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Polyimides containing cycloaliphatic segments for low dielectric material

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Abstract

New polyimides have been synthesized by the reaction of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) or/and 5-[2,5-(dioxotetrahydrofuryl)]-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DOCDA) with 4,4′-methylene dianiline (DDM). Polycondensation reactions were carried out in *N, N*-dimethylformamide solution and the resulting polyimides gave flexible free-standing films. The introduction of alicyclic moieties in the polyimide backbone improved the solubility of the resulting polymers and facilitated their processing while maintaining a high thermal stability. The dielectric constant values (measured at 10^6 Hz at room temperature), were found in the range of 3.14–2.83 and decreased with increasing of the alicyclic units content.

Keywords

polyimide, alicyclic, low dielectric constant, high thermal stability

Introduction

Aromatic polyimides exhibit excellent thermal, chemical, mechanical and electric properties, which make them useful in aerospace industry, microelectronics and engineering.[1–4] However, they have poor processability, including limited solubility in organic solvents and infusibility, which is caused by rigid polymer backbone and strong interchain interaction. To overcome this drawback, same chemical strategies appeared, like: including voluminous moieties,[5,6] use of flexible groups[1–4,7–10] or alicyclic and/or asymmetric unit.[11,12] One of the famous commercial polyimide is Kapton®, which is successfully used in aerospace industry, having dielectric constant of 3.5.[2]

The purpose of the present study was to present new polyimides with improved processability and low dielectric constant in a wide range of frequencies and temperatures. In this respect, 5-[2,5-(dioxotetrahydrofuryl)]-3-methyl-3-cyclohexen-1,2-dicarboxylic anhydride (DOCDA) was used as an alicyclic, asymmetric and flexible structure together with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4′-methylene dianiline (DDM).

Experimental

Methods

Fourier transform infrared (FTIR) measurements have been performed on KBr pellets of powder sample by using a Bruker Vertex 70 Spectrometer. ^{1}H-MNR spectra ware measured on a Bruker Avance DRX 400 at room temperature, in dimethyl sulfoxide-d_6 (DMSO-d_6) with tetramethylsilane (TMS) as an internal reference. The thermal behavior was investigated with a Mettler Toledo Instrument TGA/SDTA 851, by using 3–4 mg of polymer sample, under nitrogen atmosphere at a heating rate of 10°C min^{-1}, in the range of 25°C up to 900°C. The dielectric measurements were run on Novocontrol Dielectric Spectrometer Concept 40, in the range of −150°C up to 250°C at both 10^3 and 10^6 Hz. The polymeric films (33-42 μm thick) were inserted into a plane capacitor having gold electrodes of 20 mm diameter. The amplitude of applied voltage was 1 V.

Synthesis

Two homopolymers (**PI 1, PI 5**) and three copolymers (**PI 2, PI 3** and **PI 4**) have been synthesized by the reaction of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride

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Table 1. Solubility behavior of the polymers **PI 1**, **PI 5** and copolymers **PI 2**–**PI 4**.

Code	BTDA/DOCDA (% molar ratio)	Solvent series			
		NMP	DMAc	DMSO	THF
PI 1	100/0	– –	– –	– –	– –
PI 2	75/25	– –	– –	– –	– –
PI 3	50/50	+ –	+ –	+ –	+ –
PI 4	25/75	+ +	+ +	+ +	+ –
PI 5	0/100	+ +	+ +	+ +	+ +

NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*, *N*-dimethylacetamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran. – –, insoluble; + –, partially soluble; + +, soluble.

