Influence of Conformational Parameters on Physical Properties of Polyimides Containing Methylene Bridges

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Conformational parameters, and free and Van der Waals volume values for a group of polymers containing methylene bridges, some of them having methyl substituents as well, have been calculated and correlated with physical properties such as solubility, glass transition and decomposition temperature, tensile stress and dielectric constant which were measured for these polymers. Thus, it was shown that conformational rigidity determines the packing of macromolecules in solid state, and therefore the free volume, and glass transition temperature and dielectric constant. The presence of methyl substituents and other flexible groups such as isopropylidene, carbonyl or hexafluoroisopropylidene has a more complex effect on the values of mechanical properties.

Keywords: polyimides, thin films, conformational parameters, glass transition, dielectric constant

Aromatic polyimides belong to the class of high performance polymers due to their excellent thermal and chemical stability, good mechanical resistance and low dielectric constant. Such polymers are appropriate for use in microelectronics, aerospace, and other industries, as films and coatings, adhesives, membranes for separation of gases and liquids. Among the most important applications of polyimides are interlayer dielectrics in integrated circuits and impregnating resins in high temperature composites [1-3]. Aromatic polyimides can be processed by using their intermediate polyamidic acids which are soluble and can be cast into thin films or other thin layer articles which are afterwards converted into the final polyimide structure that is insoluble and infusible. However, this two-step process has some draw-backs: water evolved during cyclization would produce voids in the final article and thus deteriorate its physical properties; also, the cyclization of polyamidic acid to polyimide structure is never complete and the remaining non-cyclized groups would cause the degradation in time of the macromolecular chain. Therefore, much research is carried out on new polyimides which should be soluble in certain solvents and could be processed by using solutions of the already cyclized polyimides. Such polymers can be obtained by the introduction of flexible bridges [4-13], various substituents or side groups [14-20], bulky units [21-24] or other heterocycles [25-34] into the macromolecular chain. Previously, we have reported the synthesis of polyimides containing flexible methylene bridges and methyl substituents [35]. Here, we present the study of the influence of conformational parameters of polyimides containing methylene bridges on their physical properties.

Experimental part
Preparation of polymer films
Six polymers have been studied whose structures are shown in scheme 1. They were synthesized by polycondensation reaction of a diamine having methylene bridge with three aromatic diphthalic anhydrides containing isopropylidene–diphenoxy, carbonyl or hexafluoroiso-propylidene units, according to previously published method [35].
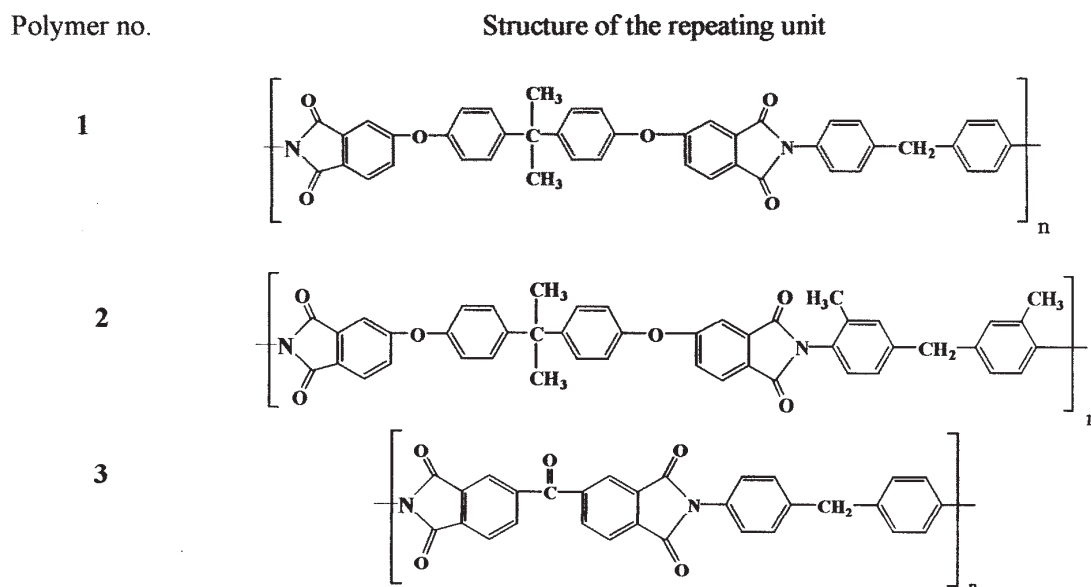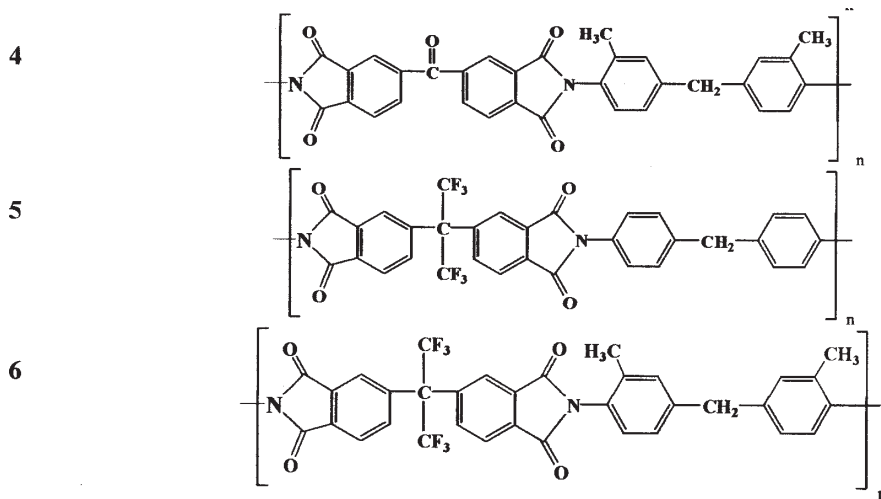
Polymer no.	Structure of the repeating unit
1	
2	
3	

