Functional Polyimides and Thin Films Based on Them

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Abstract. Soluble imide type polymers containing ether linkages, aliphatic sequences or high polar pendant groups have been obtained by solution polycondensation of aromatic diamines with various anhydrides such as 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (Epiclon), maleic anhydride or oxidiphthalic dianhydride, followed by thermal ring closure of the resulting polyamic acids. The structures of these polymers were identified by infrared and \(^1\)H-NMR spectroscopy. The viscosity and thermal behavior of these polymers were investigated. A good correlation between the polymers structure and their properties has been found. Also, the metal complexation ability of some carboxy-functionalized imide polymers was investigated. The products show remarkable film-forming ability with potential application as high performance materials.

Key words: imide type polymers, polycondensation, IR spectra, thin films.

1. General background

Electroactive polymers (EAP) are polymers whose shape is modified when a voltage is applied to them. They can be used as actuators or sensors. Electroactive polymers (EAP) can be divided into two categories: electronic EAPs and ionic EAPs. Electronic EAPs change shape or dimensions due to the migration of electrons and are usually dry, whereas ionic EAPs change shape or dimensions due to the migration of ions, contain an electrolyte and are usually wet [1–3]. As compared to electroactive ceramics and shape memory alloys, electroactive polymers are lightweight,
conformable, and tough. Recent development of electroactive polymers has offered several new candidates such as electrostrictive copolymers, electrostatic elastomers, electrostrictive liquid elastomers, electrostrictive graft elastomers or dielectric materials containing polar functional groups, for potential use as sensors in high temperature applications [4–6]. Here, a dielectric material should possess a number of other high performance characteristics such as high thermal stability, good resistance to aggressive media and good mechanical properties.

From this point of view, imide type polymers are very attractive due to their excellent thermal stability, low dielectric constant and tough mechanical properties [7, 8]. But, conventional aromatic polyimides are often categorized as insoluble, intractable and infusible materials because of their rigid backbone structure, limiting their commercial use.

Table 1. Imide type polymers PI1–PI4

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Molecular Structure</th>
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<tbody>
<tr>
<td>PI1</td>
<td><img src="image1" alt="PI1 Structure" /></td>
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<tr>
<td>PI2</td>
<td><img src="image2" alt="PI2 Structure" /></td>
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<td>PI3</td>
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<tr>
<td>PI4</td>
<td><img src="image4" alt="PI4 Structure" /></td>
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In order to overcome these deficiencies, there are different strategies including the reduction of chain crystallinity or inter-molecular charge-transfer, by using of noncoplanar or alicyclic monomers and by the introduction of flexible segments into the polymer backbone [9, 10]. Introduction of aliphatic monomers as comonomers in polyimides causes enhancement of the flexibility and transparency, improvement of solubility and decreases the dielectric constant [11]. An alternate successful approach
involves the incorporation of pendant groups onto the rigid polyimide backbone [12]. The ability to incorporate highly polar groups at high concentrations and cooperative dipole motion can generate an amorphous polymer with a large dielectric relaxation strength and piezoelectric response. Therefore, we have synthesized soluble imide type polymers containing ether linkages, aliphatic sequences or high polar pendant groups (Table 1). A study of their thermal behavior and their capability to be processed into thin films was performed. Also, the metal complexation ability of some carboxy-functionalized N-phenylmaleimide compounds was investigated.

2. Synthesis of the monomers

2,6-bis(m-amino-phenoxy)benzonitrile, an aromatic diamine, was prepared by the reaction of \( m \)-aminophenol with 2,6-dichlorobenzonitrile in N-methylpyrrolidinone (NMP) in the presence potassium carbonate, according to a published procedure [13]. It was recrystallized from a mixture of ethanol with water, or DMF with water. M.p.: 210–213\(^\circ\)C.

IR (KBr, cm\(^{-1}\)): 3450, 3360 (NH\(_2\)), 3060 (CH aromatic), 2230 (CN), 1620 (NH), 1600 (C=C aromatic), 1240 (ether). \(^1\)H-NMR (DMSO-d\(_6\), ppm): 7.2 (3H, m), 6.8 (2H, s), 6.65 (2H, s), 6.50 (2H, s), 5.10 (NH\(_2\)).