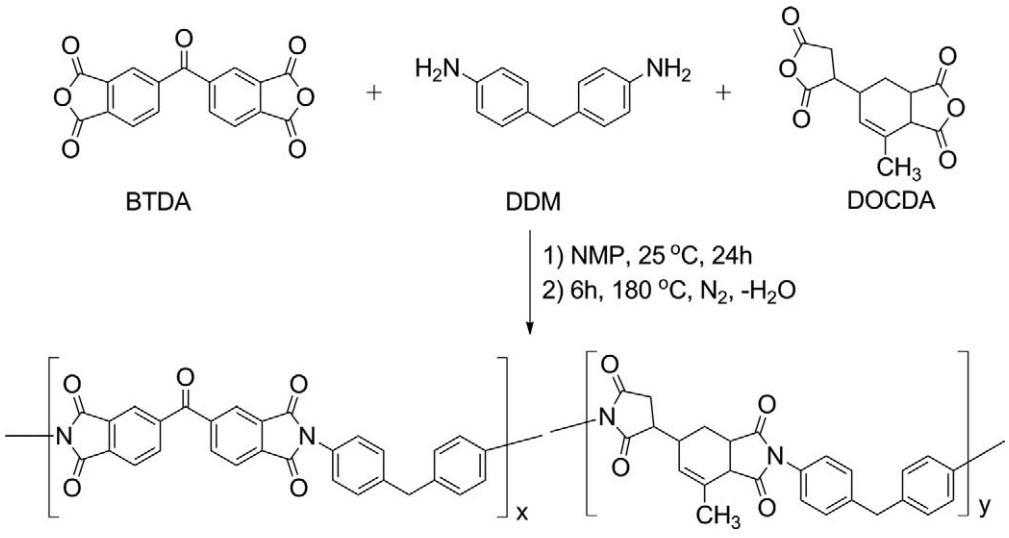

Figure 1. Synthesis of homopolymers **PI 1** ($y = 0$), **PI 5** ($x = 0$) and copolymers **PI 2**–**PI 4**.

(BTDA) or/and 5-[2,5-(dioxotetrahydrofuryl)]-3-methyl-3-cyclohexen-1,2-dicarboxylic anhydride (DOCDA) with stoechiometric amounts of 4,4′-methylene dianiline (DDM) in NMP as solvent (Figure 1). The reaction proceeded in two steps: (1) 24 h at room temperature under nitrogen atmosphere to give a precursor polyamidic acid; (2) 6 h at 180°C, under nitrogen flow for elimination of imidization water vapors, resulting in the final polyimide. The reaction mixture was precipitated in water and the resulting polymer was filtered, washed with water and methanol, and then dried for 8 h at 100°C.

Film preparation

The films for dielectric measurements were prepared by casting the polyamidic acid solutions on clean glass plates. After drying 8 h at 80°C, a program of temperature treatment was applied by using a vacuum oven, each step involving 1 h at the corresponding temperature: 80, 120, 160, 200 and 250°C. After cooling, the films were removed from the glass plates by using boiling water, and then were dried for 8 h at 100°C. The resulting film thickness was in the range of 33–42 μm.

Results and discussion

The chemical structure of the polymers and copolymers was confirmed by FTIR spectroscopy (Figure 2). Characteristic absorption bands due to specific imide moieties have been observed: 1770–1780 cm^{-1} and 1710–1720 cm^{-1} (imide I, asymmetrical C=O imide stretching), 1370–1380 cm^{-1} (imide II, C–N imide stretching), 720–740 cm^{-1} (imide IV, imide ring deformation).

^{1}H-NMR spectra of copolymer PI 4 (Figure 3) (DMSO-d_6, ppm): δ 1.236–3.565 (9H, unidentified overlapped peaks of DOCDA), 2.152 (3H, CH_3 of DOCDA), 4.034, 4.064 (2H, CH_2 of DDM), 7.20–7.757 (4H, ArH of DDM), 8.15, 8.172, 8.239 (3H, ArH of BTDA)

Figure 4 shows UV-VIS spectra (electronic spectra) of all polymeric films cast from NMP. Transparency behavior in the visible range of the spectrum was observed for all samples, with except of sample PI 1 which is poor transparent. Generally, transparency increased with the increasing

