

# Amino Acids as Substrates for Preparation of Monomers with Imide Rings

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## SYNOPSIS

The reaction of pyromellitic anhydride PMDA with some amino acids lead to monomers, which were used to synthesize new polymers. Application to glycine, D,L-alanine and  $\beta$ -alanine gave three bis-acid chlorides. These are able to condense with glycols and diamines to yield a series of new copolyimides. Amino acids of two carboxylic groups D,L-glutamic acid and D,L-aspartic acid gave, in reaction with PMDA, two similar dianhydrides (4) and (5). However, the condensation with aromatic amines lead to two different compounds. It was proved that, under the conditions studied, formation of hexa-membered imide rings was impossible while penta-membered imides formed without difficulty. Thermogravimetric analyses of these polymers were also carried out.

## INTRODUCTION

Natural amino acids are rather infrequently used for the preparation of synthetic polymers. The presence of carboxylic and amine groups yields amidic bonds in polyamino acids or polypeptides. One of the ways of synthesis of peptides is the method based on the masking of amine group by phthalic anhydride. An imide ring is formed in this reaction. The reaction between amino acid and anhydrides was used for the synthesis of bis(*N*-chloroformylmethyl)pyromellitimide (1) as described previously.<sup>1</sup>

Reaction of PMDA and glycine leads to difunctional monomers with two carboxylic end groups. These can be converted into acid chlorides. Similar monomers from PMDA and D- and L-alanine bis(*N*-chloroformyl-2-ethyl)pyromellitimides (2) were also synthesized.<sup>2</sup> The above acid chlorides were condensed with several glycols and diamines.<sup>1-3</sup> The poly(imide amide)s obtained are insoluble in organic solvents and decompose in a temperature range of 405–470°C. Poly(imide ester)s prepared from glycols are insoluble, but the use of poly(ethylene glycol)s of different molecular weight (300–6000) gives soluble thermoplastic copolyimides. The temperature range for decomposition is 385–430°C.

The condensation of (1) and (2) with polyglycols of diverse molecular weights leads to copolymers with controlled contents of imide rings in the polymer chain. This enables one to change their polarity or solubility. Since polyglycols are well known as the liquid phases for gas chromatography, these copolyimide properties allow them to be used as new chromatographic column packings.<sup>4</sup>

The obtaining of soluble and useful copolyimides from glycine and alanine encourages us to examine other amino acids as substrates for synthesis of new imide-ring-containing monomers. The present paper is devoted to the synthesis of monomers from  $\beta$ -alanine, D,L-glutamic acid, and D,L-aspartic acid. The condensation of previously described compounds (1) and (2) and monomers (3), (4), and (5) with diols and diamines are presented here, too. All monomers and copolyimides mentioned are shown in Table I.

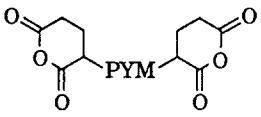
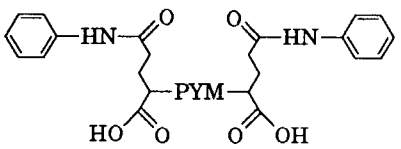
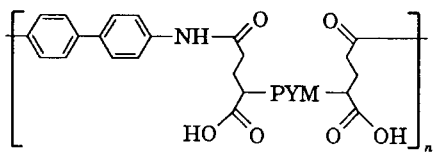
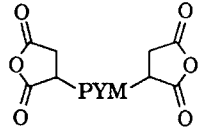
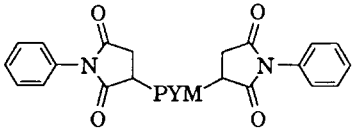
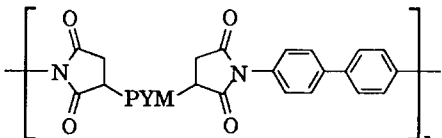
## EXPERIMENTAL

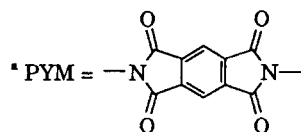
All chemicals used were analytical grade, commercial products and were used without further purification.

