MODIFIED AROMATIC POLYIMIDES WITH FLEXIBLE GROUPS

Irina BACOȘCA* a, Elena HAMCIUC a, Maria BRUMĂ a and Marta SZESZTAY b

a “Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Vodă 41 A, Iași, Roumania
b Chemical Research Center, Pusztaszeri str. 59-67, Budapest H - 1525, Hungary

Received May 18, 2009

A series of aromatic polyimides has been synthesized by solution polycondensation of 2,6-bis(4-aminophenoxy)benzonitrile with certain aromatic dianhydrides incorporating flexible units, such as ether, carbonyl or hexafluoroisopropylidene. The polyimides were easily soluble in polar organic solvents, such as N-methylpyrrolidinone, N,N-dimethylacetamide and N,N-dimethylformamide, and some of them exhibited remarkable film forming ability. All the polymers showed high thermal stability, with decomposition temperature above 400°C and glass transition above 200°C.

INTRODUCTION

Polyimides are well-known engineering plastics, offering excellent thermal, mechanical, dielectric and optical properties, along with good chemical resistance and high dimensional stability. Owing to these qualities, polyimides have been used widely in the microelectronics, film, adhesive, and membrane industries.1–3 Given the solubility of the polyamidic acid precursors they can be cast into films and thermally converted to polyimides. There are some drawbacks of the polyamidic acid approach: they are instable at room temperature and must be stored at a lower temperature, and water released during imidization can create voids in the material. Most commercial polyimides are usually infusible and insoluble in common organic solvents which have arised limits on their applications in expensive goods.4,5

The increasing demands to improve the processability have stimulated extensive research on developing new soluble polyimides that can be processed in imide form without tedious curing sequences and high temperature involved. Typical approaches include the introduction of flexible or kinked linkages,6,7 bulky substituents,8–10 noncoplanar structures,11,12 and spiro-skeletons13 into the polymer backbone. It has been generally recognized that aromatic ether linkages inserted into the chains of the polymers provide them a significant lower energy of internal rotation. In general, such a structural modification leads to lower glass transition and crystalline melting temperatures as well as significant improvement of solubility and other processing characteristics preserving the other advantageous polymer properties.14

Recently, the research of some polyimides containing pendent polar groups led to the development of promising high temperature piezoelectric materials. Up to now, however, the piezoelectric properties of polyimides have been by one order of magnitude lower than those required by practical use.15

In this article we present the synthesis of some aromatic polyimides by solution polycondensation reaction of an aromatic diamine having cyano group and two ether units with different aromatic dianhydrides incorporating flexible units, such as ether, carbonyl or hexafluoroisopropylidene. The properties of these polymers, such as solubility, inherent viscosity, thermal stability, glass transition temperature, film forming ability and their quality have been studied.
RESULTS AND DISCUSSION

Aromatic diamine I, 2,6-bis(m-aminophenoxy)benzonitrile, was prepared by the reaction of m-aminophenol with 2,6-dichlorobenzonitrile in N,N-dimethylacetamide (DMAc) with potassium carbonate, according to a published procedure (Figure 1).\textsuperscript{16}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {H2N-\textcolor{red}{O} \textcolor{blue}{C}-\textcolor{red}{O}-\textcolor{blue}{N}-\textcolor{red}{H}2\text{N}};
\end{tikzpicture}
\end{center}

\textit{Fig. 1 – Structure of 2,6-bis(m-aminophenoxy)benzonitrile I.}

The dianhydrides II, containing flexible groups such as ether, carbonyl or hexafluoroisopropilidene, have been provided by commercial sources and purified by recrystallization from acetic anhydride. Figure 2 presents the structures of the dianhydrides.

The polyimides were prepared by solution polycondensation reaction of equimolar amounts of the aromatic diamine I with aromatic dianhydrides II, in NMP as a solvent, at high temperature. The reaction was carried out under stirring in inert atmosphere. The intermediate polyamidic acid resulting in the first step (scheme 1) was not isolated.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {H2N-\textcolor{red}{O} \textcolor{blue}{C}-\textcolor{red}{O}-\textcolor{blue}{N}-\textcolor{red}{H}2\text{N}};
\end{tikzpicture}
\end{center}

\textit{Fig. 2 – Structure of the dianhydride II.}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {H2N-\textcolor{red}{O} \textcolor{blue}{C}-\textcolor{red}{O}-\textcolor{blue}{N}-\textcolor{red}{H}2\text{N}};
\end{tikzpicture}
\end{center}