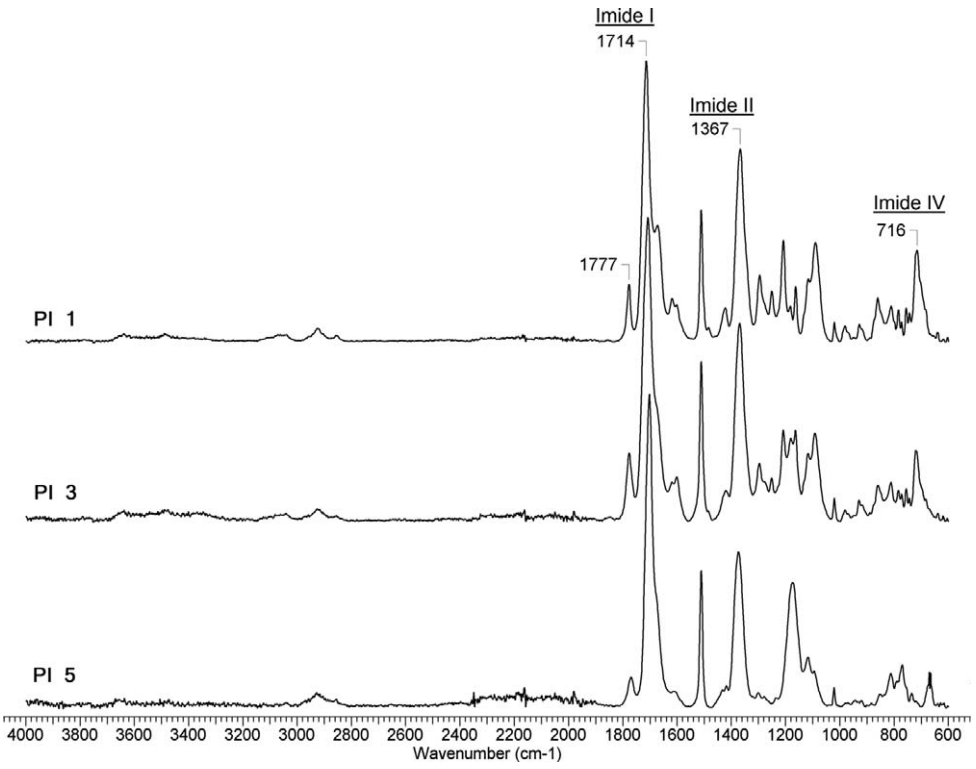

Figure 2. FTIR spectra of polymers **PI 1**, **PI 5** and copolymer **PI 3**.

