

*Dedicated to the memory of  
Professor Cristofor I. Simionescu (1920–2007)*

## INFLUENCE OF CONFORMATIONAL PARAMETERS ON PHYSICAL PROPERTIES OF SOME POLY(IMIDE-ETHER-AMIDE)S BASED ON EPICLON

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A series of poly(imide-ether-amide)s has been synthesized by solution polycondensation of a diacid chloride, based on Epiclon and *p*-aminobenzoic acid, with various aromatic diamines having ether bridges between phenylene rings. The polymers are easily soluble in polar amidic solvents such as *N*-methylpyrrolidinone or dimethylformamide. They show high thermal stability, with initial decomposition temperature above 350°C and glass transition temperature in the range of 223–238°C. Conformational rigidity parameters of some poly(imide-ether-amide)s based on Epiclon have been calculated by Monte Carlo method with allowance for hindered rotation. Several physical properties such as solubility, glass transition temperature and initial decomposition temperature are discussed in relation with the structure of the polymers and rigidity of their chains.

### INTRODUCTION

Among high performance materials, heterocyclic polymers are used in applications demanding service at enhanced temperatures while maintaining their structural integrity and a good combination of chemical, physical and mechanical properties. Some requirements to use these polymers for interlayer and intermetal dielectrics in microelectronic applications are: high thermal stability, high glass transition temperature, good mechanical properties, low dielectric constant, low coefficient of thermal expansion and low moisture absorption.<sup>1</sup> Wholly aromatic polyimides are generally the polymers of choice for these applications due to their many desirable characteristics including excellent thermooxidative stability and good mechanical properties.<sup>2–7</sup> However, their applications are restricted because of their poor solubility in organic solvents and too high glass transition temperature. Therefore, much effort has been made to modify their chemical structure in order to

enhance their physical properties with regard to a specific application or to a particular property, and improve the processability. The most widely used method for the synthesis of aromatic polyimides *via* soluble poly(amic-acid) precursors still has certain disadvantages connected with the low stability of the poly(amic-acid) solutions and their incomplete cyclization to polyimide structures.<sup>4, 5</sup>

It is known that the solubility of polymers is often increased when flexible bonds, large pendent groups or polar substituents are incorporated into the polymer backbone.<sup>8–10</sup> Aromatic poly(imide-amide)s were developed as alternative materials offering a compromise between excellent thermal stability and processability. They bring together the superior mechanical properties associated with amide groups and the high thermal stability determined by imide rings. These polymers show improved solubility in highly polar solvents, lower glass transition temperatures and easier processability compared with corresponding polyimides.<sup>11, 12</sup>

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Also, a cycloaliphatic anhydride named Epiclon, having a flexible chemical structure, is useful, like other tetracarboxylic dianhydrides, as a raw material for the production of polyimide resins. Therefore, Epiclon units have been incorporated into various polymers, mainly in aromatic copolyimides and polyesters, with the aim to enhance their solubility and render new properties.<sup>13,14</sup>

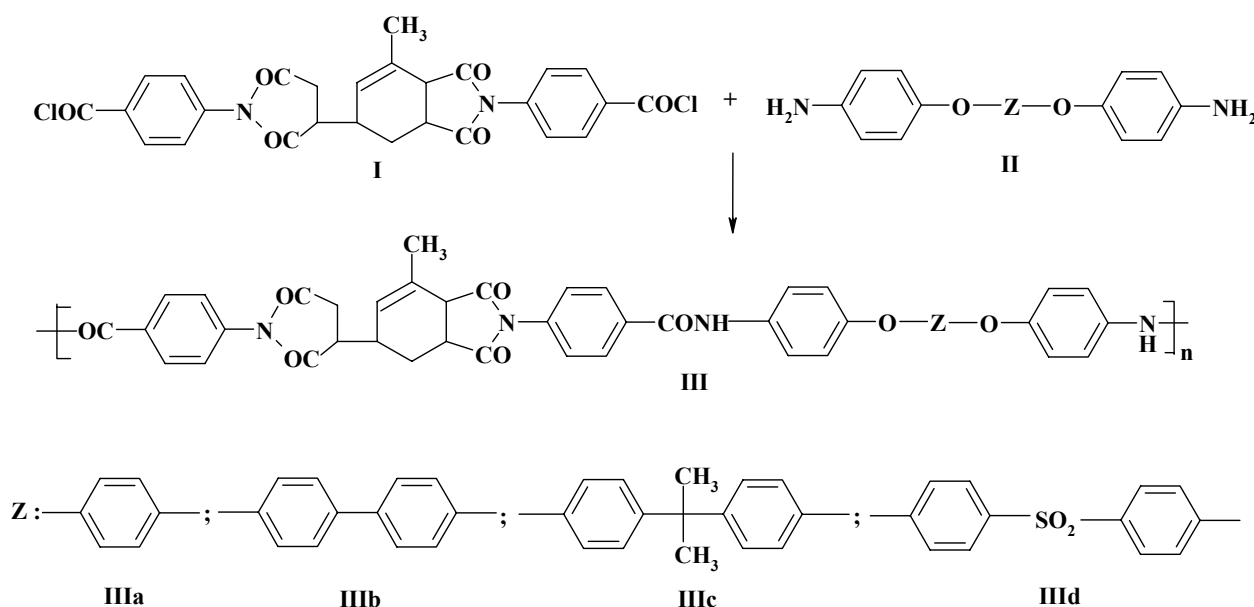
Previously we have synthesized poly(imide-amide)s by using diacid chlorides containing hexafluoroisopropylidene, methylene or dimethylsilane groups and various aromatic diamines.<sup>15-17</sup>