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4, **5**, **6**

These polymers show good solubility in N-methyl-pyrrolidinone (NMP) and other polar amidic solvents having high boiling temperature, which made possible their processing from such solutions. The films, having the thickness usually in the range of 40-60 μm, were prepared by using solutions of polymers in NMP, having the concentration of 15 %, which were cast onto glass plates and heated gradually up to 210°C until constant weight. The films were carefully taken out of the substrate and were used afterwards for various measurements.

Calculation of conformational parameters and free volume

As conformational parameters we have taken the statistical Kuhn segment A_{fr}, and the characteristic ratio C_∞. Statistical Kuhn segment was calculated with the equation (1) [36]:

$$A_{fr} = \lim_{n \to \infty} \left(\frac{<R^2>}{nl_o} \right), \qquad (1)$$

where R^2 is mean square distance between the ends of the chain calculated for all possible conformations; $L = nl_o$ is the contour length of the chain, a parameter which does not depend on the chain conformation; l_o is the contour length of a repeating unit. All the values of Kuhn segment were calculated with Monte Carlo method where the geometry of the repeating unit was assigned by using the quanto-chemical method AM1 [37].

Characteristic ratio C_∞ was calculated with the equation (2) and it shows how many repeating units are in Kuhn segment.

$$C_\infty = \frac{A_{fr}}{l_o} \qquad (2)$$

To calculate the free volume we used the method previously described [38]. We built a model of the repeating unit and its geometry was also precised by using the quanto-chemical method AM1 [37]. The atoms are described by spheres having the Van der Waals radius equal to the corresponding radius of each type of atoms (Chart 1) [39].