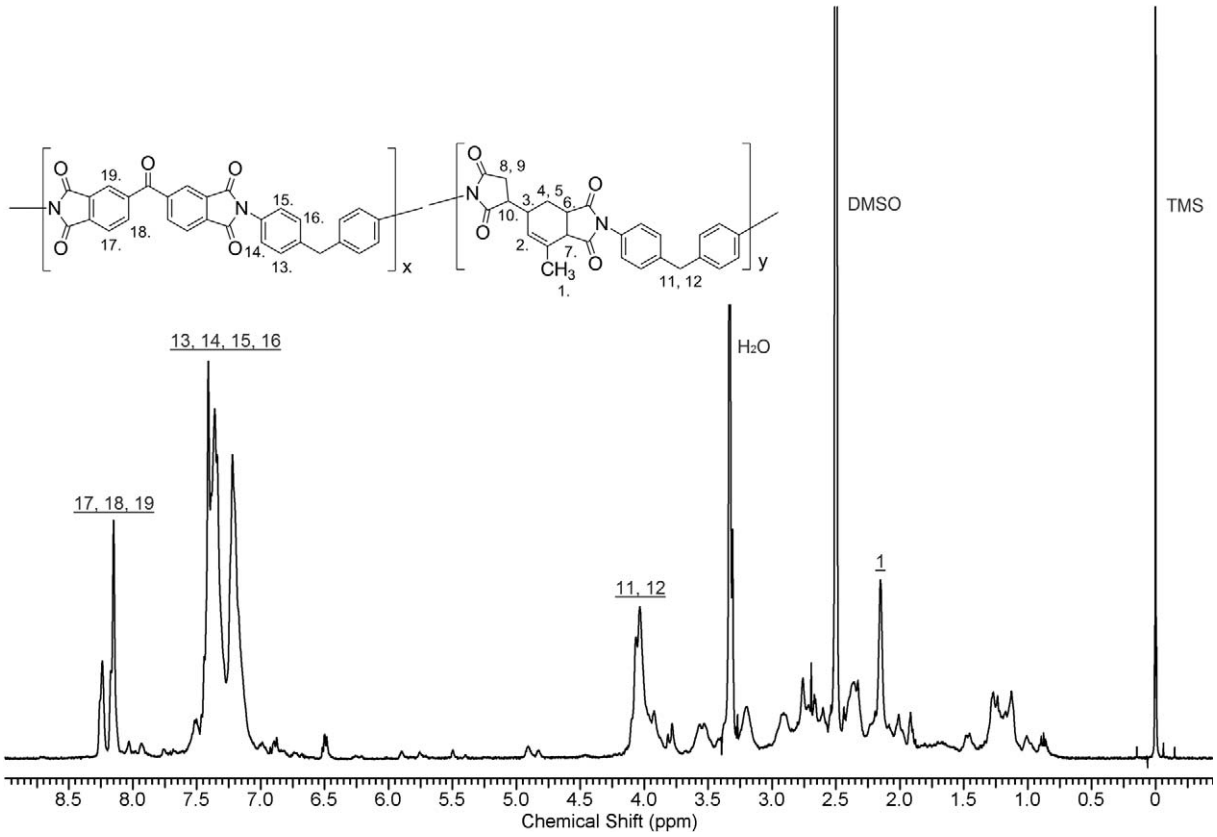

Figure 3. ^{1}H-NMR spectra of copolymer **PI 4** in DMSO-d_6.

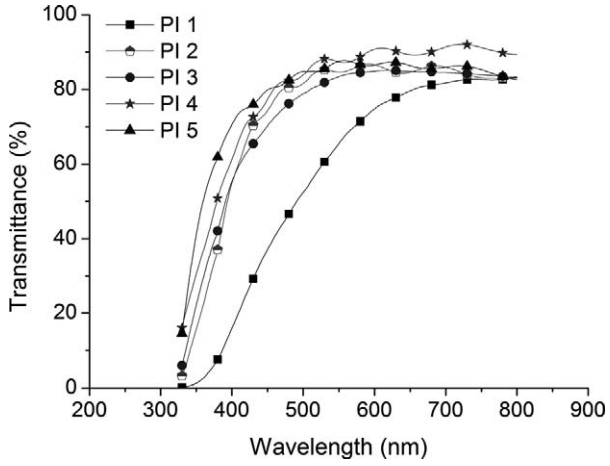

Figure 4. UV-VIS spectra of polymers **PI 1**, **PI 5** and copolymers **PI 2**–**PI 4.**

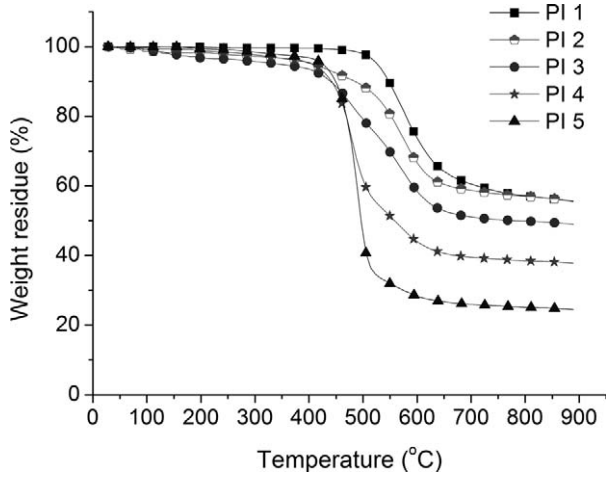

Figure 5. TGA curves of polymers **PI 1**, **PI 5** and copolymers **PI 2**–**PI 4**.

of DOCDA moieties amount. As we expected, polyimides with alicyclic structures have better transparency than aromatic polyimides, due to the prohibition of electron conjugation by the introduction of alicyclic moiety.