In the present work physical properties of some poly(imide-ether-amide)s based on Epiclon have been studied with regard to the structure and conformational rigidity of the polymer chains and their relationships have been shown. The polymers

have been synthesized by using a diacid chloride, having Epiclon units and imide groups, which reacted with certain aromatic diamines having ether bridges between phenylene rings. The conformational rigidity of the polymers was evaluated by calculating Kuhn segment by using the Monte Carlo method with allowance for hindered rotation.

## RESULTS AND DISCUSSION

Polycondensation of equimolar amounts of diacid chloride **I** and diamine **II** in NMP, at low temperature, yielded viscous solutions of poly(imide-ether-amide)s **III** (Scheme 1).



Scheme 1 – Preparation of poly(imide-ether-amide)s **III**.

The structure of polymers was identified by IR and <sup>1</sup>H-NMR spectroscopy. Strong bands at 1780 cm<sup>-1</sup>, 1720 cm<sup>-1</sup>, 1380 cm<sup>-1</sup> and 760-750 cm<sup>-1</sup> attributed to imide rings. The wide bands which appeared at 3400 cm<sup>-1</sup> were assigned to N-H stretching vibration in amide group. Characteristic absorptions appeared at 1670-1660 cm<sup>-1</sup> due to carbonyl stretching vibration (amide I) and at 1520 cm<sup>-1</sup> due to N-H deformational vibration (amide II). All the polymers exhibited IR bands at 1225-1220 cm<sup>-1</sup> due to the ether bonds. Also, <sup>1</sup>H-NMR spectra confirmed the proposed structures.

We have studied some physical properties of polymers **III**, such as solubility, glass transition temperature (*T<sub>g</sub>*) and initial decomposition

temperature (*T<sub>d</sub>*), and we have made some correlations with their conformational rigidity. The correlation between a physical property of a polymer and the conformational rigidity of its chain shows that the contribution of the conformational rigidity to this polymer property is significant.<sup>18,19</sup>

The main conformational parameter is the statistical Kuhn segment,<sup>20</sup> which equals:

$$A_{fr} = \lim_{n \rightarrow \infty} \left( \frac{\langle R^2 \rangle}{nl_0} \right),$$

where  $\langle R^2 \rangle$  is the mean square distance between the ends of the chain, averaged over all possible

conformations,  $L=nl_0$  is the chain length, and  $l_0$  is the length of the repeat unit.

Conformational rigidity characterizes the degree of macromolecular coiling and it is governed by chain geometry: lengths of virtual bonds, angles between them and the allowed rotations about these bonds. The term «virtual bonds» is used to indicate a rigid section of a chain approximated by a straight line about which rotation is possible. In a particular case, it can be an ordinary valence bond; more generally, it can contain rings as well. For polyheteroarylenes the length of virtual bonds equals the sum of segments joining the midpoints of virtual bonds and is not dependent upon chain conformation. All Kuhn segment values have been calculated using the Monte-Carlo method under the assumption of free rotation about virtual bonds, as described previously.<sup>21-23</sup>

Another conformational parameter is the number  $p$  of aromatic rings in Kuhn's segment:

$$p=(A_f/l_0)n$$

where  $n$  is the number of aromatic and heterocyclic

rings in the monomer.