N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI) was prepared according to a known procedure [14] by the reaction of maleic anhydride and \( p \)-aminosalicylic acid. The resulting N-(3-hydroxy-4-carboxy-phenyl)-maleamic acid was treated with acetic anhydride, triethylamine (TEA) and sodium acetate to perform the imidization. The product was reprecipitated from ether / \( n \)-hexane. M.p. 93–95\(^\circ\)C. IR (KBr, cm\(^{-1}\)): 3105 (CH\(_2\)); 2900-3300 (COOH); 1780, 1720 (C=O imide I); 1380, 1410 (C=O imide II); 1165 (C=O imide III); 680-710 (imide IV); 1755, 1265 (C=O ester); 1270, 1070 (C-O-C ester). \(^1\)H-NMR (DMSO-d\(_6\), ppm): 12.68 (1H, s, COOH); 7.95-7.10 (3H, m, Ar-H); 7.03 (2H, s, vinyl); 2.23 (3H, s, -CH\(_3\)).

Epiclon, which is 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, and oxydiphthalic anhydride were provided by commercial sources and were purified by recrystallization from acetic anhydride.

3. Synthesis of the polymers

Synthesis of the polymers PI1-PI3

Equimolar amounts of Epiclon and 4-(\( p \)-amino-phenoxy)-aniline or 1,4-bis(\( p \)-amino-phenoxy)benzene, respectively (scheme 1a) or oxydiphthalic dianhydride and 2,6-bis(\( m \)-amino-phenoxy)benzonitrile (scheme 1b) have been used to obtain the polyimides PI1-PI3 (Table 1). The polycondensation reactions took place in NMP under anhydrous conditions and nitrogen atmosphere. The resulting viscous solution of polyamidic acid was stirred at room temperature for 1-2 h, then it was heated at 185–200\(^\circ\)C for 2–3 h, for cyclization to the imide structure. The water resulting from the cyclization process was eliminated with a slow stream of nitrogen. Small parts
of polymer solutions PI have been cast onto glass plates to check the film forming ability. The rest of solution was poured into water to precipitate the solid polymer.

### Synthesis of the polymer PI4

Poly[N-(3-acetoxy-4-carboxy-phenyl)-maleimide] (PACPMI) was obtained by radical polymerization of the corresponding monomer, N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI), in tetrahydrofurane (THF) in the presence of N,N′-azobisizo-butyronitrile (AIBN) as a radical initiator. The composition was determined by elemental analysis [14]. The complex of this polymaleimide with cooper was then prepared by using cooper (II) acetate and PACPMI in a molar ratio 1.12:1 reported to the functional groups, which were separately dissolved in methanol in concentrations of 0.05 mol/L and were mixed by stirring. The colour of the reaction mixture quickly modified depending on the involved metal, and a solid product separated. The reaction mixture was stirred for about 2.5 h at room temperature. Then, the solid was filtered, washed with water and methanol and dried first in air stream and then in vacuum at about 70°C (Scheme 2).

### 4. Results and discussion

Polyimides PI1-PI3 were obtained by solution polycondensation of aromatic diamines with two type of dianhydrides: an alicyclic one, namely Epiclon and an aromatic one, oxidiphthalic dianhydride. The polycondensations took place in NMP, under anhydrous conditions and nitrogen atmosphere (Scheme 1).
The polymers were identified through IR spectroscopy. Characteristic absorptions appeared for imidic ring at 1780 cm$^{-1}$. The absorption peaks at 1230 cm$^{-1}$ were attributed to the aromatic ether Ar-O-Ar (Fig. 1a).

The metal complexation ability of some carboxy-functionalized maleimide structures was also studied. Thus, N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI) and poly[N-(3-acetoxy-4-carboxy-phenyl)-maleimide] (PACPMI) were prepared and complexed with a transition metal, Cu$^{2+}$ (Scheme 2).