The solubility of the polyimides was tested in some common organic solvents at room temperature and the results are presented in Table 1. While the homopolymer **PI 1** and the copolymer **PI 2** were insoluble in all the tested solvents, the copolymer **PI 4** and homopolymer **PI 5** were completely soluble in all the solvents, with the exception of sample **PI 4** in THF, where partially solubility was found.

The improvement of the solubility in the case of samples **PI 3**–**PI 5**, could be explained by an increase of the free volume induced by the presence of the voluminous alicyclic units, leading to a poor chain packing.

The thermal stability of the polymers was investigated by thermogravimetric analysis in nitrogen atmosphere (Figure 5).

Table 2. Thermogravimetric data of the polymers PI 1, PI 5 and copolymers PI 2 – PI 4.

Code	*IDT* (°C)	T_{10} (°C)	T_d (°C)	Y_c (%)
PI 1	504	540	575	60.28
PI 2	379	490	435 576	58.71
PI 3	407	447	474 572	51.35
PI 4	419	445	481 573	39.57
PI 5	431	453	490	26.02

IDT, onset temperature of thermal decomposition; T_{10}, temperature corresponding to the 10% weight loss; T_d, maximum decomposition temperature taken from DTG curve; Y_c, char yield at 700°C.

Some characteristic parameters which monitor the thermal stability of the samples are presented in Table 2. The data showed a decreasing tendency of the thermal stability for all samples, with the increase of alicyclic contents, as expected.

However, these polymers containing alicyclic units exhibit high thermal stability, with decomposition starting above 400°C, with the exception of sample **PI 2**. The presence of alicyclic units in the copolymer backbone led to the appearance of an additional decomposition peak in DTG curves at 435°C for **PI 2**, 474°C for **PI 3** and 481°C for **PI 4** (Table 2). Characteristic char yield at 700°C of studied polyimides decreases with increasing of alicyclic content, from 60.28% for **PI 1** to 26.02% for **PI 5**.

The dielectric behavior of the polyimides **PI 1**–**PI 5** was investigated in the temperature range of −150°C up to 250°C, at 10^3 and 10^6 Hz frequencies. The obtained results are presented in Table 3. The insulating properties of the samples were evaluated by using the value which is given by Equation (1):

$$\varepsilon* = \varepsilon' - i\varepsilon'' \quad (1)$$

where ε* is the dielectric constant; $\varepsilon'$is the relative dielectric constant; and ε'' is the relative dielectric loss factor

The ratio $\varepsilon''/\varepsilon'$:

$$\tan\delta = \varepsilon''/\varepsilon'$$

is known as the dissipation factor or loss tangent, where δ is the phase angle between the applied voltage and the current response.[13]

As can be seen in Table 3, the value of the relative dielectric constant (ε') showed a decreasing tendency at both 10^3 and 10^6 Hz, with the increasing of alicyclic units contents. For example, while sample **PI 1** has ε' value of 3.16, the sample **PI 5** showed an ε' value of 2.86. The dependence of the relative dielectric constant (ε') on the frequency, measured at room temperature, is shown in Figure 6. The values of relative dielectric constant of polymers decrease gradually with increasing of the frequency,

Table 3. Dielectric behavior at 25°C of the polymers **PI 1**, **PI 5** and copolymers **PI 2**–**PI 4**.

