge carrier. Poly(imid-amide)s **V** possess higher dielectric constant than polyimides **IV**. Also for polymers **V** the conductivity phenomenon appears at lower temperatures than for polymers **IV**. This can be probably explained by the presence of highly polarized carbonyl in amide groups. The dielectric constants for all the polymers at 100 Hz, 10 kHz, and 1 MHz at room temperature are presented in Table II. The values of the dielectric constant at 10 kHz were in the range of 2.94–3.08 for polyimides **IV** and 3.89–4.49 for poly(imide-amide)s **V**. As can be seen from Table II, polyimides **IV** exhibited lower dielectric constant values in comparison with the H Film—a polyimide, which is prepared from pyrromellitic dianhydride and 4,4′-diaminodiphenylether and which is one of the most common polyimides used as dielectric in microelectronics applications, having a dielectric constant of 3.5.[2,14] This can be probably explained by the presence in the main chains of bulky $Si(CH_3)_2$ groups and phenyl units as pendent groups which increase free volume and thus lowering the polarization by decreasing the number of polarizable groups per unit volume. The higher values of dielectric constant of poly(imide-amide)s are probably due to the presence of polar amide groups, traces of solvent and higher humidity absorption.

For the dielectric loss ε″ two secondary relaxations (β and γ) can be seen connected with local movements of polymer chains. Then the conductivity process arises and masks the primary relaxation connected with glass transition, which should have

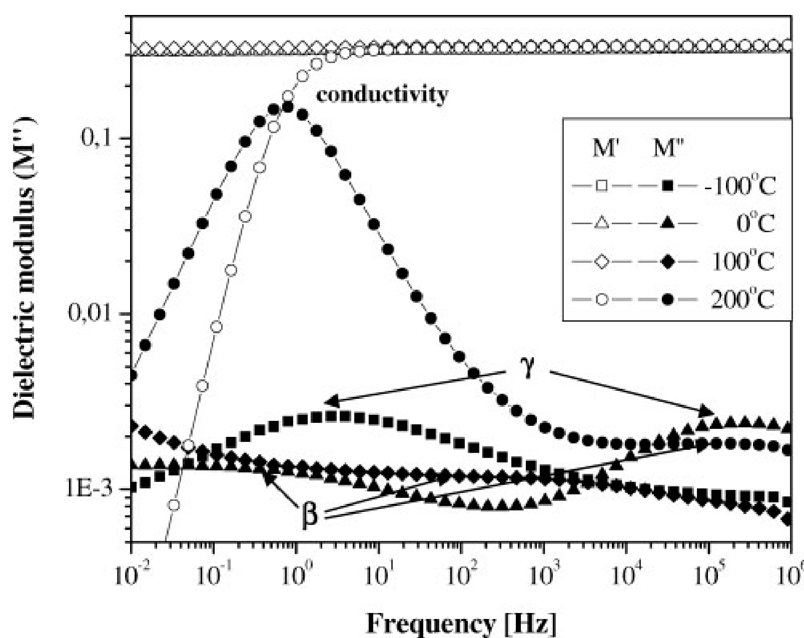


Figure 3 Dependences of real and imaginary parts of complex electric modulus versus frequency at different temperatures for the polymer **IVa**.

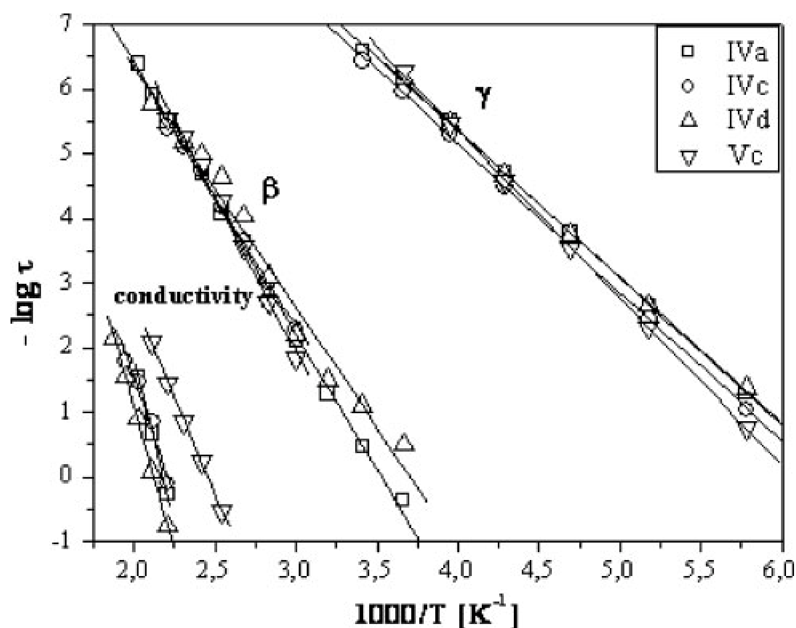


Figure 4 Activation maps for polymers **IV** and **Vc**.

place at higher temperature. One can observe that these two relaxation processes appear at similar temperatures in all samples and shift to higher frequencies with increasing temperatures. It can be also noticed that the values of the dielectric loss of poly (imide-amide)s are higher than corresponding values for polyimides, similarly as dielectric constant.

