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Optical and dielectric properties of some polymers with imidic structure

A. I. COSUTCHI, C. HULUBEI, S. IOAN*
"Petru Poni" Institute of Macromolecular Chemistry, Iasi, 700487, Romania

Three types of imidic polymers, i.e. Epiclon based polyimides, fluorinated polyimides and copolymaleimides containing azobenzene groups have been investigated. The optical and dielectric properties have been studied for several polyimides and their corresponding poly(amic acid)s and copolymaleimides. Calculations of the refractive index and specific refractive index increments are based on theoretical and experimental investigations. At optical frequencies when only electronic polarization occurs, the dielectric constants were determined from refractive indices measurements. The theoretical study indicates structural modifications for obtaining pre-established optical and dielectric properties.

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1. Introduction

The increasing need of materials for new applications, requires polymers with diverse architectures, leading to specific properties. Polyimides represent a very important class of high-performance synthetic polymers, whose specific properties such as thermal, thermo-oxidative stability, high mechanical strength, good processability and superior chemical resistance recommend them for a large range of applications [1-3]. However, their poor solubility in organic solvents and their very high softening temperature make them intractable and limit their applications. So far, major effort has been devoted to synthesizing soluble polyimides in organic solvents, while preserving their good thermal stability. Some methods have been put forward to improve their solubility. Current attempts to produce soluble and processable polyimides involve the introduction of asymmetrical [4] or non-coplanar structures [5,6] into the backbone. It is known that one of the most successful approaches increasing the solubility and processability without sacrificing the high thermal stability is the introduction of bulky and unsymmetrical groups, flexible bonds, large pendent or polar substituents into the polymer backbone [7-8]. Therefore, it is expected that the combination of imide units, rings, flexible bonds and epiclon moieties and a cycloaphatic anhydride with flexible and asymmetrical structure into one single macromolecule, would develop new synthetic polymers, which provide a compromise between processability and the physical and thermal characteristics. Epiclon has been used as raw material for polyimides to enhance their new properties [9-11].

The nature of most polyimidic materials challenges many applications that require specific characteristics, such as those related to wetting or adhesion, in microelectronics. High adhesion of the polyimide film to different inorganic interfaces, such as cooper, silicon and aluminum, is important for reliable electronic packaging. The minimal water uptake of these materials is advantageous for dielectric performance, since the absorbed water significantly increases the dielectric constant [12]. The excellent dielectric properties of polyimides recommend them as ideal dielectric insulators for semiconductors and wire-coatings materials, or as substrates for flexible printed circuits. These properties also recommend them for applications in opto-electronics, telecommunications or modern aerospace and aviation industry, as structural or sub-structural components in supersonic aircraft and missile airframes [13-17].

A special class is represented by maleimide type polymers, which have also found use in electronics for the aerospace and aircraft industry. They evidence good stability and at high transition temperatures, due to the polar five-membered imide ring structure [18,19]. The tractability, high thermal stability, high durability, good water resistance, fire and radiation resistance [20] are other important properties of theirs. Maleimide type polymers are very useful in microelectronics as thermally-stable photoresists in lithography or image-marking processes [21,22] or for optical and catalytic activities [23,24]. Functional copolymers based on *N*-substituted maleimides or different types of maleimide/vinyl ether UV - curable systems with thermal stability and photosensitive properties have been reported [25-27]. The materials containing azobenzene derivatives have found applications in optical data storage, holography, photo-switching of optical elements, and alignment of liquid crystals (LC). Also, azobenzene moiety has been used as a photochromic mesogen in a variety of systems [28-30]. Within the large range of photosensitive materials, azobenzene derivatives demonstrate relatively high values of induced anisotropy, caused by a high-absorption dichroism in azobenzene units.

Previous publications in the field have presented the synthesis and some properties of new soluble polyimides

[7,31,32]. The products have been characterized from the view point of their chemical structure, thermal behavior and solution properties. This paper presents a theoretical study on the optical and dielectric properties of epiclon based polyimides, ideal fluorinated polyimide structures and fuctional maleimide copolymers in order to evaluate and predict their applicability in microelectronics and aircraft industry. Some theoretical results are compared with the experimental data.