	10^3 Hz			10^6 Hz		
Code	ε'	tan $\delta \times 10^{-3}$	$R_{spec} \times 10^{11}$	ε'	tan $\delta \times 10^{-3}$	$R_{spec} \times 10^{8}$
PI 1	3.16	1.57	3.61	3.14	0.55	10.4
PI 2	2.99	1.55	3.88	2.96	1.11	5.5
PI 3	2.97	1.64	3.70	2.94	1.70	3.7
PI 4	2.98	1.60	3.89	2.87	1.03	6.1
PI 5	2.86	1.32	7.77	2.83	0.17	38.2

ε', relative dielectric constant; tan δ, dissipation factor; R_{spec}, specific resistivity.

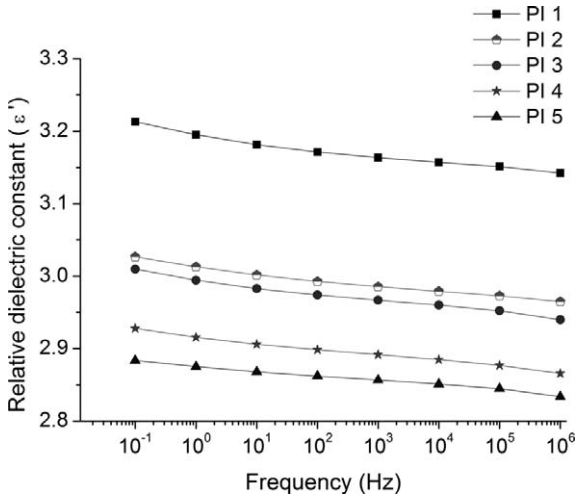

Figure 6. The dependence of the dielectric constant values on frequency, for the polymers **PI 1**, **PI 5** and copolymers **PI 2**–**PI 4** at room temperature.

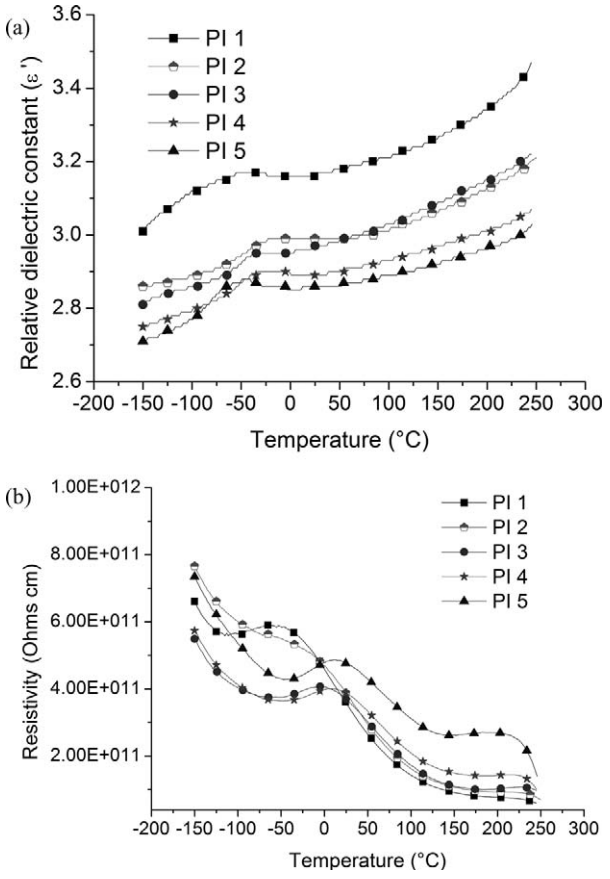

Figure 7. The temperature dependence of: (a) the relative dielectric constant; (b) volume resistivity for polyimides **PI 1**–**PI 5** at 10^3 Hz.

because the response of the electronic, atomic and dipolar units vary with frequency.[14] This decreasing effect of dielectric constant could be due, on one hand, to the interruption of extended conjugation along the macromolecular chain which lowers the dipole size[15] and, on the other hand, to the increasing of the free volume of the macromolecules.[16]