### Synthesis of Monomers

Bis(*N*-chloroformylmethyl)pyromellitimide (1) was obtained according to our previous description<sup>1</sup>: mp 234°C.

Table I Structure of the Compounds Studied

Monomer A	Monomer B	Polymer	
ClOC-CH <sub>2</sub> -PYM-CH <sub>2</sub> -COCl	(1) <sup>a</sup> PEG-2000	$\text{-(CO-CH}_2\text{-PYM-CH}_2\text{-CO-(CH}_2\text{CH}_2\text{O)}_n\text{)-}$	(8)
	Benzidine	$\text{-(CO-CH}_2\text{-PYM-CH}_2\text{-CO-NH-}\langle\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\rangle\text{-NH)-}$	(11)
ClOC-CH(CH <sub>3</sub> )-PYM-CH(CH <sub>3</sub> )-COCl	(2) PEG-2000	$\text{-(CO-CH(CH}_3\text{)-PYM-CH(CH}_3\text{)-CO-(CH}_2\text{CH}_2\text{O)}_n\text{)-}$	(9)
	Benzidine	$\text{-(CO-CH(CH}_3\text{)-PYM-CH(CH}_3\text{)-CO-NH-}\langle\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\rangle\text{-NH)-}$	(12)
ClOC-CH <sub>2</sub> CH <sub>2</sub> -PYM-CH <sub>2</sub> CH <sub>2</sub> -COCl	(3) PEG-2000	$\text{-(CO-CH}_2\text{CH}_2\text{-PYM-CH}_2\text{CH}_2\text{-CO-(CH}_2\text{CH}_2\text{O)}_n\text{)-}$	(10)
	Benzidine	$\text{-(CO-CH}_2\text{CH}_2\text{-PYM-CH}_2\text{CH}_2\text{-CO-NH-}\langle\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\rangle\text{-NH)-}$	(13)
	(4) Aniline		(6) <sup>b</sup>
	Benzidine		(14)
	(5) Aniline		(7) <sup>b</sup>
	Benzidine		(15)



<sup>b</sup> Model compounds.

D,L-bis(*N*-chloroformyl-2-ethyl)pyromellitimide (2) was obtained according to our previous paper<sup>3</sup>: mp 212–214°C.

β-Alanine (0.90 g, 10.5 mmol) was dissolved in 15 mL of pyridine–acetic acid mixture (2 : 3). PMDA (1.09 g, 5 mmol) was added with stirring. The mixture was refluxed for 2 h and, after cooling to room temperature, crystals of bis(*N*-carboxy-1-ethyl)pyromellitimide precipitated, mp 330°C (dec). The crude crystals were dissolved in a mixture of 10 mL SOCl<sub>2</sub> and 0.1 mL DMF and refluxed under ni-

trogen atmosphere for 10 min and then were mixed for 48 h at room temperature. The crystals of bis(*N*-chloroformyl-1-ethyl)pyromellitimide (3) were filtered and washed with dry hexane and dried under vacuum at 50°C. Yield 0.9 g (35%) mp 192°C. The structure was confirmed by elemental analysis:

Calcd. from formula (3)

C 38.71% H 2.01% N 5.64% Cl 14.31%

Found C 38.78% H 2.08% N 5.60% Cl 14.24%

D,L-glutamic acid (3.0 g, 21 mmol) was dissolved in 25 mL of pyridine-acetic acid mixture (1 : 1). PMDA (2.18 g, 10 mmol) was added with stirring. The mixture was refluxed for 1 h. Next, 15 mL of solvent was distilled off. Ten milliliters of acetic anhydride was added and heated for 5 min. After cooling crystals of D,L-bis(*N*-2-glytaric anhydride)pyromellitimide (4) were filtered and washed with dry hexane and dried under vacuum at 100°C. Yield 3.5 g (67%), dec. 305°C. The structure was confirmed by elemental analysis:

