

УДК 541.64

OPTICALLY ACTIVE POLY(AMIDE IMIDE)S

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The carboxyimides were prepared by the reaction of selected anhydrides (trimellitic, pyromellitic, benzophenone-3,3',4,4'-tetracarboxylic, bicyclo-[2,2,2]-octen-2-tetracarboxylic) with (α -amino acids: L-Ala, D-Ala, L-Val, L-Abu, L-Phe, L-Leu and L-Trp). These carboxyimides are for the first time synthesized and characterized. All the compounds gave NMR and IR spectra consistent with their assigned structures. Acid chlorides were prepared by refluxing these acids with thionyl chloride. The synthesized acids and acid chlorides were condensed with aromatic amines. Low molecular weight poly(amide imide)s were obtained.

Introduction

The optically active polymers are materials of great interest due to the introduction of chiral centers into polymer chain, which may cause some new physical properties. The introduction of chiral structural units into polyimide systems may play an important role in molecular arrangement. A very useful monomer in the synthesis of chiral poly(ester amide)s and poly(amide imide)s is trimellitic anhydride.

The purpose of this our work was to obtain optically active poly(amide imides) through introduction of the chiral carbon atom from amino acids to the main chain of the polymer.

Experimental

All the reagents were commercial products and were used without purification. The carboxyimides were prepared by the reaction of selected anhydrides: trimellitic (TDA), pyromellitic (PMDA), benzophenone-3,3',4,4'-tetracarboxylic (BTDA), bicyclo-[2,2,2]-octen-2-tetracarboxylic (BOTDA), and α -amino acids: L-alanine (L-Ala), D-alanine (D-Ala), L-valine (L-Val), L-2-aminobutyric acid (L-Abu), L-Phenylalanine (L-Phe), L-Leucine (L-Leu) and L-Tryptophane (L-Trp), (scheme 1). A flask was charged with 20 mmol of trimellitic anhydride or 10 mmol of dianhydrides, 20 mmol of α -amino acid and 50 ml of anhydrous acetic acid. The mixture was stirred at 120°C for 3-7 h. About half of the acetic acid was evaporated and a precipitate which formed upon cooling was filtered off, and purified by recrystallization.

In the synthesis of poly(amide imide)s, such diamines as 4,4'-diaminodiphenylmethane (MDA), 1,4-phenylenediamine (PPD), 4,4'-oxydianiline (ODA), 1,3-phenylenediamine (MPD), 2,3,5,6-tetramethyl-1,4-phenylenediamine (DAD) and 4',4''-(hexafluoroisopropylidene)bis(4-phenoxyaniline) (BDAF) were used.

Method 1 (scheme 2 and 3). Syntheses were carried out by the literature method [1]. Thionyl chloride (6.2 mmol) was added to 3 mmol of diimide-dicarboxylic acid, and the reaction mixture was stirred for 3.5 h. An excess of thionyl chloride was evaporated under vacuum. Solution of diamine (3 mmol) in 10 ml of DMF and 0.5 ml of pyridine was then added. Reaction was carried out in an ice-water bath for 3 h. The resulting mixture was rapidly poured, with stirring, into methanol. The precipitated polymer was washed with methanol, collected by filtration and dried under reduced pressure for 24 h.

Method 2 (scheme 4). According to the method reported in the literature [2], a mixture of 0.8 mmol of diimide-dicarboxylic acid, 0.8 mmol of diamine, 0.25 g calcium chloride, 0.8 ml of triphenyl phosphite, 0.7 ml pyridine, and 2.5 ml of NMP was heated with stirring at 100°C for 1 h. After addition of another 1 ml of NMP, the reaction was continued for another 1 h. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, producing a precipitate that was washed thoroughly with methanol, collected on a filter, and dried in vacuum. Product was then extracted with methanol in Soxhlet apparatus.

