

# Rapid synthesis of optically active poly(amide–imide)s by direct polycondensation of aromatic dicarboxylic acid with aromatic diamines

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Received 26 October 2001; received in revised form 20 February 2002; accepted 7 March 2002

## Abstract

4,4'-(Hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-*L*-leucine-*p*-amidobenzoic acid) (**2**) was prepared from the reaction of 4,4'-(hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-*L*-leucine) diacid chloride with *p*-aminobenzoic acid. The direct polycondensation reaction of monomer (**2**) with *p*-phenylenediamine (**2a**), 4,4'-diaminodiphenylsulfone (**2b**), 2,4-diaminotoluene (**2c**), 2,6-diaminopyridine (**2d**), *m*-phenylene diamine (**2e**), benzidine (**2f**), 4,4'-diaminodiphenylether (**2g**) and 4,4'-diaminodiphenyl methane (**2h**) was carried out in a medium consisting of triphenyl phosphite, *N*-methyl-2-pyrrolidone, pyridine, and calcium chloride. The homogeneous mixture was heated at 220 °C for 1 min under nitrogen. The resulting poly(amide–imide)s (PAIs) having inherent viscosities 0.27–0.78 dl/g were obtained in high yield and are optically active and thermally stable. All of the above polymers were fully characterized by IR spectroscopy, elemental analyses and specific rotation. Some structural characterization and physical properties of this new optically active PAIs are reported.

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**Keywords:** 4,4'-(Hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-*L*-leucine-*p*-amidobenzoic acid); Poly(amide–imide)s; Optically active polymers; Direct polycondensation; Thermally stable polymers

## 1. Introduction

Wholly aromatic polyamides (aramides) exhibit a number of useful properties such as high thermal stability, chemical resistance, and low flammability, and they have excellent mechanical properties as fibers [1,2]. However, the poor solubility and high softening or melting temperature caused by the high crystallinity and high stiffness of the polymer backbones lead to difficult processability of these aramides. The need for engineering plastics circumventing these problems recently increased. A successful approach commonly used to increase the processability of aramides is the introduction of flexible

links [3,4] or asymmetric units [5–7] into the aramid backbone.

In our earlier publications, we have synthesized optically active polymers by different methods [8–13], such as modification of polybutadiene with optically active substituted urazole group [8], Diels–Alder-ene reactions [9,10] and reaction of an optically active monomer with several diamines and diols via solution and microwave polymerization [11–13].

In our effort to develop easily processable high-performance polymers, the present work describes a successful synthesis of 4,4'-(hexafluoroisopropylidene) *N,N'*-bis(phthaloyl-*L*-leucine-*p*-amidobenzoic acid) and its use to prepare aramides by the polycondensation of this aromatic dicarboxylic acids with different aromatic diamines. We describe here the preparation and basic characterization of poly(amide–imide)s (PAIs) based on this new dicarboxylic acid.

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## 2. Experimental

### 2.1. Materials

All chemicals were purchased from Fluka Chemical Co., Aldrich Chemical Co. and Riedel-deHaen AG. 4,4'-(Hexafluoroisopropylidene)-bis(phthalic anhydride) was kindly obtained from Hoescht–Celanese as electronic grade material and was used as received. 4,4'-Diaminodiphenyl methane (**2h**) was purified by recrystallization from water. *p*-Phenylenediamine (**2a**), 2,4-diaminotoluene (**2c**), 2,6-diaminopyridine (**2d**), *m*-phenylene diamine (**2e**), benzidine (**2f**), and 4,4'-diaminodiphenylether (**2g**) were purified by sublimation. The other diamines were used as obtained without further purification. *N*-methyl pyrrolidine (NMP) and pyridine were distilled before use. Triphenyl phosphite (TPP) and calcium chloride were used as received.

### 3. Monomer synthesis

#### 3.1. 4,4'-(Hexafluoroisopropylidene)-bis(phthaloyl-*L*-leucine) diacid chloride (**1**)

4,4'-(Hexafluoroisopropylidene)-bis(phthaloyl-*L*-leucine) diacid chloride (**1**) was prepared by the condensation of *L*-leucine with 4,4'-(hexafluoroisopropylidene) bis(phthalic anhydride), followed by reaction with thionyl chloride, according to the previously reported procedure [11]. The yield of the diacid chloride **1** was 96.1%, m.p. = 118 °C and  $[\alpha]_{\text{D}}^{25} = -29.92^{\circ}$  (0.052 g in 10 ml *N,N*-dimethylformamide (DMF)).