The parameter  $p$  was included because in the previous works the correlation of physical properties with the number of aromatic rings in Kuhn segment was shown.<sup>20,22,24</sup> The conformational parameter  $p$  takes into account the both factors: aromatic character of polyheteroarylenes and their rigidity. Since many physical properties such as glass transition temperature of polyheteroarylenes are determined by the presence of aromatic rings or heterocycles in the polymer backbone, the introduction of this parameter is very useful for comparison of polymers with different structures but containing the same heterocycle.<sup>25</sup>

In order to calculate Kuhn's segment, models of all polymers under study have been constructed using the PCMODEL molecular editor, and their geometry adjusted using the semi empirical quantum chemistry method AM1. Kuhn's segments and polymer lengths have been calculated using Monte-Carlo method. Table 1 presents some properties of polymers **III** and their calculated conformational parameters.

Table 1

Properties of poly(imide-ether-amide)s **III**

Poly-mer	$\eta_{inh}$ (dL/g)	Mw (g/mol)	Mn (g/mol)	Mw/Mn	$T_g$ (°C)	$T_d$ (°C)	$l_0$ (Å)	$A$ (Å)	$p$
<b>a</b>	0.26	53300	33100	1.61	238	350	36.36	24.96	4.80
<b>b</b>	0.31	66000	41500	1.59	223	370	40.08	27.93	5.57
<b>b'</b>	0.31	66000	41500	1.59	223	370	40.08	23.40	4.67
<b>c</b>	0.35	50000	31500	1.59	234	370	41.03	25.41	4.78
<b>d</b>	0.28	48600	29200	1.66	226	380	41.35	22.34	4.32

$T_g$  = glass transition temperature;  $T_d$  = initial decomposition temperature = temperature of 5% weight loss;  $l_0$  = contour length over repeating structural unit;  $A$  = Kuhn segment;  $p$  = conformational rigidity parameter.

The inherent viscosities, measured in NMP solution, were in the range of 0.3-0.4 dL/g (Table 1). The molecular weight of polymers was determined by gel permeation chromatography (GPC). The values of weight-average molecular weight Mw are in the range of 48600 – 66000 g/mol, the number-average molecular weight Mn in the range of 29200 – 41500 g/mol, and the polydispersity Mw/Mn in the range of 1.59 – 1.66 (Table 1).

The solubility of the polymers correlates well with their conformational rigidity. Polymers were

soluble in polar aprotic solvents such N-methylpyrrolidone (NMP) or N,N-dimethylformamide (DMF). The good solubility is due to the high flexibility of the macromolecular chains, which is in agreement with relatively low values of the Kuhn segment, in the range of 22.34-27.93 Å (Table 1). This flexibility is determined by the presence of Epiclon units and ether linkages into the structure of polymers. The good solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

Generally, the glass transition temperature ( $T_g$ ) of polymers increases with increasing chain rigidity. As is mentioned in the literature,<sup>20</sup> if the dependence is linear with a good factor of convergence, this equation can be used for the

theoretical estimation of glass transition temperature for polymers having similar structures.

Figure 1 shows the dependency of the glass transition temperature upon Kuhn's segment and the number of rings in it, for polymers **III**.