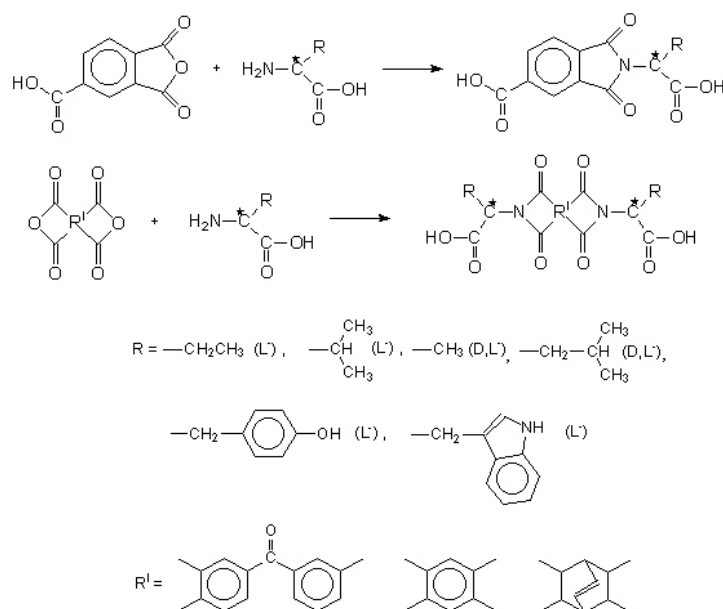
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Melting points were determined by using a Büchi B-540 capillary melting point apparatus. ^1H NMR spectra were taken on a Varian 200 MHz and Mercury 400 MHz spectrometers. IR spectra were recorded in the range $4000\text{-}600\text{ cm}^{-1}$.

Results

The diimide-dicarboxylic acids were prepared by condensation of the corresponding α -amino acids with the anhydride according the following scheme:



Scheme 1.

Products of the synthesis were crystallized from a proper solvent and their melting points were determined (Table 1). The structure of the products was confirmed by means ^1H NMR and IR spectroscopy.

Synthesis 1. ^1H NMR (DMSO- d_6 , δ in ppm): 0.87 (3H, t, methyl, $J=7.5$ Hz), 2.16 (2H, m, methylene, $J=7.5$ Hz), 4.7 (1H, q, methine), 8.0-8.4 (3H, m, aromatic) and 13.2-13.6 (2H, carboxylic); IR (KBr): 3486 cm^{-1} (-OH, carboxylic acid), 3075 cm^{-1} ($\text{C}_{\text{arom.}}\text{-H}$, stretching), 1775 cm^{-1} (C=O, asym. stretching), 1714 cm^{-1} (C=O, sym. stretching), 1382 cm^{-1} (C-N, stretching) and 739 cm^{-1} (C=O, bending).

Table 1. Melting points of obtained products

Synthesis	Anhydride	Amino acid	Recrystallization	M.p. [$^{\circ}\text{C}$]
1	TDA	L-Abu	MeOH:H ₂ O 7:3	192-196
2	TDA	L-Val	Hexane	183-186
3	PMDA	L-Abu	MeOH:H ₂ O 7:3	196-199
4	PMDA	L-Ala	MeOH:H ₂ O 7:3	293.5-296
5	PMDA	L-Val	MeOH:H ₂ O 7:3	263r.
6	TDA	D-Ala	Hexane	179-183
7	PMDA	D-Ala	MeOH:H ₂ O 7:3	293.5-296
8	BTDA	L-Ala	EtOH:H ₂ O 9:1	289-293 r.
9	BTDA	D-Ala	EtOH:H ₂ O 9:1	290-295 r.
10	TDA	L-Phe	EtOH	241-242
11	TDA	L-Leu	EtOH:H ₂ O	227-228
12	TDA	L-Trp	EtOH	145-147
13	BOTDA	L-Leu	EtOH	298-300

Synthesis 2. ^1H NMR (DMSO- d_6 , δ in ppm): 1.58-1.61 (6H, d, methyl, $J=7.2$ Hz), 4.7-4.8 (2H, q, methine, $J=7.2$ Hz), 8.29 (4H, s, aromatic) and 12-14 (2H, carboxylic); IR (KBr): 3480 cm^{-1} (-OH,

carboxylic acid), 1764 cm^{-1} (C=O, asym. stretching), 1704 cm^{-1} (C=O, sym. stretching), 1391 cm^{-1} (C-N, stretching) and 734 cm^{-1} (C=O, bending).