\textit{Scheme 1 – Preparation of the polymers III and IV.}

The structure of polymers was established by FTIR spectroscopy. Thus, the conversion of polyamidic acid to the fully cyclized polyimide was confirmed by the disappearance of the amidic bands. Figure 3 shows the FTIR spectra of polyamidic acid IIIb and the corresponding polyimide.
**Modified aromatic polyimides**

**IVb**, as an example. In all FTIR spectra of polymers **IV** strong bands appearing at 1780 cm\(^{-1}\) and 1730 cm\(^{-1}\) were assigned to symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide rings. Absorption band at 1380 cm\(^{-1}\) is due to C–N stretching of imide rings, and absorption band at 730 cm\(^{-1}\) due to imide ring deformation. The absorption peak at 1230 cm\(^{-1}\) is attributed to the aromatic ether Ar-O-Ar. All polymers exhibit an absorption band at 2220 cm\(^{-1}\) due to the presence of CN groups. Polymers **IIIb** and **IVb** present characteristic absorption bands at 1180 and 1210 cm\(^{-1}\) due to hexafluoroisopropylidene (6F) groups.

The cyclization of polyamidic acids to the corresponding imide structures was also evidenced by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA of the polyamidic acids showed a first weight loss at about 120°C due to the evolution of absorbed water, a second weight loss in the range of 130-230°C due to the evolution of water resulting from the thermal cyclization to imide structure and a third weight loss above 400°C due to the degradation of the resulting polyimide.

The DSC curves of the polyamidic acids **III** exhibited a broad endotherm at about 100°C due to the evolution of absorbed water. All the samples showed an endotherm just above 190°C. According to thermogravimetric analyses, the polyamidic acid underwent thermal cyclization in the same range of the DSC endotherm.

![Fig. 3 – FTIR spectra of polyamidic acid IIIb and corresponding polyimide IVb.](image)

The polyimides **IV** are soluble in polar organic solvents such as *N*-methylpyrrolidinone, dimethylsulfoxide or dimethylformamide, except polymer **IVe**, based on a dianhydride having no flexible groups, which precipitated during cyclization reaction. The polyimide **IVb** containing 6F groups was also soluble in less polar solvents like chloroform and tetrahydrofuran. The good solubility of these polymers is explained by the structural modification, the flexible bridges such as ether, carbonyl, hexafluoroisopropylidene, cyano, disturbing the packing of the polymers and making the shape of the respective macromolecules to be far from a linear rigid rod characteristic to conventional polyimides, as can be seen in figure 4. The disturbed packing of macromolecular chains facilitates the diffusion of small molecules of solvents between the polymer chains which leads to better solubility. Their good solubility allowed the imidization process to be performed in solution so that the final polymers were obtained as imidized products, which is more convenient than using polyamidic acids.

The inherent viscosity of the polymers, in NMP was in the range of 0.14-0.38 dL/g (Table 1). The molecular weights of the polymers were estimated by GPC according to universal calibration. The data of estimated molecular weights (Table 2) show a fairly high molecular weight of polymer **IVd**, while those of the other two polymers, **IVa** and **IVb** are quite low. All these values correlate well with the data obtained for inherent viscosity. Thus the polymer **IVd**
shows the highest inherent viscosity (0.38 dL/g). At the same time, the polymers show a narrow distribution of molecular weight as indicated by the value of Mw/Mn ranging between 1.2 and 2.2. Figure 5 presents the molecular weight distribution curves of polymers IIIb and IVb.

![Model molecule of polymer IVc](image)

**Table 1**

Solubility and inherent viscosity of polymers III and IV

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>NMP</th>
<th>DMF</th>
<th>DMSO</th>
<th>THF</th>
<th>CHCl₃</th>
<th>Py</th>
<th>ηinh</th>
<th>dL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIIa</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>0.183</td>
<td></td>
</tr>
<tr>
<td>IIIb</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>0.183</td>
<td></td>
</tr>
<tr>
<td>IIIc</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>0.180</td>
<td></td>
</tr>
<tr>
<td>IIId</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>0.251</td>
<td></td>
</tr>
<tr>
<td>IIIe</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>0.193</td>
<td></td>
</tr>
<tr>
<td>IVa</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>0.259</td>
<td></td>
</tr>
<tr>
<td>IVb</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>0.173</td>
<td></td>
</tr>
<tr>
<td>IVc</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>0.139</td>
<td></td>
</tr>
<tr>
<td>IVd</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>0.380</td>
<td></td>
</tr>
<tr>
<td>IVe</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

ηinh = inherent viscosity (determined in NMP solution at 20 °C, at a concentration of 0.5 g/dL); ++ = soluble at room temperature; + = soluble upon warming; - = insoluble.