The formation of complex which separated as precipitate from the reaction mixture was confirmed by elemental and spectral analyses. It is difficult to verify by IR analysis the participation of the ester groups of the ACPMI and PACPMI in metal coordination because the characteristic band of ester group is overlapped with imide bands, in the range 1680–1780 cm$^{-1}$. No significant displacements of the other C=O (1190 cm$^{-1}$) and C-O-C (1090 cm$^{-1}$) ester groups are visible (Fig. 1b). Otherwise, based on the insolubility of the reaction product we can assume that the formation of the chelate polymer of salt type is favorized. The absorption band in the range of 3300–3500 cm$^{-1}$ reveals the presence of water, either as lattice or in coordination sphere.

The thermal stability of the cooper complex PI4 was evaluated by thermogravimetry. The presence of water was also evidenced in TGA curves (Figure 2) which showed weight losses in the range of 100–200°C assigned both to the loss of crystallization water (100–150°C) and coordination water (150–200°C) removal [14].

The thermal behavior of the polyimides PI1-PI3 was evaluated by thermogravimetric analysis and differential scanning calorimetry (table1). The polymers did not show significant weight loss below 300°C. They began to decompose in the range of 280°C–438°C and showed 10% weight loss in the range of 341°C–470°C (Table 1). One can assume that the degradation process could begin in the aliphatic segment of the backbone and then propagates to the entire structure. No significant weight loss was observed up to 430°C for PI3 (Fig. 3).
Fig. 1. a) IR spectra of the polyimides PI 1 and PI 3; b) Comparative IR spectra of PACPMI and its copper complex PI4.
Therefore, the polyimides PI1 to PI3 exhibited high thermal stability. The values of their glass transition temperature, $T_g$, is in the range of 203–275°C (Table 2).
Table 2. Properties of polyimides PI1, PI2 and PI3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ar</th>
<th>Mn (g/mol)</th>
<th>IDT&lt;sup&gt;a&lt;/sup&gt; (°C)</th>
<th>T&lt;sub&gt;10&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI1</td>
<td></td>
<td>48200</td>
<td>281</td>
<td>341</td>
<td>275</td>
</tr>
<tr>
<td>PI2</td>
<td></td>
<td>75000</td>
<td>280</td>
<td>368</td>
<td>230</td>
</tr>
<tr>
<td>PI3</td>
<td></td>
<td>84700</td>
<td>438</td>
<td>470</td>
<td>203</td>
</tr>
</tbody>
</table>

<sup>a</sup>Temperature of 5% weight loss in TGA curves;  
<sup>b</sup>Temperature of 10% weight loss in TGA curves;  
<sup>c</sup>Glass transition temperature determined from DSC curves.

These polyimides exhibited good solubility in polar aprotic solvents such as NMP, DMF and DMA and the solutions gave flexible, tough, thin films. Their good solubility is due to the presence of flexible and assymmetrical structure of Epiclon segment as well as the ether bridge, which lead to more flexible shapes of the macromolecular chains. Thus, it is prevented the strong packing through hydrogen bonds and it is facilitated the diffusion of small molecules of solvent (Fig. 4) [15].

![Model molecules of polyimide PI 3.](image)

5. Conclusions

Soluble polyimides containing flexible assymmetrical Epiclon units, nitrile pendant groups and ether bridges were prepared by polycondensation at high tempera-
ture. These polymers are soluble in polar aprotic solvents and can be cast into thin and very thin films from such solutions. The polyimides $\text{PI1-PI3}$ show high thermal stability with decomposition temperature being above $300^{\circ}C$ and glass transition in the range of $203-275^{\circ}C$. $\text{N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI)}$ and poly[$\text{N-(3-acetoxy-4-carboxy-phenyl)-maleimide} (\text{PACPMI})$ have been used for complexation with transition metals, such as cooper. The copper complex, $\text{PI4}$, based on the poly[$\text{N-(3-acetoxy-4-carboxy-phenyl)-maleimide}$. was insoluble in common organic solvents while the corresponding monomer complex was easily soluble. The films prepared from these polymers had a strong adhesion to glass and silicone substrates. These characteristics make the present polymers potential candidates for applications as high performance materials.

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References