Synthesis 3. ^1H NMR (DMSO- d_6 , δ in ppm): 0.88-0.92 (6H, d, methyl, $J=6.7$ Hz), 1.95-2.15 (1H, m, methine, $J=6.5$ Hz), 4.1-4.2 (1H, q, methine), 7.6-8.4 (3H, m, aromatic) and 13.2 (2H, carboxylic); IR (KBr): 3229 cm^{-1} (-OH, carboxylic acid), 1769 cm^{-1} (C=O, asym. stretching), 1709 cm^{-1} (C=O, sym. stretching), 1410 cm^{-1} (C-N, stretching) and 773 cm^{-1} (C=O, bending).

Synthesis 4. ^1H NMR (DMSO- d_6 , δ in ppm): 0.85-0.92 (6H, t, methyl), 1.95-2.30 (4H, m, methylene), 4.7-4.8 (2H, q, methine), 8.34 (2H, s, aromatic) and 12-14 (2H, carboxylic); IR (KBr): 3304 cm^{-1} (-OH, carboxylic acid), 3164 cm^{-1} ($\text{C}_{\text{arom.}}\text{-H}$, stretching), 2976 and 2927 ($\text{C}_{\text{aliph.}}\text{-H}$, asym. and sym. stretching), 1770 cm^{-1} (C=O, asym. stretching), 1704 cm^{-1} (C=O, sym. stretching), 1387 cm^{-1} (C-N, stretching) and 734 cm^{-1} (C=O, bending); $[\alpha]_D^{20} = -45.7^\circ$ (dioxane, 2.94 g/100ml).

Table 2. Poly(amide imide)s prepared from diimide-dicarboxylic acids and aromatic diamines

Diimide-dicarboxylic acids	Amine	Method of synthesis	Viscosity [0,5% in DMF]
PMDA + L-Ala	PPD	1	0.03
PMDA + L-Abu*	MDA	1	0.08
PMDA + L-Abu	MPD	1	0.05
TDA + L-Abu	PPD	1	0.03
TDA + L-Abu	ODA	1	0.03
TDA + L-Abu	MDA	1	0.03
TDA + L-Abu**	DAD	1	0.06
TDA + L-Abu	BDAF	2	0.15
PMDA = L-Ala	BDAF	2	0.21

* - $[\alpha]_D^{20} = -3.333^\circ$ (MDA, 3.00 g/100ml)

** - $[\alpha]_D^{20} = -1.866^\circ$ (DDA, 3.00 g/100ml)

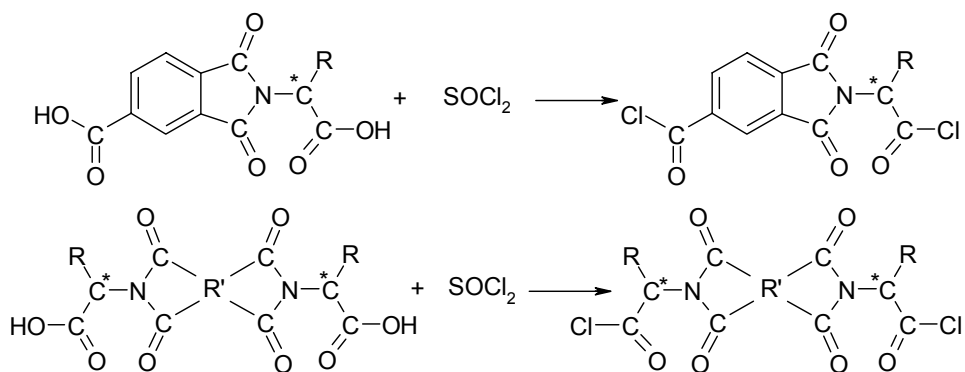
Syntheses 8 and 9. ^1H NMR (DMSO- d_6 , δ in ppm): 1.56-1.59 (6H, d, methyl, $J=7.3$ Hz), 4.87-4.99 (2H, q, methine, $J=7.3$ Hz), 8.05-8.26 (6H, m, aromatic) and 13.17 (2H, carboxylic); IR (KBr): 3246 cm^{-1} (-OH, carboxylic acid), 3066 cm^{-1} ($\text{C}_{\text{arom.}}\text{-H}$, stretching), 1780 cm^{-1} (C=O, asym. stretching), 1712 cm^{-1} (C=O, sym. stretching), 1389 cm^{-1} (C-N, stretching) and 731 cm^{-1} (C=O, bending).

