

# Synthesis and Characterization of Polyimides Containing 4,4'-Hexafluoroisopropylidene-Bisphthalic

Daniel Liu Chun Hung, Tong-Ing Ho, Der-Jang Liaw and Been-Yang Liaw

**Abstract:** This paper presents the synthesis and characterization of polyimides, which contain a 4,4'-hexafluoroisopropylidene-bisphthalic anhydride (6FDA) unit in the backbone. These polyimides are a result of the use of the traditional method of "one step". The reactions occur between equimolar of a dianhydride and an aromatic diamine in presence of the solvent dimethylacetamide (DMAc), then cyclo-dehydrated by adding the acetic anhydride and pyridine. In this work, the 6FDA was used as the dianhydride and four different diamines were investigated: 3,3',5,5'-Tetramethyl-2,2-bis[4-(4-aminophenoxy) phenyl] propane; 2,2-bis[4-(4-aminophenoxy)-phenyl] hexafluoropropane; 1,3-bis(4-aminophenoxy)benzene and 2,2'-dimethyl-4,4'-bis(4-aminophenoxy)biphenyl. The four polyimides (PA, PB, PC and PD) were characterized by tensile strength, infrared, inherent viscosity, Differential Scanning Calorimeter (DSC) to get the glassy transition temperature (T<sub>g</sub>) and Gel Permeation Chromatograph (GPC) to obtain the average molecular weight (M<sub>n</sub>).

**Keyword:** *Synthesis, polyimides, dianhydride, diamine, characterization, 6FDA*

## Introduction

Various applications of polymeric material are specifically needed in rustic environments, mainly at high temperature, because the polymers present manifold inherent properties such as chemical inert, elasticity, light weight, easy formability, low permeability and others. In addition, polymeric materials are also commonly required to be thermal and mechanical resistant as possible. For example, in space vehicles polymers have been used under radiation and temperature changes in outer space. Many other applications of polymeric material can be seen, such as components of cable insulation,

seals and gaskets, pipes, hoses, radiation shielding, coatings, electrical housings, structural components and many others<sup>[1]</sup>.

The changes of mechanical properties of polymers are strongly influenced by chemical structure of polymers mainly chemical composition and molecular configuration of polymers. These can provide the different mechanical behaviors among polymers. In particular, polymers containing aromatic rings in the main chain have received special attention, due to the presence of aromatic rings, which turn these polymers more resistant.

This paper presents the synthesis and characterization of polyimides containing 6FDA unit in

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the backbone, resulted from reactions between equimolar of a dianhydride and an aromatic diamine. In addition, aryl ether linkages inserted in aromatic polymer main chains allow to reduce the chain rigidity without great modification on thermal stability.

Aromatic polyimides are a class of polymers generally not processable by conventional thermoplastic or hot-melt techniques. However, polyimides are exceptionally thermally stable and have high glass transition temperatures. The polyimides are also resistant to the attack of common organic solvents<sup>[2]</sup>. In addition, it is well known that, in general, polyimides present high thermal stability and mechanic resistance<sup>[3-5]</sup>.

Several authors<sup>[6-8]</sup> have shown that the incorporation of 6FDA in aromatic ether linkages polymer main chain leads generally the polymer to have lower glass transition temperature and crystalline melting temperature, as well as significant improvement in solubility without great modification in thermal stability.

## Experimental

### Materials

N,N-Dimethylacetamide (DMAc), N,N-Dimethylformamide (DMF) and pyridine were dehydrated by  $\text{CaH}_2$  overnight and then distilled under reduced pressure. Acetic anhydride was purchased from Merck and was used as received. 4,4'-hexafluoroisopropylidene bisphthalic anhydride (6FDA) was recrystallized from acetic anhydride. 2,2-bis[4-(4-aminophenoxy)phenyl]propane and 2,2-Bis[4-(4-aminophenoxy)-phenyl]hexafluoropropane were supplied from Wakayama Seika Co. Ltd and used without further purification. 1,3-bis(4-aminophenoxy)benzene was purchased from CHRISKEV and used as received. 2,2'-dimethyl-4,4'-bis(4-amino-phenoxy)biphenyl was synthesized and purified according to the method reported<sup>[8]</sup>.