Chart 1. Repeating unit introduced in the box.
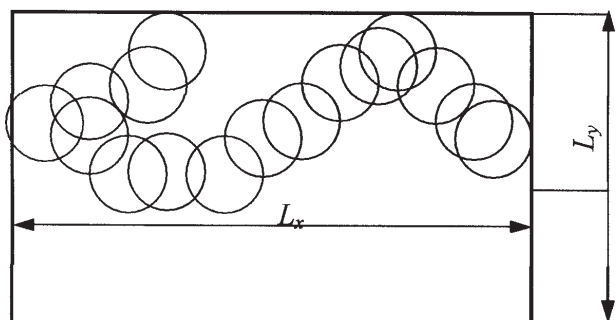
This model was situated in a 3D rectangular box having the axes L_x, L_y, L_z which are given by the equation (3):

$$L_x = x_{max} + R_{max} - (x_{min} - R_{max}) = x_{max} - x_{min} + 2R_{max} , \qquad (3)$$

where x_{max} and x_{min} are the maximum and the minimum values of the coordinates of atom corresponding to the repeating unit, R_{max} is the maximum value of the radius of atom corresponding to the repeating unit. L_y and L_z were determined in the same way. The volume of this model was calculated with Monte Carlo method. For that, in the volume corresponding to the parameters of the box, random points were generated. The number of random points, landing in the repeating unit, is m. In the beginning of calculation m is equal zero. For each random point the following conditions were verified:

$$| r_d - r_i | \leq R_i, \qquad i = 1...N,$$

where N is the number of atoms in the repeating unit, $|r_d - r_i|$ is the distance between a given point and any other point in the repeating unit. In case of achievement of this conditions for at least one atom, procedure of verification stopped, number of successful events began with $m+1$, and next random point was generated.

Van der Waals volume (V_w) was calculated with the formula (4):

$$V_w = (m / M) \, V_{box} \qquad (4)$$

where M is the total number of all points, V_{box} is the volume of the box.

The free volume (V_f) was calculated with the formula (5):

$$V_f = \frac{1}{\rho} - \frac{N_A \bullet V_w}{M_o} \qquad (5)$$

where N_A is the number of Avogadro, ρ is the density of polymer, M_o is the molecular weight of the repeating unit. The value V_f, thus calculated, shows the volume which is not occupied by the macromolecules in one cm³ of polymer film.

Measurement of glass transition and decomposition temperature

The glass transition temperature (Tg) of the polymers was measured by differential scanning calorimetry, using a Mettler DSC 12E apparatus. The samples were heated at a rate of 15°C/min under nitrogen to above 300°C. Heat flow versus temperature scans from the second heating run were ploted and used for reporting the Tg. The mid-point of the inflection curve resulting from the second

heating run was assigned as Tg of the respective polymers. The precision of this method is ±7 – 10°C.

The decomposition temperature (Td) of the polymers was measured by thermogravimetric analysis (TGA), using a Mettler Toledo model TGA/DTA 851. The samples were heated under nitrogen flow (20 cm³/min) at a heating rate of 10°C/min, from 25 to 900°C. The onset temperature on the TGA curve was taken as decomposition temperature of the respective polymers.

Measurement of dielectric constant

Dielectric spectroscopy measurements of polymer films in the frequency range of 10^{-1}–10^6 Hz have been performed using a Novocontrol Dielectric Spectrometer, CONCEPT 40 (GmbH Germany). Polymer films were placed in a flat parallel plate capacitor arrangement having gold plated electrodes with 20 mm diameter. The amplitude of AC applied voltage was 1 V.

Measurement of mechanical properties

The mechanical properties of the polymer films were determined by stress-strain measurements at room temperature on an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5 kN load cell and activate grips, which prevented the slippage of the sample before break. The cross head speed was 50 mm/min.

Measurement of density

To measure the density of polyimide films we used the hydrostatic weighing method. The study was performed with an equipment for density measurement and an electronic analytic balance Ohaus AP 250D, precision of 10^{-5} g, from Ohaus Corp. US which was connected to a computer. With this equipment we measured the change of sample weight during the experiment, with a precision of 0.001 g/cm³ in the value of density. Ethanol was taken as a liquid with known density. The studied polyimides did not absorb and did not dissolve in ethanol, which for these polymers had a low diffusion coefficient. Since the density of ethanol depends on temperature, every time it was measured using pycnometer. The characteristic diffusion times were in the domain of 10^4 – 10^5 s, which are 1-2 order of magnitude higher than the time of density measurement. This is why the sorption of solvent and the swelling of the film must have only insignificant influence on the value of the measured density. All measurements of the density were performed at 23°C. The density was calculated with the equation (6):
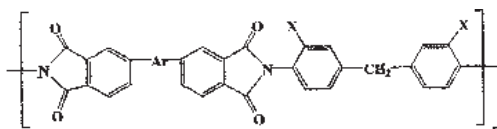
$$\rho_s = W_a / (W_a - W_l) \, \rho_l , \tag{6}$$

where ρ_s is density of the sample, W_a is the weight of the sample in air, W_l is the weight of the sample in liquid, ρ_l is the density of liquid. The error of density measurements was 0.1 – 0.3 %.