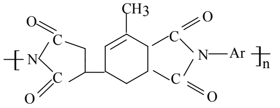
2. Experimental

Polyimides have been obtained by the polycondensation reaction of equimolar amounts of 5 - (2,5 - dioxotetrahydrofurfuryl) - 3 - methyl - 3 - cyclohexenyl-1,2 dicarboxylic acid anhydride (Epiclon) with four different diamines: 1,4- benzene diamine (1), 4,4'-methylenedianiline (2), 4,4'-ethylenedianiline (3), 1,4-bis(p-aminophenoxy)benzene (4). The reactions were carried out in N-methylpyrrolidinone (NMP) as a solvent, under inert atmosphere. The concentration of the reaction mixture was adjusted to 12-15 % total solids. The first step of this reaction, performed at room temperature,led to poly(amic acid)s. In the second step, the polymer solution was heated at 180-190 ºC to perform cyclodehydration of the poly(amic acid) to the corresponding polyimide structure (PI1-4) [7,32,33].

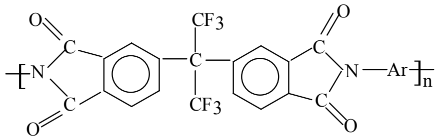
Copolymaleimides (PMI) have been synthesised by radical polymerization of N-(4-formyl-fenoxy-4'-carboylphenyl)maleimide with styrene (PMI1) followed in a chemical modification reaction with *p*-aminoazobenzene (PMI2) [34,35]. This special class of maleimides evidences good stability at high transition temperatures due to the polar five - membered imide ring structure, tractability, high thermal stability, high durability, good water resistance, fire and radiation resistance. Also, unsynthesized fluorinated polyimide structures (PIF) were considered for this comparative study.

The investigated structures are presented below.

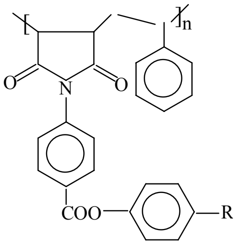
PI:



PIF:



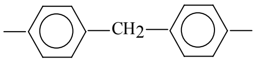
PMI:



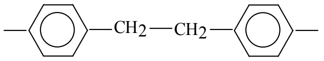
where Ar is:

for PI1:

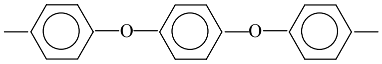
for PI2:



for PI3



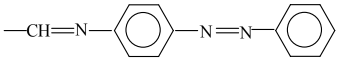
for PI4



and R is:

for PM1: —CHO

for PM2:



The number average molecular weights M_n for polyimides and copolymaleimides were determined by gel permeation chromatography (GPC) measurements in N,N-dimethylformamide (DMF), on a PL EMD-950 evaporative light scattering detector apparatus.

The refractive indices of the polymer solutions are considered as additive functions of the solvent (w_{DMF}) and polymer ($w_{polymer}$) compositions (equation 1). The refractive indices of the studied samples were determined from the refractive index 1.427 for DMF and from the refractive indices of the polymer solutions, using Abbe refractometer, with an experimental error of approx. ±4% .

$$n_{solution} = n_{DMF} w_{DMF} + n_{polymer} w_{polymer} \qquad (1)$$

The specific refractive index increments of the solutions, dn/dc, in DMF at 25°C were measured with a Zeiss interferometer in the standard way.

The molecular weight of the chain units and the number average molecular weights for the studied samples are presented in Table 1.

Table 1. Molecular weight of the structural unit, m_u*, number average molecular weight,* M_n*, of polyimides (PI1-4) and copolymaleimides (PMI1-2).*

Sample	m_u	M_n
PI1	336	57000
PI2	426	50000
PI3	440	70000
PI4	520	75000
PMI1	436	3300
PMI2	614	3300

3. Results and discussion

3.1. Refractive index and specific refractive index increments

The refractive index of epiclon based polyimides, fluorinated polyimides and maleimide copolymers were determined by equations (2-4), according to Lorenz-Lorentz [36,37], Gladstone-Dale [38] and Vogel [39] approximations, respectively.

$$R_{u,LL} = V_u \left(n_{2,LL}^2 - 1\right)/\left(n_{2,LL}^2 + 2\right) \tag{2}$$

$$R_{u,GD} = V_u \left(n_{2,GD} - 1\right) \tag{3}$$

$$R_{u,V} = n_{2,V} m_0 \tag{4}$$

where $n_{2,LL}, n_{2,GD}$ and $n_{2,V}$ represent the refractive indices of the polymer according to different approximations, R_u is the molar refractivity and V_u is the molar volume.