### Polymerization

To a 100 mL of three necked flask equipped with a magnetic stirrer, a reflux condenser, thermometer and argon inlet, was added 1.261g (5mmol) of diamine (1,3-bis(4-aminophenoxy)benzene) and 10 mL of solvent DMAc. Under argon atmosphere, 90%wt of amount equimolar (2.220g, 5 mmol) of

dianhydride (6FDA) was added into the reaction mixture, with vigorous stirring. Ten minutes later, 50%wt of dianhydride was added into the reactor, and finally after another 10 minutes the rest of dianhydride was added. During this time interval, an increase of the viscosity of the solution was observed. In order to facilitate the stirring of the solution, DMAc solvent was added such much as necessary. Remain the reaction at room temperature during 3 hours. During this period polyamic acid is formed, as shown in Figure 1. To the reaction mixture 2 mL of pyridine and 4 mL of acetic anhydride were added in order to cycle-dehydrate the amic acid. The reaction mixture was maintained at room temperature for one hour, then heated up to 120°C for another two hours. The reaction mixture was trickled into excess methanol with vigorous stirring. The white precipitate was collected and washed thoroughly with hot water and methanol. Subsequently, it was dried in an oven at 100°C. In order to form polymer films, the polymer was dissolved in DMAc (0.5g of polymer/10mL of solvent) forming a yellow solution, then the solution was poured in a plan surface and dried in a vacuum oven at 200°C for several hours.

### Measurements

IR spectra were recorded within the range of 4000-400  $\text{cm}^{-1}$  for the polymers in a JASCO IR-700 spectrometer. The inherent viscosities of the all polymers were measured using Ubbelohde viscometer at 30°C. Differential scanning calorimetry analysis was carried out in a differential scanning calorimeter (Du Pont 2100) at a heating rate of 20°C  $\text{min}^{-1}$ . Molecular weights of polyimides were measured by GPC, using 0.1mg of polymer in a 1mL of Tetrahydrofuran (THF) solution as an eluent, and after calibration with the standard polystyrenes. Tensile properties were determined from stress-strain curves obtained from a Orientec Tensilon device with a load cell of 10 kgf. A gauge of 3 cm and a strain rate of 2  $\text{cm}\cdot\text{min}^{-1}$  were used in this study. Measurements were performed at room temperature with film specimens of 0.5 cm wide, 6 cm long and thickness of 1 mm.

## Results and Discussion

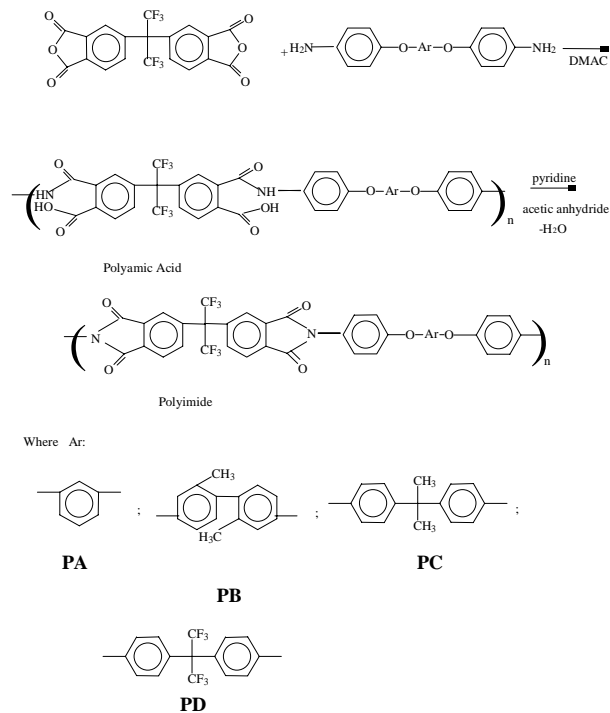
Four polyimides were studied and obtained by the traditional method of "one step", as shown in