The strong low-frequency dispersion for ε′ and sharp increase in ε″ are the characteristics of charge carrier systems. The localized charge carriers under an applied alternating electric field can hop to neighboring localized sites like the reciprocating motion of a jumping dipole or can jump to neighboring sites, which form a continuous connected network allowing the charges to travel through the entire physical dimensions of the polymer sample and causing the electric conduction. During the motion of charge carriers, the applied electric field will be a subject of decay. Such relaxation of electric field is termed electric field relaxation and the relaxation of the charge system is termed conductivity relaxation.[15]

To analyze the conductivity relaxation of the polymer films, the complex permittivity was converted to the complex dielectric modulus $M^*(\omega) = 1/\varepsilon^*(\omega)$ according to an equation described in the literature.[16] The real (M') and imaginary (M'') parts of the dielectric modulus can be calculated from ε′ and ε″

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}; \quad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$

The frequency dependencies of the real (M') and imaginary (M'') parts of the dielectric modulus for polymer **IVa** are shown in Figure 3, as determined for different temperatures.

We can see that on the M'' diagrams beside two relaxation processes visible in ε″ dependencies, the conductivity relaxation is seen. These relaxations are almost the same in all samples. The activation map is the best for a comparison of all samples as well as is necessary for calculation of activation energy. Relaxation times (τ) of these three processes at various temperatures have been determined from maxima position of M'' at frequency scale ($\tau = 1/\omega_{max}$). The activation plots are shown in Figure 4. In Table III the activation energies of relaxation process calculated on the bases of these diagrams are presented. It is well seen that polymers **IV** differ slightly from polymer **Vc**. The activation energies of secondary relaxations of polymer **Vc** are slightly higher than polymers **IV** and in these last the conductivity relaxation appears at higher temperatures, what was mentioned earlier.

CONCLUSIONS

The introduction of silicon together with phenylquinoxaline groups and ether linkages in the main chain

TABLE III
Activation Energies of Relaxation Phenomena Calculated from $M''(\omega)$ Dependencies

Polymer	E_a of γ relaxation (kJ/mol)	E_a of β relaxation (kJ/mol)	E_a of conductivity relaxation (kJ/mol)
IVa	43.6	80	190
IVc	44.0	76	150
IVd	43.3	71	170
Vc	47.9	109	186

of aromatic polyimides and poly(imide-amide)s gave polymers with remarkable solubility in some organic solvents and high molecular weights, thus being appropriate for processing into thin transparent films from solutions. These polymers have high thermal stability and a large interval between glass transition temperature and decomposition temperature, which may be advantageous for their processing by a thermoforming technique. The polymer films have a low dielectric constant and good mechanical properties, which make them potential candidates for future high performance applications in microelectronics or in related fields.

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References

1. Maier, G. Prog Polym Sci 2001, 26, 65.
2. Sroog, C. E. Prog Polym Sci 1991, 16, 561.
3. Hasegawa, M.; Horie, K. Prog Polym Sci 2001, 26, 259.
4. Hergenrother, P. In Encyclopedia of Polymer Science and Engineering; Mark, H., Wiley: New York, 1988; Vol. 13, p 55.
5. Bruma, M. In Handbook of Thermoplastics; Olabisi, O., Ed.; Marcel Dekker: New York, 1997; p 771.
6. Korshak, V. V.; Krongauz, E. S.; Belomoina, N. M.; Raubach, H.; Hein, D. Acta Polym 1983, 34, 213.
7. Korshak, V. V.; Krongauz, E. S.; Belomoina, N. M.; Bruma, M.; Diaconu, I.; Simionescu, C. I. Angew Makromol Chem 1986, 144, 129.
8. Pratt, J. R.; Thames, S. F. J Org Chem 1973, 38, 4271.
9. Hamciuc, E.; Bruma, M.; Schulz, B.; Kopnick, T. High Perform Polym 2003, 15, 347.
10. Hamciuc, E.; Schulz, B.; Kopnick, T.; Kaminorz, Y.; Bruma, M. High Perform Polym 2002, 14, 63.
11. Schulz, B.; Hamciuc, E., Kopnick, T.; Kaminorz, Y.; Bruma, M. Macromol Symp 2003, 199, 391.
12. Hamciuc, C.; Hamciuc, E.; Bruma, M.; Klapper, K.; Pakula, T.; Demeter, A. Polymer 2001, 42, 5956.
13. Hamciuc, C.; Hamciuc, E.; Bruma, M.; Klapper, K.; Pakula, T. Polym Bull 2001, 47, 1.
14. Liang, T.; Makita, Y.; Kimura, S. Polymer 2001, 42, 4867.
15. Lee, H. T.; Chuang, K. R.; Chen, S. A.; Wei, P. K.; Hsu, J. H.; Fann, W. Macromolecules 1995, 28, 7645.
16. Macedo, P. B.; Moynihan, C. T.; Bose, R. Phys Chem Glasses 1972, 13, 171.