Synthesis 10. ^1H NMR (DMSO- d_6 , δ in ppm): 3.25 and 3.33 (2H, t, methylene), 4.93 (1H, d, methine), 8.24 (1H, s, aromatic), 7.89 (1H, d, aromatic), 8.33 (1H, d, aromatic), 6.50 (2H, d, aromatic), 6.86 (2H, d, aromatic), 8.92 (1H, s, OH); IR (KBr): 3480 cm^{-1} (-OH, carboxylic acid), 1764 cm^{-1} (C=O, asym. stretching), 1704 cm^{-1} (C=O, sym. stretching), 1391 cm^{-1} (C-N, stretching) and 734 cm^{-1} (C=O, bending).

Synthesis 11. ^1H NMR (DMSO- d_6 , δ in ppm): 0.92 (6H, d, methyl, $J=7.2$ Hz), 1.44 (1H, m, methine, $J=7.2$ Hz), 1.87 and 2.21 (2H, t, methylene), 4.75 (1H, d, methine), 8.32 (1H, s, aromatic), 7.97 (1H, d, aromatic), 8.40 (1H, d, aromatic), and 12-14 (2H, carboxylic); IR (KBr): 3480 cm^{-1} (-OH, carboxylic acid), 1764 cm^{-1} (C=O, asym. stretching), 1704 cm^{-1} (C=O, sym. stretching), 1391 cm^{-1} (C-N, stretching) and 734 cm^{-1} (C=O, bending).

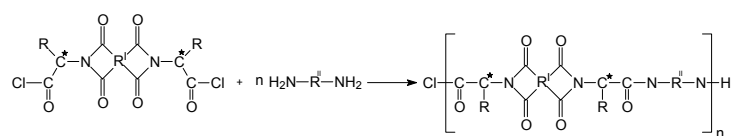
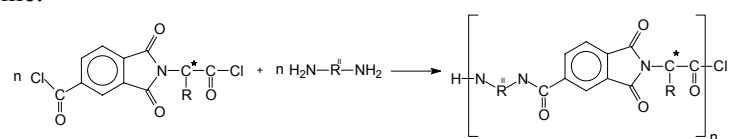
Synthesis 12. ^1H NMR (DMSO- d_6 , δ in ppm): 3.57 (2H, d, methylene), 5.07 (1H, t, methine), 8.20 (1H, s, aromatic), 7.90 (1H, d, aromatic), 8.33 (1H, d, aromatic), 6.96 (1H, s, aromatic), 6.88 (1H, s, aromatic), 7.44 (1H, d, aromatic), 7.17 (2H, m, aromatic), 10.65 (1H, s, NH); IR (KBr): 3480 cm^{-1} (-OH, carboxylic acid), 1764 cm^{-1} (C=O, asym. stretching), 1704 cm^{-1} (C=O, sym. stretching), 1391 cm^{-1} (C-N, stretching) and 734 cm^{-1} (C=O, bending).

Synthesis 13. ^1H NMR (DMSO- d_6 , δ in ppm): 0.83 (12H, d, methyl, $J=7.2$ Hz), 1.27 (2H, m, methine, $J=7.2$ Hz), 1.67 and 1.91 (4H, t, methylene), 4.43 (2H, d, methine), 3.22 (4H, d, methine), 3.51 (2H, s, methine), and 6.01 (2H, s, methine); IR (KBr): 3480 cm^{-1} (-OH, carboxylic acid), 1764 cm^{-1} (C=O, asym. stretching), 1704 cm^{-1} (C=O, sym. stretching), 1391 cm^{-1} (C-N, stretching) and 734 cm^{-1} (C=O, bending).