Results and discussions

Table 1 shows the chemical structure of the repeating unit and some of the physical properties of the studied polymers. For these polymers we calculated the Kuhn segment A_{fr}, characteristic ratio C_∞, Van der Waals volume V_w and free volume V_f, and we measured their density ρ_s in ethanol. By using the values of density and Van der Waals volume, the free volume of each of the studied polymers was calculated with equation (4) and it is shown in table 1.

The solubility of these polymers correlates well with their conformational rigidity. The polymers were soluble in polar aprotic solvents such as N-methylpyrrolidinone or dimethylformamide. The good solubility is due to the high flexibility of the macromolecular chains, which is in agreement with relatively low values of Kuhn segment, in the range of 25.3-29.1Å(table 1). This flexibility is determined by the presence of methylene bridges and other linkages such as isopropylidene, carbonyl or hexafluoro-isopropylidene. The good solubility makes the present polymers potential candidates for practical applications in spin-coating and casting processes.

Poly mer	Ar	X	ρ (g/cm³)	Td (°C)	Tg (°C)	l_o (Å)	A_{fr} (Å)	C_∞	V_w (Å³)	V_f (cm³/g)	ε_o
1		–	1.200	493	200	32.32	25.3	0.787	625.359	0.2915	3.138
2		CH₃	1.169	479	228	32.32	26.2	0.811	656.092	0.3056	2.953
3		–	1.398	508	–	24.53	28.3	1.143	426.696	0.1889	3.340
4		CH₃	1.337	498	278	24.53	28.7	1.177	460.613	0.2085	3.180
5		–	1.546	509	275	22.37	28.5	1.281	488.651	0.1648	2.845
6		CH₃	1.488	501	287	22.37	29.1	1.319	522.676	0.1793	2.780

Table 1
PHYSICAL PROPERTIES OF THE STUDIED POLYIMIDES

ρ = density of polymer film; l_o = contour length of a repeating unit; A_{fr} = Kuhn segment; C_∞ = characteristic ratio; V_w = Van der Waals volume; V_f = free volume; ε_o = dielectric constant

The dependence of glass transition temperature on Kuhn segment is presented in figure 1. This dependence shows usual behavior: with the increase of Kuhn segment, the glass transition increases [39-42]. Since all the points are situated on a straight line, which is described by the equation y=324+20.85x with a high correlation coefficient R=99.17%, we can calculate the Tg of polymer **3** which could not be detected experimentally. Thus, the calculated value of Tg is 262°C, which is correctly situated on the diagram showing the dependence of Tg on free volume (fig. 2). This dependence represented in figure 2 shows that with the increase of free volume, the Tg decreases because the higher free volume allows the molecular fragments to change their conformation which leads to an increased mobility of polymer chains with heating.

Figure 3 shows the dependence of free volume on conformational rigidity. This dependence is linear with a high correlation coefficient and it confirms that with the increase of rigidity of polymer matrix, the free volume decreases.