The relative dielectric constant ε' depends on both number and degree of mobility of polarisable units. Due to the fact that mobility of polarizable units depends on the temperature, the relative dielectric constant ε' also depends on the temperature (Figure 7(a)). The value of the dielectric constant decreased with decreasing carbonyl group content from BTDA moieties, while the modification of ε' with temperature is smaller. The published papers[17–21] on related alicyclic polyimides, reported dielectric constant values based on refractive index measurement, in the range of 2.55–2.83, at 10^6 Hz and 25°C using Maxwell equation. The polyimides studied in the present paper show comparable dielectric constant values; 2.88–2.83 for alicyclic polyimide **PI 5**, in a larger frequency domain, of 10^{-1}–10^6 Hz (25°C), and 2.71–3.03 in a larger temperature range of −150 to 250°C (10^3 Hz). Furthermore, at temperatures higher than 0°C the sample **PI 5** exhibited the highest internal resistivity, in concordance with the increasing of DOCDA content (Figure 7(b)).

Figure 8 showed the dependence of dissipation factor (tan δ) values on the temperature at 10^3 Hz frequency. All the samples exhibited two peaks along different temperature domains. The small peak, around −60°C, the so-called γ relaxation, was assigned to crankshaft motion of the entire polymer backbone. The second peak at around 175°C, the so-called β relaxation, was attributed to rotation around backbone bonds.[16,17] In addition, the studied samples exhibit low dissipation energy under the form of heat ($\tan \delta < 2 \cdot 10^{-3}$). From the dependence of dissipation factor on temperature, at 10^3 Hz it was found that the dielectric losses due to the local heating decreased by increasing the alicyclic content in the polymer composition. This phenomenon could be associated with a decrease of intra- and intermolecular charge transfer interaction (CTC). All these results recommend the investigated polymers as potential candidates for use as high performance dielectric materials.

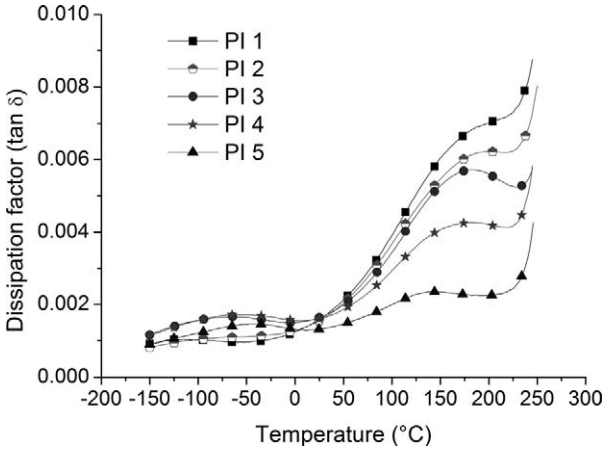

Figure 8. Temperature dependence of β and γ relaxation at 10^3 Hz.

Conclusions

Two polymers and three copolymers containing BTDA and DOCDA units have been synthesized by using DDM as aromatic diamine. Polycondensations were carried out in solution and the resulting polyimides gave flexible free-standing films. The introduction of alicyclic moieties in the polyimide backbone improved their solubility in both aprotic dipolar solvents and tetrahydrofurane. Films cast from NMP solutions showed transparency in UV-VIS range of spectrum. The transparency increased with the content of alicyclic moieties. The samples showed high thermal stability, with initial decomposition temperature being above 400°C. Dielectric measurements showed a decreasing tendency of the value of dielectric constant with increasing of alicyclic unit content. The polyimides based on equimolecular amounts of alicyclic dianhydrides and methylene-dianiline showed a dielectric constant value of 2.86, significantly lower than that of commercial Kapton® polyimide, usually taken as a reference. These properties recommend the present polyimides as good candidates for RF electronics and microelectronics, both as interlayer substrate and insulator.