**Table 2**

Molecular weights for polyimides IV

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mn, g/mol</th>
<th>Mw, g/mol</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVa</td>
<td>48 000</td>
<td>59 600</td>
<td>1.2</td>
</tr>
<tr>
<td>IVb</td>
<td>10 000</td>
<td>20 000</td>
<td>2.0</td>
</tr>
<tr>
<td>IVd</td>
<td>85 000</td>
<td>189 000</td>
<td>2.2</td>
</tr>
</tbody>
</table>

![Molecular weight distribution of polymers IIIb (---) and IVb (---)](image)
The thermal stability of the polyimides \textbf{IV} was investigated by thermogravimetric analysis. All polymers exhibited high thermal stability, with insignificant weight loss up to 440°C. They start to decompose in the range of 438-520°C as evidenced by the temperature of 5% weight loss (T_5); the temperature of 10% weight loss (T_{10}) was in the range of 470-560°C (Table 3). The thermal behaviour of these polymers is similar to that of related polyimides without cyano groups based on benzophenonetetra-carboxylic dianhydride, 4,4’-oxydiphthalic anhydride and hexafluoroisopropylidene diphthalic dianhydride.\textsuperscript{17,18} The polymer \textbf{IVe} based on biphenyltetra- carboxylic dianhydride exhibited the highest thermal stability, having T_5 = 520°C and T_{10} = 560°C. It can be observed that there is a large interval between the glass transition and decomposition temperatures which makes these polymers attractive for thermo-forming processing.

All polyimides except polymer \textbf{IVe} possess film-forming ability. Their solutions in NMP having a concentration of about 10-14% were cast onto glass substrates and dried to yield free standing films having a thickness of 30-50 µm. Dynamic mechanical analysis (DMA) of free standing films made from polyamidic acids and the corresponding polyimides was performed to get more information about the imidization reaction and of the phenomena which take place during the heating process. As an example, two typical DMA curves are shown in figure 6.

\begin{table}[ht]
\centering
\caption{Thermal properties of polymers \textbf{IV}}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Polymer & T_5, °C & T_{10}, °C & W_{500}, % & T_{max}, °C & T_g, °C \\
\hline
\textbf{IVa} & 512 & 557 & 4 & 615 & 226 \\
\textbf{IVb} & 491 & 550 & 4.8 & 609 & 235 \\
\textbf{IVc} & 520 & 560 & 4.4 & 602 & 232 \\
\textbf{IVd} & 438 & 470 & 17 & 541 & 203 \\
\textbf{IVe} & 445 & 512 & 7.8 & 580 & 263 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{15} T_5 = temperature of 5\% weight loss; \textsuperscript{16} T_{10} = temperature of 10\% weight loss; \textsuperscript{17} W_{500} = weight loss at 500 °C; \textsuperscript{18} T_{max} = temperature of maximum decomposition; \textsuperscript{19} T_g = glass transition temperature.

Figure 6a presents the storage modulus (E’) and the loss modulus (E’’) and figure 6b the loss factor tangent (tan δ) dependences on temperatures for films of polyamidic acid \textbf{IIIc} and polyimide \textbf{IVc}. The drops in E’ curves and the peaks on E’’ and tan δ indicate the physical transitions which take place in the structure of the polymers. At low temperatures the polymers show a plateau in the E’ dependence, above 10^9 Pa, which is typical for the glassy structures, a region where the macromolecules are in the “frozen” state. The value of the storage modulus in the glassy region of the polyimide \textbf{IVc} is higher than that of the polyamidic acid \textbf{IIIc}, which demonstrates that the chains lose flexibility through the imidization process. The peak maximum of the polyamidic acid from the E’’ curve has a value of about 170°C showing the beginning of the glass transition temperature (T_g) for polyamidic acid \textbf{IIIc}; this value can be also found on the tan δ curve (Figure 6b). The glass transition
temperature of the polyimide structure IVc (216°C) is higher than that of polyamidic acid IIIc, value which can also be found in the E' and tanδ curves.