The equations are based on the assumption that the molar volume, V_u, and the molar refraction, R_u, of the chain repeating unit are additive functions of composition [equations (5) and (6)] [40-42].

$$V_u = \sum_i a_i \cdot V_i \tag{5}$$

$$R_u = \sum_i a_i \cdot R_i \tag{6}$$

where V_i and R_i are the contributions of group, and a_i is the number of groups i in the repeating unit.

The increments of various substructures R_i and V_i were taken from the literature [41,42,43,44] (Table 2).

Table 2. Increments of various substructures R_i and V_i

Increment	R_i (cm^3/g)	V_i (cm^3)	R_i/V_i
p-C_6H_4 (aromatic)	25.235	65.912	0.383
CF_3	6.149	40.274	0.153
CH_3	5.901	25.798	0.229
CH_2	4.504	15.528	0.290
OH	8.290	32.491	0.255
C=O	4.590	13.170	0.349
-O- (ether)	1.625	9.052	0.180
CONH	8.256	21.660	0.381
CCH_3	7.875	22.645	0.347

R_u, V_u and n_2 calculations are listed in Tables 3 and 4.

Table 3. Molar refraction, R_u, molar volume, V_u, and ratio R_u/V_u of PI1-4, PIF1-4 and PMI1-2.

Samples	R_u (cm^3/g)	V_u (cm^3)	R_u/V_u
PI1	82.076	209.163	0.392
PI2	111.815	290.603	0.385
PI3	116.319	306.131	0.380
PI4	135.796	359.091	0.378
PIF1	112.935	329.580	0.343
PIF2	142.674	411.022	0.347
PIF3	147.178	426.550	0.345
PIF4	166.655	479.510	0.348
PMI1	113.353	299.021	0.379
PMI2	182.654	456.022	0.401

The experimental values of the refractive index for these polymers slightly differ from those calculated with the Lorenz-Lorentz equation, on considering the corresponding group contributions to the molar refraction and to the molar volume. The differences are higher when the theoretical values are determined by Vogel and by Gladstone and Dale equations, respectively.

Table 4. Theoretical and experimental values of the refractive index for PI1-4, PIF1-4 and PMI1-2.

Samples	$n_{2,LL}$	$n_{2,GD}$	$n_{2,V}$	n_{exp}
PI1	1.713	1.392	0.244	1.715
PI2	1.691	1.385	0.262	1.683
PI3	1.685	1.380	0.264	1.747
PI4	1.681	1.378	0.261	1.679
PIF1	1.601	1.343	0.214	-
PIF2	1.611	1.347	0.231	-
PIF3	1.606	1.345	0.233	-
PIF4	1.612	1.348	0.234	-
PMI1	1.683	1.379	0.260	
PMI2	1.733	1.401	0.297	

On the other hand, the values of the refractive index for epiclon based polyimides and fluorinated polyimides are less influenced by the Ar groups. Also, the radical with extended conjugation, R, increases the refractive index of copolymaleimides, comparatively with the aldehyde group. Thus, the refractive index of the studied samples increases in the following order: PIF<PI<PMI

Table 5. Theoretical and experimental data for specific refractive index increments of PI1-4, PIF1-4 and PMI1-2 in DMF at 25˚C.

Samples	$\left(\frac{dn}{dc}\right)_{LL}$	$\left(\frac{dn}{dc}\right)_{exp}$
PI1	0.227	-
PI2	0.180	0.170
PI3	0.180	0.173
PI4	0.176	0.174
PIF1	0.109	-
PIF2	0.122	-
PIF3	0.121	-
PIF4	0.125	-
PMI1	0.176	-
PMI2	0.227	-

The specific refractive index increments were evaluated by Huglin equation (7) [45] in which the refractive index of polymers was calculated by Lorenz-Lorentz approximation.

$$\left(\frac{dn}{dc}\right)_{LL} = \bar{v}_2 \left[\frac{n_{2,LL}^2 - 1}{n_{2,LL}^2 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2}\right] \cdot \frac{\left(n_1^2 + 2\right)^2}{6 n_1} \tag{7}$$

where n_1 is the refractive index of the solvent, v_2 is the specific volume of polymer in solid state and $\bar{v}_2$ is the partial specific volume of polymer in solution; generally,

$\overline{v}_2$ is approximated by v_2 on assuming that the solvent effect on $\overline{v}_2$ may be neglected. The specific volume of polymers was calculated by equation (8), with V_u from Table 3 and m_u from Table 1.

$$v_2 = \frac{V_u}{m_u} \qquad (8)$$

Table 5 shows the results of theoretical evaluation, comparatively with the experimental data. The errors observed between the theoretical and the experimental data are between 1-5 % being due to the absorption effect which had affected the experimental data.