When looking at figures 1-3, a contradiction appears in pairs of polymers **1** with **2**, **3** with **4**, **5** with **6**: with increasing rigidity it is expected to have an increase of glass transition temperature and a decrease of free volume. However, when going to polymers containing methyl substituents - **2**, **4** and **6** - the rigidity, given by A_{fr}, increases, and both glass transition temperature and free volume increase, as well. Such a behaviour is explained in the following way: the introduction of methyl substituents on phenylene rings
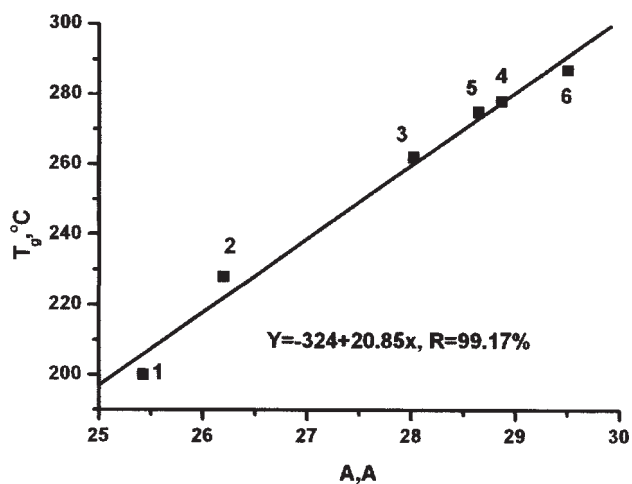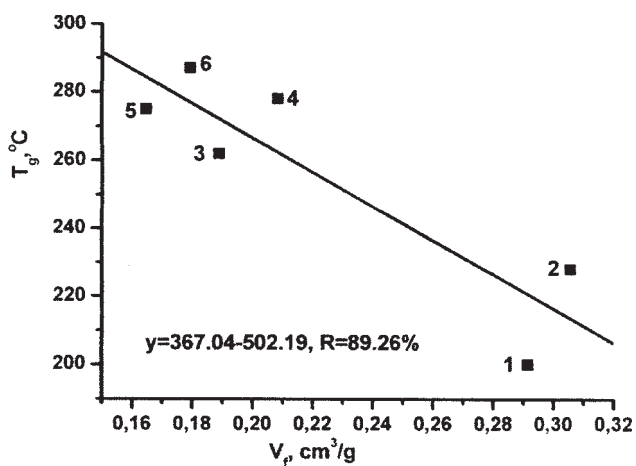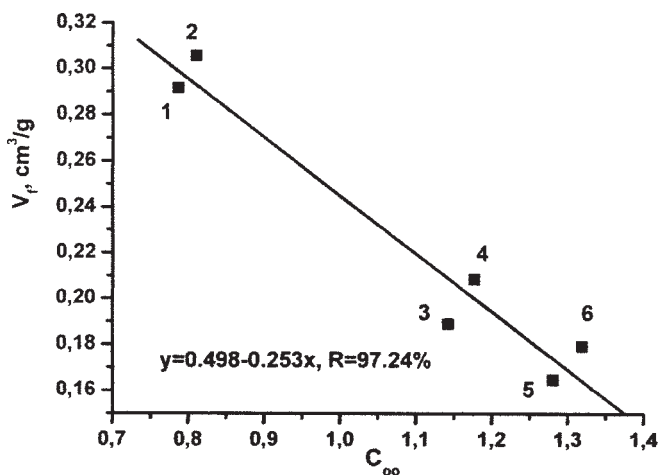

Fig. 3. Dependence of free volume V_f on characteristic ratio C_∞

in orto-position towards the bond between imide and phenylene rings leads to the increase of hindrance of rotation; therefore, the rigidity increases, the amount of conformational isomers and their mobility decrease when heating, and as a consequence the glass transition temperature increases. On another side, the methyl substituents do determine a loosing of packing, but the polymer can not benefit of the increased free volume because the rotation hindrance does not allow the production of conformations which should occupy that free volume when heating. This is why the glass transition temperature of polymers containing methyl substituents does not decrease, but it increases in each pair of polymers. Thus, the competition between these two processes, increased free volume and increased rotation hindrance/ conformational rigidity, gives a particular behavior of glass transition temperature.