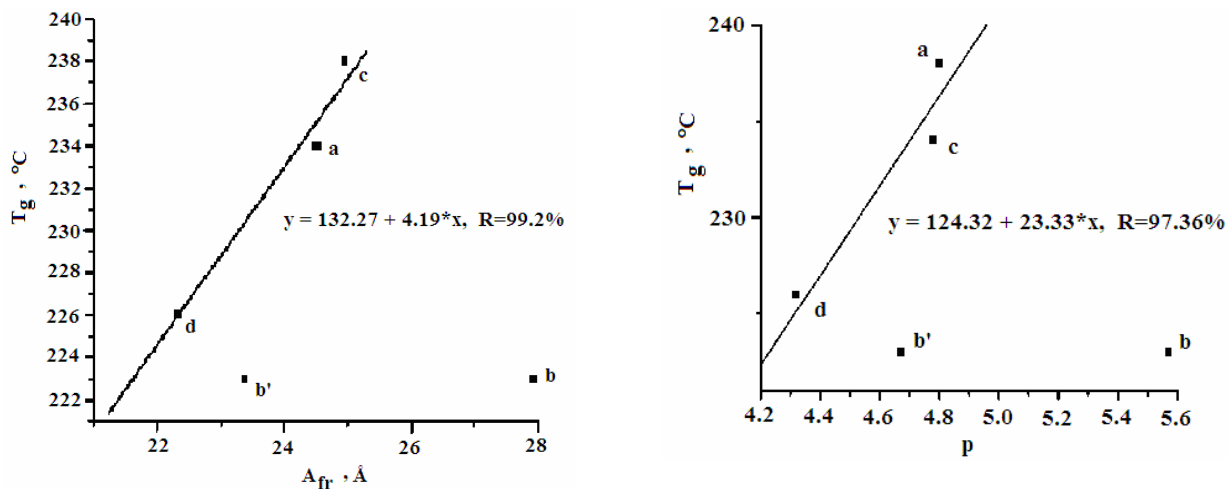


Fig. 1 – The dependence of glass transition temperatures of polymers **III** on Kuhn's segment (top) and on the number of rings in Kuhn's segment  $p$  (bottom).

As seen in Fig. 1, most polymers demonstrate linear dependence, with high correlation coefficients, and the coefficient of correlation with Kuhn's segment is higher than with the  $p$  value. The polymer **IIIb** drops out of both dependencies. Analogous behavior is observed for the temperatures of 5% weight loss, but with a smaller correlation coefficient (Fig. 2). Molecular weight values in this group of polymers are very close to each other. One may suppose that defective structures arise during synthesis: some *ortho*-

carboxy-amidic units are not cyclized to imide structure. To check this assumption, Kuhn segment for the polymer **IIIb'** having the structure shown in Fig. 3 has been calculated. During the incomplete cycle formation Kuhn's segment diminished, but still does not fit the dependence. Based on these calculations one may confirm that cyclized and non-cyclized structures coexist during polymer synthesis. Earlier, partial cyclization of parabane rings has been observed experimentally.<sup>20</sup>

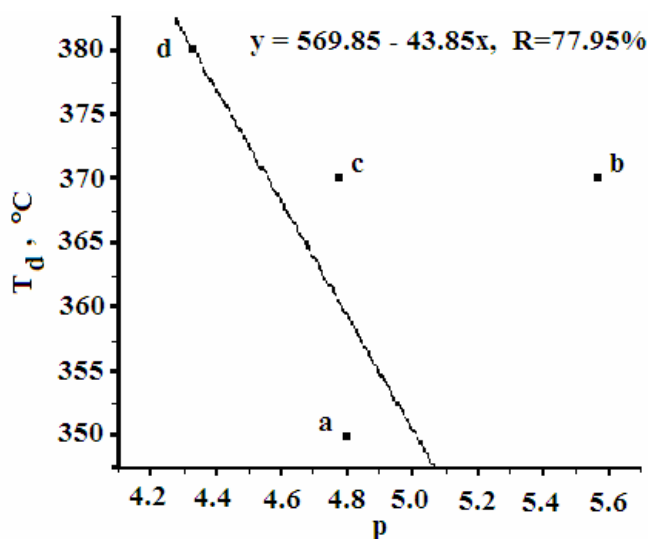
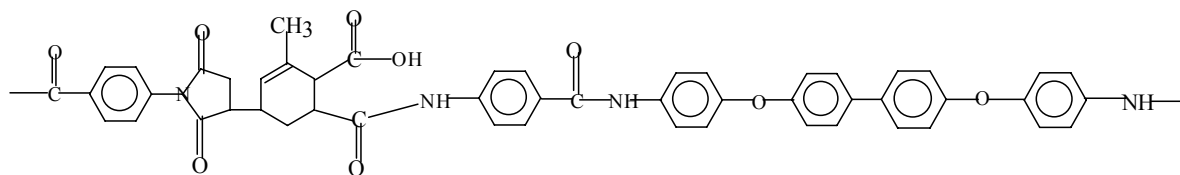


Fig. 2 – The dependence of the decomposition temperature  $T_d$  of polymers **III** on the number of rings in Kuhn's segment  $p$ .



IIIb'

Fig. 3 – The structure of polymer IIIb'.

Previously, it was shown that there is a relationship between glass transition ( $T_g$ ) and decomposition ( $T_d$ ) temperatures for several polymers.<sup>26</sup>

$$T_d = aT_g$$

The value of  $a$  for polyamides and polyimides lies in the range of 1.15-1.25 depending on the structure of the polymer repeating unit. Given the dependence between the glass transition temperature and the conformational rigidity, it would be reasonable to assume the existence of a relation between decomposition temperature and the conformational rigidity.