References

1. Gosh MK and Mittal KL (eds). *Polyimides: fundamentals and applications*. New York: Marcel Dekker, 1991.
2. Sroog CE. Polyimides. *Prog Polym Sci* 1991; **16**: 561–694.
3. Yu S, Wong TKS, Hu X, et al. Synthesis and characterization of porous silsesquioxane dielectric films. *Thin Solid Films* 2005; **473**: 191–195.
4. Maier G. Low dielectric constant polymers for microelectronics. *Prog Polym Sci* 2001; **26**: 3–65.
5. Hamciuc E, Lungu R, Hulubei C, et al. New poly(imide-ether-amide)s based on epiclon. *J Macromol Sci, Part A: Pure Appl Chem* 2006; **43**: 247–258.
6. Hulubei C, Hamciuc E and Bruma M. New polyimides based on epiclon. *Rev Roum Chim* 2007; **52**: 1063–1069.
7. Bruma M, Sava I, Mercer F, et al. Synthesis and properties of fluorinated poly(ester-imide)s. *High Perform Polym* 1995; **7**: 411–420.
8. Murray TJ. Poly(amide-imide)s: wire enamels with excellent thermal and chemical properties. *Macromol Mater Eng* 2008; **293**: 350–360.
9. Hamciuc E, Sava I, Bruma M, et al. New poly(amide-imide)s containing cinnamoyl and azobenzene group. *Polym Adv Technol* 2006; **17**: 641–646.
10. Rusu RD, Damaceanu MD and Bruma M. Comparative study of soluble poly(keto-naphthylimide)s. *Rev Roum Chim* 2009; **54**:1015–1022.
11. Tsuda Y, Kuwahara R, Fukuda K, et al. Soluble polyimides and copolyimides based on alicyclic dianhydride having cyclohexene and tetralin moieties. *Polym J* 2005; **37**: 126–132.
12. Choi K-Y, Yi MH and Jin MY. Synthesis and characterization of novel polyimides from alicyclic dianhydride. *Korea Polym J* 1996; **4**: 117–124.
13. Feger C and Franke H. Polyimides in high performance electronics packaging and optoelectronic applications. In: Ghosh MK and Mittal KL (eds.) *Polyimides: fundamentals and applications*. New York: Marcel Dekker, 1996.
14. Deligoz H, Yalcinyuva T, Ozgumus S, et al. Electrical properties of conventional polyimide films: effects of chemical structure and water uptake. *J Appl Polym Sci*, 2006; **100**: 810–818.
15. Mathews AS, Kim I and Ha CS. Synthesis, characterization and properties of fully aliphatic polyimides and their derivatives for microelectronics and optoelectronics applications. *Macromol Res* 2007; **15**: 114–128.
16. Zhang Y, Ke S, Huang H, et al. Dielectric relaxation in polyimide nanofoamed films with low dielectric constant. *Appl Phys Lett* 2008; **92**: 052910(1–3).
17. Eichstadt AE, Ward TC, Bagwell MD, et al. Synthesis and characterization of amorphous partially aliphatic polyimide copolymers based on bisphenol-A dianhydride. *Macromolecules* 2002; **35**: 7561–7568.
18. Matsumoto T. Nonaromatic polyimides derived from cycloaliphatic monomers. *Macromolecules* 1999; **32**: 4933–4939.
19. Matsumoto T. Colorless full-alicyclic polyimides with low dielectric constant, *J Photopolym Sci Technol* 2001; **14**: 725–730.
20. Zhubanov BA, Kravtsova VD, Iskakov RM, et al. Polymeric composites based on alicyclic polyimide and polyaniline. *Russian J Appl Chem* 2008; **81**: 2151–2154.
21. Watanabe Y, Shibasaki Y, Ando S, et al. A new positive-type photosensitive alkaline-developable alicyclic polyimide based on poly(amic acid silylester) as a polyimide precursor and diazonaphthoquinone as a photosensitive compound. *Chem Mater* 2002; **14**: 1762–1766.