**Table 1.** Tensile Strength of polyimides.

Polymer	TS (MPa)	EL (%)	MO (GPa)
PA	90	5.5	2.4
PB	97	6.4	2.4
PC	62	5.4	1.5
PD	75	7.5	1.6

Figure 1. This reaction occurs between equimolar of diamine and dianhydride in presence of the solvent (DMAc) and then cyclo-dehydrated by adding the acetic anhydride and pyridine.

Table 1 shows the measured data of tensile strength (TS), elongation (EL) and modulus (MO) of polyimides. Each value is an average of five measurements. One can observe the different property values among polyimides, indicating the influence of distinct structures of polymers. The polymer PB has shown a higher strength than the other polymers. The incorporation of 2,2'-disubstituted biphenylene in a para-linked polymer chain provides the phenyl rings that are forced by the 2,2'-disubstitution into a noncoplanar conformation, reducing the force of intermolecular. Even so, this force reduction is not enough to gain the effect due to stereoregularity. The polymers PC and PD present structural character lightly branched, which impedes the approach of

**Figure 1.** Illustration of polymerization of Polyimides

other molecules. The presence of fluor atoms in polymer PD leads the appearance in the molecule of polymer a attraction force, and this force is a consequence of strong difference of electronegative between carbon atom and the referred atom of fluor, resulting in a region dipolar in the chain.

Table 2 shows the values of glassy transition temperature (Tg), inherent viscosity ( $\eta_{inh}$ ) and average molecular weight (Mn). It is well known that the presence of aromatic rings contributes to polymers to thermal strength of polymers. Through these data of Tg, the polymer PA presents the lowest Tg (246°C), indicating to be less thermal resistant than the other polymers and presenting more part amorphous. Note that this PA has less concentration of aromatic rings in the molecule. However, studied polyimides which presented Tgs nearby the 250°C, comparatively with another engineering polymers, polyamides for instance present Tg less than 100°C, so they are considered good values.

As shown in tensile strength, the viscosity of polyimides PA and PB are more strength and presented higher viscosity property.

The use of gel permeation chromatography (GPC) allows to determine quickly the distribution of polymer molecular weight and the number-average molecular weight (Mn) of studied polyimides.

One observe that molecular weights are different among different chemical structures of polymers. Once the polymers were degraded, it reflects directly in polymer properties this fact confirms the behavior of mechanical and thermal properties above presented.

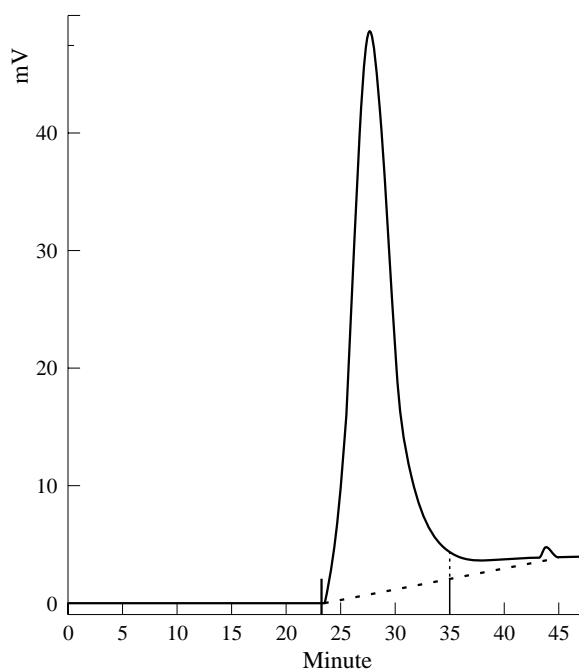
Figure 2 shows a typical graphic of molecular weight distribution of polyimide PA.