All polymers exhibited high thermal stability. The initial decomposition temperature  $T_d$  was in the range of 350-380°C (Table 1).

It can be observed from Fig. 2 that the decomposition temperature does not depend significantly on the chain rigidity of these polymers. This fact is probably due to the presence of amide units in the macromolecular chains which are more sensitive to thermal degradation and the decomposition is mainly determined by these groups. A similar behavior was reported for related heterocyclic polymers containing amide groups.<sup>27</sup>

## EXPERIMENTAL

### Synthesis of the polymers

Poly(imide-ether-amide)s based on Epiclon, **III**, have been synthesized by low temperature solution polycondensation of equimolar amounts of diamine **II** with the diacid chloride **I**, which resulted from the reaction of Epiclon with *p*-aminobenzoic acid followed by treatment with thionyl chloride.<sup>28</sup> The reaction was performed under anhydrous conditions in a nitrogen atmosphere, in *N*-methylpyrrolidone (NMP) as a solvent and with pyridine as an acid acceptor, as depicted in scheme 1. The relative amounts of monomers and NMP were adjusted to maintain a solid content of 9-12 %. A typical reaction was carried out as follows: In a 100 mL three-necked flask, equipped with mechanical stirrer and nitrogen gas inlet and outlet, 1.08 g (0.0025 mol) of 4,4'-bis(*p*-aminophenoxy)-diphenylsulfone, **IId**, 22 mL NMP and 1 mL Py were placed and the mixture was stirred under nitrogen until complete dissolution. The solution was cooled to -10°C and 1.3475 g (0.0025 mol) of diacid chloride **I** were added with rapid

stirring. The content of the flask was kept below 0°C for 15 min. The cooling bath was then removed and the reaction mixture was allowed to reach the room temperature after which it was stirred for another 4 h. Half of the resulting viscous polymer solution was cast onto a glass plate and after evaporating the solvent at 120°C, 160°C, 180°C and 210°C, each for 1h, a flexible transparent film was obtained which was stripped off the plate by immersion in hot water for 2 h. It was used for different measurements. The other half of the polymer solution was diluted to about 6% by addition of more NMP and the polymer was precipitated by pouring into water. The precipitated product was filtered, washed twice with water and with ethanol under stirring and dried under vacuum at 100°C for 1 h.

### Measurements

Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices) apparatus without correction. Infrared spectra were recorded with a Specord M 80 spectrometer in transmission mode, at 4 cm<sup>-1</sup> resolution, by using monomers or precipitated polymers ground in potassium bromide pellets. The <sup>1</sup>H-NMR spectra were recorded on a JEOL 60 MHz spectrometer for polymer solution in dimethylsulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) using tetramethylsilane (TMS) as internal standard. The inherent viscosities ( $\eta_{inh}$ ) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20°C, at a concentration of 0.5 g/dL. The molecular weight were determined by gel permeation chromatography (GPC) using a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards of known molecular weight were used for calibration and dimethylformamide as the mobile phase. Thermogravimetric analyses (TGA) were performed on a MOM derivatograph (Hungary) in air, at a heating rate of 12°C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperatures of 10% weight loss ( $T_{10}$ ), were also recorded. The glass transition temperatures ( $T_g$ ) of the precipitated polymers were determined with a Mettler differential scanning calorimeter DSC 12E. The samples were heated from ambient temperature to above 300°C at a heating rate of 10°C/min under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflection curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers. The Kuhn segments were calculated by using the Monte Carlo method as described earlier.<sup>21-23</sup>

## CONCLUSIONS

A series of poly(imide-ether-amide)s based on Epiclon have been synthesized by using a diacid

chloride, having Epiclone units and imide groups, which reacted with certain aromatic diamines having ether bridges between phenylene rings. The physical properties such as solubility, glass transition temperature and initial decomposition temperature were studied and correlated with the conformational rigidity of their chains. The solubility of the polymers correlates well with Kuhn segment values. The glass transition temperature increases with increasing chain rigidity, being in the range of 223-238°C, excepting the polymer which contains biphenyl unit in the segment coming from the diamine monomer. The decomposition temperature is high, above 350°C, and it does not show a significant dependence on the chain rigidity. The large interval between glass transition and decomposition temperature may be advantageous for their processing by a thermoforming technique. The polymers can also be processed from solutions into flexible thin films. All these properties, associated with an easy processability, make the present polymers potential candidates for practical applications in microelectronics or related advanced fields.

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