Figure 4 shows the dependence of decomposition temperature, that is temperature when the decomposition starts, on conformational rigidity, A_{fr}. It can be seen that the points are situated on two straight lines: the polymers which do not contain methyl substituents are situated on the top-line, while those containing methyl substituents are situated on the bottom line, both dependences having a high correlation coefficient. It means that by introduction of methyl substituents the thermal stability decrease. It can also be seen that the order of stability is the same in both groups of polymers, and the decrease of decomposition temperature is of 14, 11 and 7°C, respectively, showing the stability of the bridge between imide rings: the most stable are the polymers containing hexafluoroisopropylidene bridge and the less stable are those containing isopropylidene one.
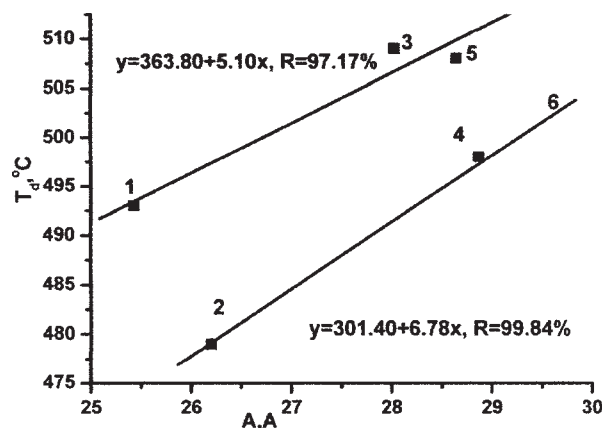

Fig. 1. Dependence of glass transition temperature **Tg** on Kuhn segment A_{fr}

Fig. 2. Dependence of glass transition temperature **Tg** on free volume V_f

Fig. 4. Dependence of decomposition temperature on Kuhn segment

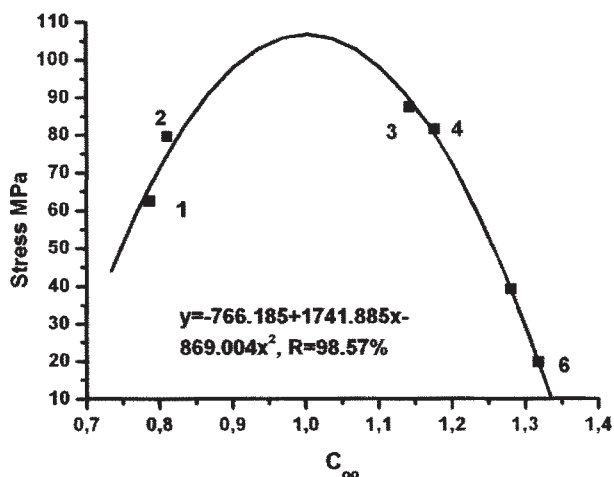| Polymer	Elongation at break (%)	Tensile stress (MPa)
1	4.4	62.4
2	8.8	79.5
3	4.2	87.4
4	4.4	81.5
5	-	-
6	2.3	19.7

Fig. 5. Dependence of tensile stress on characteristic ratio C_∞

Table 2 presents the mechanical properties of the polyimide films. Figure 5 shows the dependence of tensile stress on the characteristic ratio. This dependence is described by an equation of second order having a high correlation coefficient. It allows to calculate the value of mechanical resistance of polymer **5** which was not determined experimentally. It is equal to 39.2 MPa. According to figure 5, it follows that the most resistant films will be those obtained from the polymer having a value of characteristic ratio close to 1, which means that Kuhn segment is formed only by one repeating unit. In this case a tight packing of the repeating units takes place in the polymer matrix.
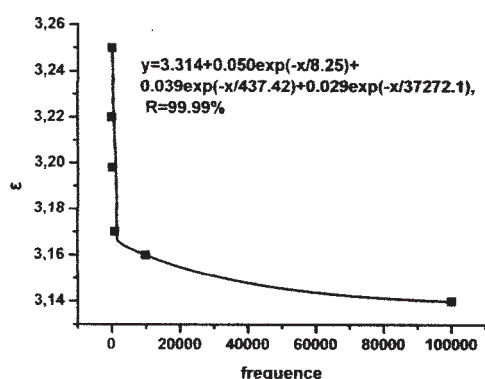
Table 3 shows the values of dielectric permitivity ε at various frequencies. To compare the values of dielectric permitivity of different polymers, we examine its value at the frequency equal to zero. Figures 6a-f show the dependence of ε on frequency.