#### 3.2. 4,4'-(Hexafluoroisopropylidene)-*N,N'*-bis(phthaloyl-*L*-leucine-*p*-amidobenzoic acid) (**2**)

Into a 25 ml round-bottomed flask fitted with a magnetic stirrer was placed a solution of 2 g ( $2.83 \times 10^{-3}$  mol) diacid chloride (**1**) in 5 ml DMF. The reaction mixture was cooled in an ice water bath. To this solution 0.78 g ( $5.65 \times 10^{-3}$  mol) *p*-aminobenzoic acid in 7 ml DMF was added dropwise. After the reagents had dissolved completely, the cooling bath was removed and the reaction was allowed to stir at room temperature for an overnight. Then it was heated at 120 °C on an oil bath for 8 h. The mixture was then cooled and poured into 100 ml of water. The precipitate was collected by filtration, washed thoroughly with water and dried at 80 °C for 10 h, to yield 2.20 g (85.8%) of monomer (**2**)  $T_{\text{dec}}$  239 °C;  $[\alpha]_{\text{D}}^{25} = -25.62^{\circ}$  (0.05 g in 10 ml DMF); IR (KBr): 3700–2150 (m, br), 1775 (s), 1715 (s, br), 1380 (m, br), 720 (s)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CHCl}_3$ , TMS):  $\delta$  1 (d, 12H), 1.28–1.83 (m, br, 2H), 1.83–2.7 (m, 4H), 5.1 (dd, 2H,  $J_1 = 7.2$  Hz,  $J_2 = 4.5$  Hz), 7.42–8.43 (m, br, 14H), 9.55 (br, 2H) ppm.

Elemental analysis: calculated for  $\text{C}_{45}\text{H}_{38}\text{N}_4\text{O}_{10}\text{F}_6$ , C (59.48%), H (4.21%), N (6.16%); found, C (57.7%), H (4.3%), N (5.1%); corrected, C (59.46%), H (4.29%), N (5.26%).

### 4. Polymer synthesis

A typical preparation of aromatic PAIs was as follows: 0.1 g ( $1.10 \times 10^{-4}$  mol) of diacid (**2**), 0.012 g ( $1.10 \times 10^{-4}$  mol) of diamine (**3a**) and 0.014 g ( $1.26 \times 10^{-4}$  mol) of calcium chloride were placed in a 10 ml round-bottomed flask and then added 0.2 ml NMP, 0.062 ml TPP, and 0.055 ml of pyridine. The mixture was heated at 220 °C for 1 min under nitrogen. The viscous reaction mixture was poured into 75 ml of methanol. The precipitated polymer was collected by filtration, and was dried at 80 °C for 15 h under vacuum to leave 0.106 g (98.2%) of polymer **4a**.

Other PAIs were synthesized by the above procedure.

#### 4.1. Polymer (**4a**)

IR (KBr): 3350 (m, br), 2960 (m), 1780 (s), 1720 (s, br), 1670 (s, br, sh), 1380 (s), 720 (m)  $\text{cm}^{-1}$ .

#### 4.2. Polymer (**4b**)

IR (KBr): 3340 (m, br), 2950 (m), 1780 (s), 1720 (s, br), 1670 (s, br, sh), 1595 (s), 1520 (s, br), 1380 (s), 1310 (m, br), 1105 (s), 720 (m)  $\text{cm}^{-1}$ .

#### 4.3. Polymer (**4c**)

IR (KBr): 3350 (m, br), 2960 (m), 1780 (s), 1720 (s, br), 1670 (s, br, sh), 1380 (s), 720 (m)  $\text{cm}^{-1}$ .

#### 4.4. Polymer (**4d**)

IR (KBr): 3400 (s, br), 2960 (m), 1780 (s), 1720 (s, br), 1670 (m, br, sh), 1380 (s), 720 (m)  $\text{cm}^{-1}$ .

#### 4.5. Polymer (**4e**)

IR (KBr): 3350 (m, br), 2960 (m), 1780 (s), 1720 (s, br), 1670 (s, br, sh), 1380 (m), 720 (m)  $\text{cm}^{-1}$ .

#### 4.6. Polymer (**4f**)

IR (KBr): 3340 (m, br), 2960 (m), 1780 (s), 1720 (s, br), 1670 (s, br, sh), 1375 (m), 718 (m)  $\text{cm}^{-1}$ .

#### 4.7. Polymer (**4g**)

IR (KBr): 3340 (m, br), 2950 (m), 1780 (s), 1720 (s, br), 1670 (m, br), 1380 (m), 720 (m)  $\text{cm}^{-1}$ .

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