Thin films were deposited by spin-coating technique on glass plates using 1% dilute polymer solutions. The quality of these films was studied by atomic force microscopy (AFM). All the films prepared showed a smooth surface, practically with no defects. The root mean square roughness is in the range of 5-10 Å, close to that of the substrate. A typical AFM image is shown in Figure 7.

**EXPERIMENTAL**

**Preparation of the monomer**

Aromatic diamine I, 2,6-bis(m-aminophenoxy)benzonitrile, was prepared by the reaction of m-aminophenol with 2,6-dichlorobenzonitrile in N,N-dimethylacetamide (DMAc) with potassium carbonate, according to a published procedure. It was recrystallized from a mixture of ethanol with water. M.p.: 136-138°C. The diamine structure was confirmed by FTIR and 1H NMR spectroscopy. The FTIR spectrum of the diamine presented characteristic bands of absorption at 3469 and 3380 cm⁻¹ due to the presence of the amine groups, at 3053 cm⁻¹ the band of the C-H aromatic linkage, at 2232 cm⁻¹ the characteristic band of the CN stretching and at 1243 cm⁻¹ the band for the aromatic ether Ar-O-Ar. 1H NMR spectrum of the diamine I showed characteristic peaks at 5.3 ppm due to protons of amine groups and at 6.23-7.64 ppm due to aromatic protons.

**Preparation of the polyimides**

The polyimides were prepared by solution polycondensation reaction of equimolar amounts of aromatic diamine I, with an aromatic dianhydride II, in NMP as a solvent, at high temperature. Thus, the solid dianhydride was added to the solution of diamine in NMP at room temperature and the reaction was run for 5 h, giving the corresponding polyamidic acid. About 4 mL of the resulting polyamic acid solution was precipitated into 50 mL of water. A fibrous product resulted which was thoroughly washed with 100 mL water, filtered and dried under vacuum. The second step was performed by heating the polyamic acid solution at 185-190°C for 6 h. The final polyimides IV were isolated by precipitation in water. The solid product was filtered, washed with water under stirring and dried at 120°C for 6 h, 180°C for 1 h and at 200°C for 1 h.

**Measurements**

Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices) apparatus with no correction. Inherent viscosities were determined at 20°C for solutions of polymers (0.5 g/dL) in NMP, using an Ubbelohde viscometer.

The molecular weight distribution (MWD) was determined by GPC using a Waters Millipore chromatograph equipped with a Water 515 pump, UltraStyragel columns and a Viscotek parallel differential refractometer/viscometer detector. Universal calibration was made with polystyrene standards. The mobile phase was DMF with a flow rate of 1.5 mL/min. Measurements were carried out at room temperature.

The FTIR spectra were recorded on a Perkin-Elmer spectrometer using KBr pellets.

1H NMR spectra were recorded on a Varian EM-390 Spectrometer, at 90 MHz, for solutions in deuterated dimethylsulfoxide (DMSO-d₆).

Thermogravimetric analysis (TGA) was performed on a MOM–type Derivatograph made in Budapest, Hungary, operating in air at a heating rate of 12°C/min.

The glass transition temperature (Tg) was measured on a Mettler DSC 12E apparatus in nitrogen with a heating rate of 20°C/min. The mid-point of the inflection curve resulting from the typical second heating cycle was considered as the Tg of polymers.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 4.

Dynamic mechanical analysis was performed on a Perkin-Elmer Diamond device equipped with a standard tension attachment. The run conditions were conducted at a frequency of 1 Hz and a heating rate of 3°C/min from 0 to 300°C using film samples of 10 × 10 × 0.04 mm.

The quality of the films was investigated by AFM. The images were taken in air, on a SPM SOLVER Pro-M instrument.

**CONCLUSIONS**

A series of polyimides with flexible groups was prepared by polycondensation at high temperature using an aromatic diamine having ether and cyano...
Modified aromatic polyimides 1029

groups and different aromatic dianhydrides containing flexible moieties. These polymers are soluble in polar aprotic solvents, and can be cast into thin films from such solutions giving smooth films with no defects. The good solubility of the polymers is due to the improved flexibility of the macromolecular chains. The polyimides show high thermal stability with decomposition temperature above 440ºC and glass transition in the range of 226-263ºC.

Acknowledgements: We thank Mariana Cristea and Iuliana Stoica from “Petru Poni” Institute of Macromolecular Chemistry, Iași, Roumania for DMA and AFM analyses, respectively. The financial support provided by the Roumanian Ministry of Education and Research through the Program PN II, Project 11008/2007, is gratefully acknowledged.

REFERENCES