These dependences are described by an exponential function of second order. The free term of this equation is the dielectric permitivity when the frequency is equal to zero. This is the dielectric constant ε_o of a given polymer. If we draw the dependence of dielectric constant of the studied polymers on the characteristic ratio, we can see that the points are situated in pairs (fig. 7). The value of ε_o of the polymers containing methyl groups is lower than
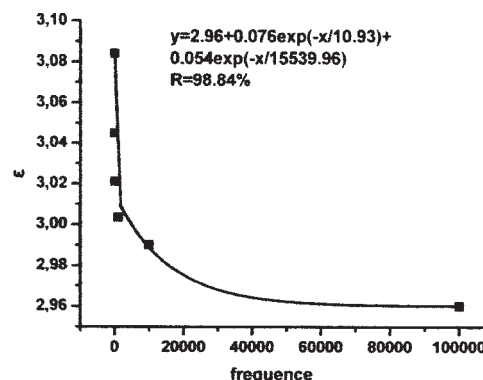
Polymer	1 Hz	10 Hz	100 Hz	1 kHz	10 kHz	100 kHz
1	3.25	3.22	3.198	3.17	3.16	3.14
2	3.084	3.045	3.021	3.0033	2.99	2.96
3	3.48	3.449	3.42	3.40	3.38	3.34
4	3.32	3.29	3.26	3.24	3.22	3.18
5	2.91	2.89	2.87	2.86	2.85	2.84
6	2.88	2.85	2.83	2.82	2.80	2.78

a (Polymer **1**)

b (Polymer **2**)

c (Polymer **3**)

$$y=3.34+0.072\exp(-x/14.66)+0.073\exp(-x/15694.9)$$
$$R=98.96$$

d (Polymer **4**)

$$y=3.18+0.071(-x/15.41)+0.073(-x/15710.58)$$
$$R=98.97\%$$

e (Polymer **5**)

$$2.84+0.041\exp(-x/12.14)+0.019\exp(-x/16108.19)+0.014(-x/588.89)$$
$$R=99.99\%$$

f (Polymer **6**)

$$y=2.78+0.058\exp(-x/10.64)+0.047\exp(-x/11033.97)$$
$$R=99.67\%$$
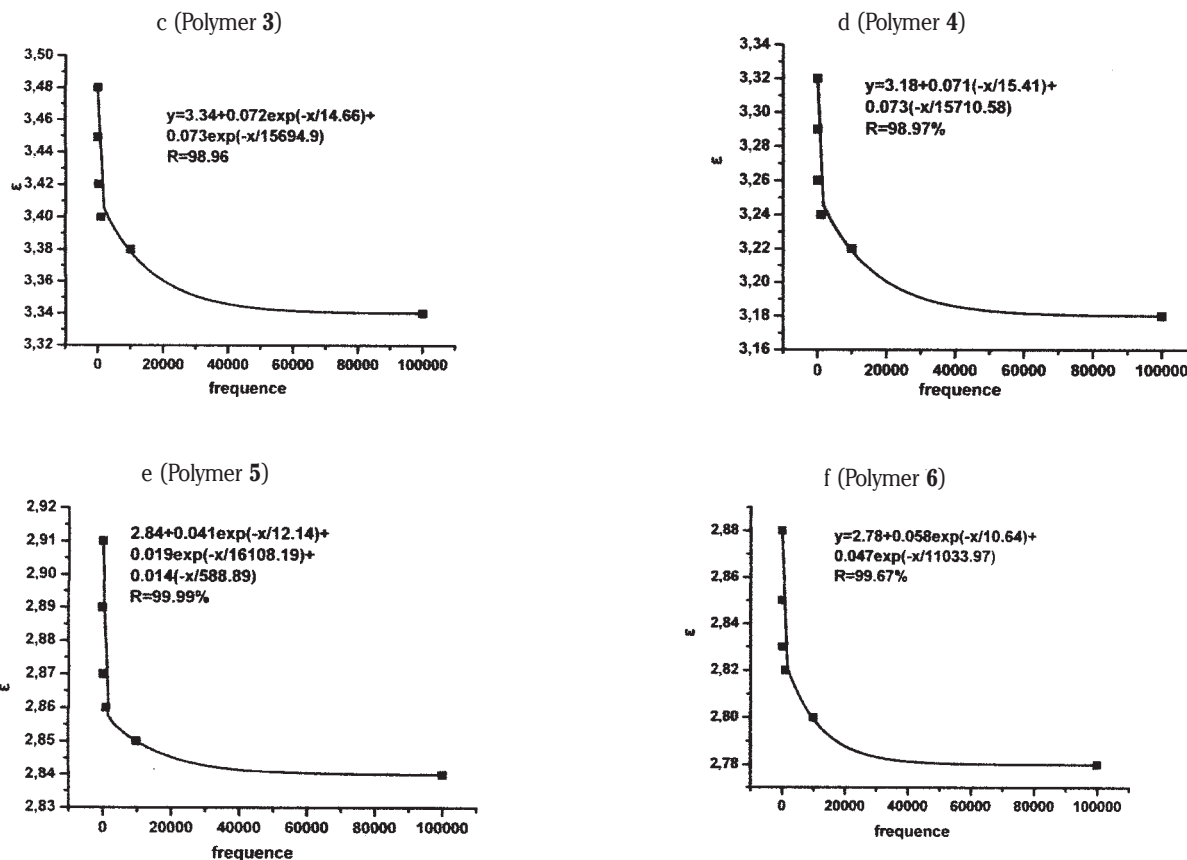
Fig. 6a-f. Dependence of dielectric permitivity on frequency
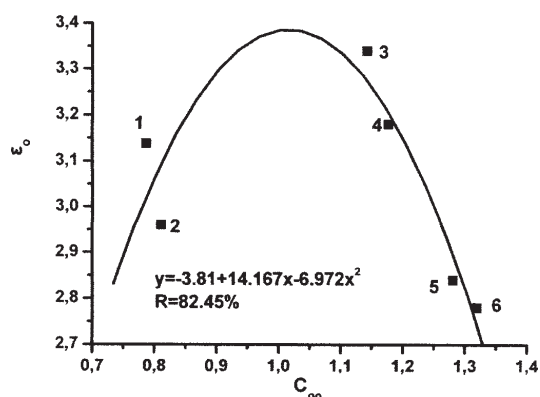