3.2. Dielectric constant

The methods used for the determination of the dielectric constant are based on the theoretical and experimental evaluation of the refractive index. Materials with relatively low dielectric constants provide effective electrical barrier properties, and this behavior has led them to be referred as “dielectrics”. A lower dielectric constant indicates that the respective material is suited for protection and insulation in microelectronics. In multilevel electronics packaging, an important function of a dielectric material is to block the electromagnetic interactions between parallel metal conducting lines, which operate independently. For assuming an effective blocking the material should have low electrical conductivity/permitivity.

The dielectric constant, ε, is used to describe a material's ability to store the charge, when used as a capacitor device. Materials with dielectric constants below 4.0, which correspond to the value of the standard SiO_2 insulator, have been recognized by the electronics industry as being superior in electrical performance to ceramics [46].

Generally, the literature shows that for polyimides ε decrease gradually with increasing frequency (Figure 1). This variation is attributed to the frequency dependence of the polarization mechanisms which include the dielectric constant. The magnitude of the dielectric constant is dependent on the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field. At optical frequencies (approx. 10^{14} Hz), only the lowest mass species, the electrons, are efficiently polarized. At lower frequencies, the atomic polarization of nuclei, which move more slowly, also, contribute to the dielectric constant. Atomic polarization of induced dipoles such as a carbonyl group may occur in infrared (10^{12} Hz) or lower frequency regimes. Dipole polarization represents the redistribution of charge when a group of atoms with a permanent dipole align in response to the electric field. In solid state, the alignment of permanent dipoles requires considerably more time than electronic or atomic polarization, occurring at microwave (10^9 Hz) or lower frequencies. The contribution of each polarization mode to the dielectric constant is expressed in equation (9).

$$\varepsilon = \varepsilon_{electronic} + \varepsilon_{atomic} + \varepsilon_{dipolar} \qquad 9)$$

At optical frequencies, when only electronic polarization occurs, the dielectric constant, ε_∞, is related to the refractive index by Maxwell's identity, according to equation (10):

$$\varepsilon_\infty = n_2^2 \qquad (10)$$

A comparison between ε_∞ and the dielectric constant measured at frequencies lower than optical frequency, may assure a basic understanding of the influence of the molecular structure on the dielectric properties in the studied poly(amic acid)s, polyimides, fluorinated polyimides and copolymaleimides.

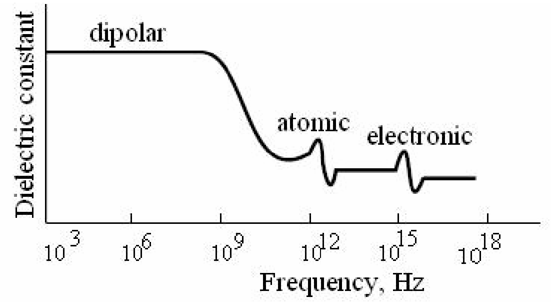


Fig. 1. Frequency response of dielectric mechanisms

At optical frequencies, the dielectric constant, ε_∞, was evaluated from equation (10) with the refractive index Lorenz-Lorentz from equation (2). The results obtained from theoretical and experimental data for dielectric constants are presented in Table 6.

Table 6. Theoretical and experimental values of optical dielectric constants for PI1-4, PIF1-4 and PMI1-2.

Sample	$\varepsilon_{\infty,LL}$	$\varepsilon_{\infty,exp}$
PI1	2.934	2.941
PI2	2.860	2.832
PI3	2.839	3.052
PI4	2.826	2.819
PIF1	2.563	-
PIF2	2.595	-
PIF3	2.579	-
PIF4	2.599	-
PMI1	2.833	-
PMI2	3.003	-

Fig. 2 plots the ratio of molar fraction R_i (proportional to the induced dipole moment) to molar volume V_i for different atoms present in organic polymers. There is a broad range of values for each atom, due to the different binding structures and to varying chemical environment in different organic or inorganic compounds.