It is well known that the dissolved polymer molecules flow past the porous beads, they can diffuse into the internal pore structure of the gel to an extent depending on their size and pore-size

**Table 2.** Characteristics of polyimides

Polymer	Tg (°C)	$\eta_{inh}$ (dL/g) <sup>a</sup>	Mn (10 <sup>4</sup> )
PA	246	1.20	5,2
PB	271	1.20	5,8
PC	258	0.92	4,3
PD	262	0.83	6,9

<sup>a</sup> In DMAc at 30°C, c=0.5g/dL



**Figure 2.** Curve of Molecular Weight Distribution of PA.

distribution of the gel. Larger molecules can enter only in a small fraction of the internal portion of the gel, or are completely excluded; smaller polymer molecules penetrate a larger fraction of the interior of the gel. Therefore, the larger molecules spend less time inside of the gel, and it flows faster through the column. Thus, the peaks of distribution curves of lower Mn are dislocated successively to longer time.

### Infrared results

The characterization of polyimides by IR is showed in Table 3. All the polymers studied present characteristic peaks of a typical polyimide. They present strong peaks of absorption near 1770 and 1720  $\text{cm}^{-1}$ , which correspond to asymmetric and symmetric stretching of carbonyl group of imide, respectively. The band near 1370  $\text{cm}^{-1}$  is attributed to the stretching of C-N (C-N-C) and near 1250  $\text{cm}^{-1}$  corresponds to the stretching of C-O-C.

Furthermore, the traditional bands of polyamic acid, intermediate product of synthesis of

**Table 3.** IR characterization of polyimides

Absortion peaks	Polymers			
	PA	PB	PC	PD
C=O(Imide ring)	1774, 1718	1774, 1718	1774, 1718	1775, 1722
C-N-C	1372	1372	1373	1375
C-O-C	1253	1233	1239	1243

polyimides, did not appear in the spectra, indicating the good formation of polyimides.

### Conclusion

The four polyimides were successfully synthesized in this work. IR spectra analysis showed all typical peaks of polyimides. All the studied polyimides presented good thermal strength with glassy transition temperatures (Tgs) varying between 246 and 271°C. The inherent viscosity varied from 0.83 to 1.2 g/dL, the tensile strength from 62 to 97 MPa and Mn varied from  $4.3 \times 10^4$  to  $6.9 \times 10^4$ . The polyimide PB shows more tensile strength and the highest Tg, indicating the incorporation of 2,2 dimethyl biphenylene, even with aim to reduce intermolecular force, the chemical structure, i.e., stereoregularity influences more significantly in mechanical properties of polymers.

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### References

1. Clough, R. - *Radiation-Resistant Polymers*, Encyclopedia of Polymer Science and Engineering, Vol. 13, p. 667 (1985).
2. Deanin, R. D. - *Polymer Structure Properties and Applications*, Cahners, Boston, Chap. 8, p. 457 (1972).
3. Wilson, M.; Stenzenberger, H. D. & Hergenrother, P. M. - *"Polyimides"*, Blackies & Son, Glasgow and London, (1990).
4. Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N., *Macromolecules* (1991).
5. Park, J. W.; Lee, M.; Lee, M. H.; Liu, J. W.; Kim, S. D.; Chang, J. Y.; Rhee, S. B.; *Macromolecules* 27, 3459 (1994).
6. Schmidt, W. and Guo, D. - *Makromol. Chem.*, 189, 2029 (1988).
7. Sinta, R.; Minns, R. A.; Gaudiana, R. A. & H. G. Rogers, *Macromolecules*, 20, 2374 (1987).
8. Liaw, D. J.; Liaw, B. Y. & Jeng, M. Q. - *Polymer*, 39, 1597 (1998).