$$y=-3.81+14.167x-6.972x^2$$
$$R=82.45\%$$

Fig. 7. Dependence of dielectric constant on characteristic ratio

that of the related polymers which do not contain methyl groups. By introduction of methyl groups, the packing of the polymer chain becomes loose and the free volume increases for the pairs of polymers: from 0.2915Å to 0.3056 Å, for polymers **1** and **2**, respectively; from 0.1889 Å to 0.2085Å, for polymers **3** and **4**, respectively, and from 0.1648Å to 0.1793 Å, for polymers **5** and **6**, respectively (table 1). As a consequence the dielectric constant of the polymers containing methyl groups **2**, **4** and **6** is lower than that of the related polymers **1**, **3** and **5** which do not contain methyl groups.

Conclusions

A series of six polyimides containing methylene bridges and three of them having methyl substituents as well have been studied with regard to the effect of conformational parameters on their physical properties such as solubility, glass transition and decomposition temperature, mechanical resistance and dielectric constant.

The good solubility of these polymers, in certain organic solvents, correlates well with the low values of their Kuhn segment. The glass transition temperature, being in the range of 200-287°C, is increasing with increasing values of

conformational rigidity. The introduction of bulky methyl substituents does not lead to a decrease of glass transition temperature, although it leads to the increase of free volume, and by contrary the glass transition temperature increase due to the hindrance of rotation around imide-phenylene rings bonds produced by those methyl substituents.

The decomposition temperature slightly decreases by the introduction of methyl substituents, but it is still high, above 479°C. A slight increase of decomposition temperature was observed when hexafluoroisopropylidene groups were incorporated in the macromolecular chain.

The increase of free volume of polymers containing methyl substituents leads to the decrease of dielectric constant compared with related polymers which do not contain such substituents. The influence of free volume on tensile stress is diverse, because this property is also influenced by the other flexible groups which are present in the polymer chain such as isopropylidene, carbonyl or hexafluoroisopropylidene.

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