One can assume that the dielectric constants obtained for partial aliphatic epiclon based polyimides, fluorinated polyimides and functional copolymaleimides are low, reflecting the influence of the different binding structures.

It can be seen that the fluorine atoms from the PIF samples decreases with the dielectric constant, due to the high electronic conjugation trough steric hindrance and the inductive deactivation effect [47]. It is possible that the nitrogen atom from the high conjugated radical R (from PMI2) should play an important role, which can be observed in the resulting dielectric constant value. Thus, the inequality transmitted by the refractive index to $\varepsilon_{\infty,LL}$, PIF<PI<PMI, is justified by the polarizability of samples.

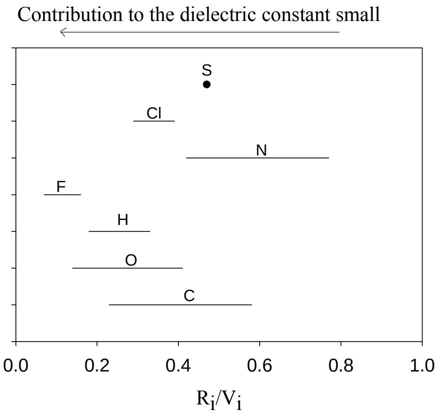


Fig. 2. Contribution of different atoms to the dielectric constant of a compound

4. Conclusions

One of the extremely important roles in polyimide applications is the control balance between the dielectric constants of the different substructures, for obtaining the desired electrical properties. Thus, for multiple applications, knowledge on the dielectric properties before the preparation process of polyimides is necessary.

The present paper evaluates the optical and dielectric properties of polyimides on the basis of theoretical and experimental data.

It is observed that the ratio of molar refraction, proportional to the induced dipole moment, to molar volumes for different atoms present in studied samples, is reflected in the variation of the refractive index, specific refractive index increment or in the dielectric constant. Theoretical values of the refractive index are close to the experimental data, within the range of experimental errors, and increase in the following order: PIF<PI<PMI

It is also observed that the Ar groups have introduced insignificant differences in the dielectric constant values for the studied polymers. By their special conjugation, the pendent groups of copolymaleimides affect the dielectric constant. Specific atoms, such as fluorine, decrease the dielectric constant.