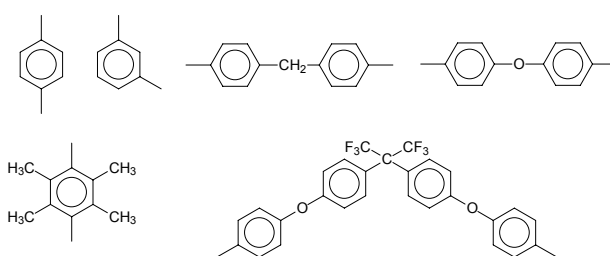


Scheme 2.

We adopted here two methods of poly(amide imide)s synthesis. It was found that the most effective is direct polycondensation of imide-dicarboxylic acid with diamine in the presence of triphenyl phosphite and pyridine.

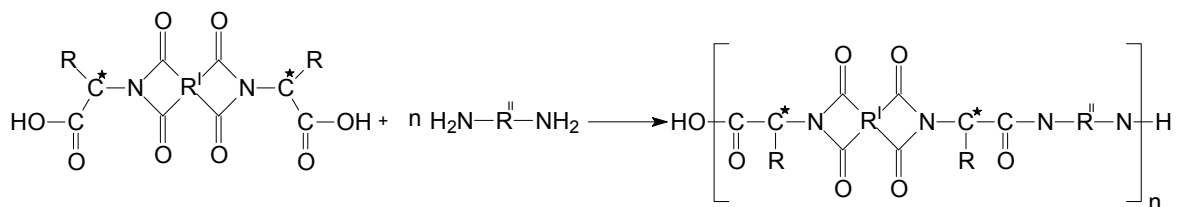
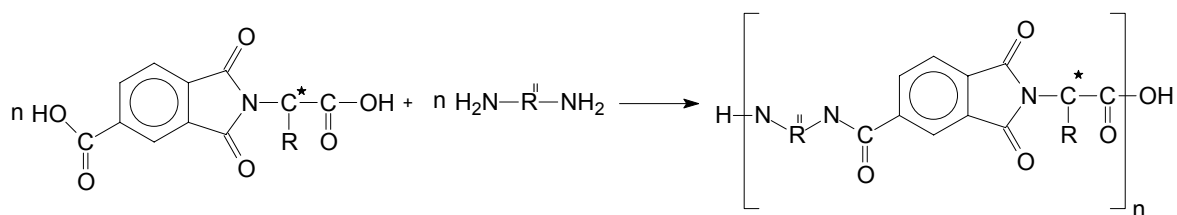


where R'' =



(R, R' see scheme 1)

Scheme 3.



Scheme 4.

Conclusions

The new optically active dicarboxylic acids containing imide groups were prepared by the reaction of anhydrides with optically active α -aminoacids. Poly(amide imide)s of low molecular weight were obtained. The most effective method is the direct polycondensation of imide-dicarboxylic acid with diamine in the presence of triphenyl phosphite and pyridine.

Acknowledgements

This work was realized under financial support of The State Committee of Scientific Research in Warsaw (Grant number 3 T09B 048 17).

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Поступила в редакцию 16 июля 2005 г.

Вісник Харківського національного університету. 2005. №669. Хімія. Випуск 13(36).
Е. Борицки, М. Вильчек, А.Ю. Колендо, Н.Н. Юхименко. Оптически активные поли(амидоимиды).

Взаимодействием ангидридов тримеллитовой, пирромеллитовой, бензофенон-3,3',4,4'-тетракарбоновой, бицикло-[2,2,2]-октен-2-тетракарбоновой кислот с оптически активными α -аминокислотами получены и охарактеризованы новые дикарбоксиимиды. Их строение подтверждено данными ПМР и ИК спектроскопии. Взаимодействием с тионил хлоридом синтезированы соответствующие хлорангидриды. Их конденсацией с ароматическими диаминами, а также прямой конденсацией карбоксиимидов с ароматическими диаминами в присутствии трифенилфосфина и пиридина, синтезированы оптически активные низкомолекулярные поли(амидоимиды).