References

[1] C. E. Strong, Prog. Polym. Sci., **16**, 561 (1991).
[2] S. J. Huang, A. E. Hoyt, Trends Polym. Sci. **3**, 262 (1995).
[3] J. de Abajo, J. G. de la Campa, Adv. Polym. Sci. **140**, 23 (1999).
[4] H. B. Zheng, Z. Y. Wang, Macromolecules **33**, 4310 (2000).
[5] I. K. Spiliopoulos, J. A. Mikroyannidis, Macromolecules, **31**, 1236 (1998).
[6] G-S Liou, J. Polym. Sci. A, **36**, 1937 (1998).
[7] E. Hamciuc, R. Lungu, C. Hulubei, M. Bruma, J. Macromol. Sci. Part A: pure and Appl. Chem. **43**, 247 (2006).
[8] G. C. Eastmond, J. Parprotny, R. S. Irwin, Macromolecules, **29**, 1382 (1996).
[9] C. Mao, C. Zhanh, Y. Qiu, A. Zhu, J. Shen, S. Lin, Appl. Surf. Sci., **228**, 26 (2004).
[10] J. Yip, K. Chan, K. M. Sin, K. S. Lau, Mater. Res. Innovat., **6**, 73 (2002).
[11] K. Gotoh, Y. Nakata, M. Tagawa, M. Tagawa, Colloid. Surf. A- Physicochem. Eng. Asp. **224**, 163 (2003).
[12] L. D. Dunson, PhD Thesis, Virginia (2000).
[13] M. K. Ghosh, K. L. Mittal, Polyimides: Fundamentals and Applications, Marcel Dekker (1996).
[14] M. Bruma, E. Hamciuc, I. Sava, M. D. Iosip, J. Robison, Proceedings of the 6 th European Technical Symposium, Polyimides and Other High Performance Polymers, Montpellier, France, Ed. M. J. M. Abadie and B. Sillion, 2003, p.162.
[15] NASA-CP10039, HITEMP Review 1989 Advanced High Temperature Engine Materials Technology Program, NASA, Washington, DC (1989).
[16] R. D. Vannuci, D. Malarik, 22nd Int. SAMPE Tech. Conf., **175** (1990).
[17] K. C. Chuang, R. D. Vannuci, I. Ansari, L. L. Cerny, D. Scheiman, J. Polym. Sci., **32,** 1341 (1994).
[18] J. M. G. Cowie, Alternating Copolymers, Plenum, New York (1985).
[19] Z. M. O. Rzaev, Progr. Polym. Sci., **25**, 163 (2000).
[20] I. J. Lee, H. W. Choi, Y. C. Nho, D. H. Suh, J. Appl. Polym. Sci., **88**(9), 2339 (2003).
[21] C. D. Ahn, Polymeric Materials Encyclopedia, Ed. J. C. Salamone, CRC Press, Boca Raton, FL, USA **4**, 2621 (1996).
[22] R. W. Blevin, R. S. Daly, S. R. Turner, Encyclopedia of Polymer Science and Engineering, Ed. Wiley-Interscience, New York, vol. **9**, 47 (1987).
[23] G. Wulff, S. Krieger, Macromol. Chem. Phys, **195**, 3665 (1994).
[24] Y. K. Lee, S. Kitamura, K. Onimura, H. Tsutsumi, T. Oishi, J. Polym. Sci. Part A: Polym. Chem., **42,** 6157 (2004).
[25] S. H. Jin, H. U. Seo, D. H. Nam, W. S. Shin, J. H. Choi, U. C. Yoon, J. W. Lee, J. G. Song, D. M. Shin, Y. S. Gal, J. Mat. Chem. **15**, 5029 (2005).
[26] C. Decker, C. Bianchi, Polym. Int., **52**, 722 (2003).
[27] S. Şenel, Z. M. O. Rzaev, E. Pişkin, Polym. Int. **52**, 713 (2003).
[28] S. Kurihara, S. Nomiyama, T. Nokana, Chem. Mat. **12**, 9 (2000).

[29] C. Kaufmann, W. Muller, F. Vogtle, S. Weinman, S. Abramson, B. Fuchs, Synthesis, **12**, 849 (1999).
[30] G. Clavier, F. Ilhan, V. M. Rotello, Macromolecules, **33**, 9173 (2000).
[31] C. Hulubei, E. Hamciuc, Bull. Inst. Polyt. Iasi, **Tom LI (1)**, 295 (2005).
[32] D. Macocinschi, A. Taranu, C. Hulubei, S. Ioan Rev. Roum. Chim., proof (2006).
[33] S. Ioan, A. I. Cosutchi, C. Hulubei, D. Macocinschi, G. Ioanid, Polym. Eng. Sci., in press
[34] Roumanian Academy Project –GAR, no. 40, 2005-2006.
[35] C. Hulubei, M. Morariu, High Perform. Polym. **12**, 367 (2000).
[36] L. V. Lorenz, Wied. Ann. Phys., **11**, 70 (1880).
[37] Lorentz H. A., Wied. Ann. Phys., **9**, 641 (1880).
[38] J. H. Gladstone, T. P. Dale, Trans. R. Soc., London, **A148**, 887 (1958).
[39] V. Vogel , J. Chem. Soc., 1833 (1948).
[40] D. J. Goedhart, Procedings of International GPC Seminar, Monaco, 12 (1969).
[41] D. W. van Krevelen, Properties of Polymers, Elsevier: Amsterdam (1972).
[42] W. Groh, A. Zimmermann, Macromolecules, **24**, 6660 (1991).
[43] G. Schultz, C. Wehstedt , R. Gnauck, Plaste u Kautsch, **32**, 153 (1985).
[44] G. Neumann, R. Becker, Plaste u Kautsch **23**, 26 (1976).
[45] M. B. Huglin, Polymers Handbook, Eds. J. Brandrup, E. H. Immergut, John Willey, New York, Chap. VII (1989).
[46] S. K. Moore, Low-dielectric Hits the Road, Chemical Week, June 23 (1999).
[47] R. Hariharan, S. Bhuvana, M. Sarojadevi, High Perf. Polym, **18**, 181 (2006).

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[*] Corresponding author: ioan_silvia@yahoo.com