Calcd. from formula (4)

C 51.92% H 2.88% N 6.73%

Found C 51.90% H 2.92% N 6.65%

PMDA (1.09 g, 5 mmol) was dissolved in 20 mL of pyridine acetic acid mixture (3 : 2) and 1.35 g (11 mmol) of D,L-aspartic acid was added with stirring. The mixture was refluxed for 0.5 h and after cooling white crystals were filtered and dried. The crystals were refluxed with 10 mL of SOCl<sub>2</sub> for 5 min and stirred for 2 h at room temperature. The crystals of D,L-bis(*N*-2-succinic anhydride)pyromellitimide (5) were filtered and dried under vacuum at 100°C. Yield 1.6 g (70%), dec. 260°C. The structure was confirmed by elemental analysis:

Calcd. from formula (5)

C 48.25% H 2.01% N 7.03%

Found C 48.22% H 2.09% N 7.10%

### Synthesis of Model Compounds

Monomer (4) (0.22 g, 0.5 mmol) was dissolved in 1 mL of dry DMF; then 0.095 g (1.05 mmol) of aniline was added and refluxed for 0.5 h. Next, 25 mL of water was added. The crude deposit was crystallized from 80% ethanol, mp 237°C, yield 0.1 g (30%). The structure of bis[*N*-2-glutaric(mono-*N*-anilide)]pyromellitimide (6) was confirmed by <sup>1</sup>H-NMR, IR spectroscopy, and elemental analysis:

Calcd. from formula (6)

C 64.64% H 4.37% N 9.42%

Found C 64.72% H 4.31% N 9.49%

Monomer (5) (0.206 g, 5 mmol) was dissolved in 1 mL of DMF and refluxed with aniline (0.095 g,

0.5 mmol) for 0.5 h. After cooling, the crude product was crystallized from DMF, dec. ca. 400°C. Yield 0.055 g (20%). The structure of bis[*N*-succinic-(*N*-phenylimide)]pyromellitimide (7) was confirmed by <sup>1</sup>H-NMR, IR spectroscopy, and elemental analysis:

Calcd. from formula (7)

C 64.05% H 3.20% N 9.96%

Found C 64.00% H 3.22% N 9.91%

### Synthesis of Polymers

Poly(imide ester)s (8, 9, 10) were synthesized from monomers (1, 2, 3) and poly(ethylene glycol)-2000 according to the previously described method.<sup>2,3</sup> Poly(imide amide)s (11, 12, 13) were synthesized from monomers (1, 2, 3) and benzidine according to our paper.<sup>1</sup> Anhydride (4) (0.44 g, 1 mmol) was dissolved in 2 mL of hot DMF and cooled to room temperature, benzidine (0.184 g, 1 mmol) was then added. The reacting mixture was stirred for 2 h. After this time the viscous solution was poured into methanol. The polymer (14) was filtered, washed with hot acetone, and dried at 25°C in vacuum. Yield 0.5 g (80%).

Anhydride (5) (0.412 g, 1 mmol) and benzidine (0.184 g, 1 mmol) were dissolved in 2 mL of dry DMF and stirred for 2 h. Then the solution was poured into methanol. The polymer (15) was filtered, washed with hot acetone, and dried at 250°C in vacuum. Yield 0.41 g (70%).

### Measurements

Viscosity measurements were performed on a Höppler viscometer in chloroform solution for (8, 9, 10) and in DMF for (14):  $c = 0.5$  g/100 mL at 25°C. Infrared spectra were recorded on a Carl Zeiss spectrofotometer UR-20 using KBr discs. <sup>1</sup>H-NMR spectra were recorded on a Tesla 100 MHz spectrometer in deuterated acetone. Thermogravimetric studies were done in a dynamic inert gas atmosphere using a DuPont 1090 TG analyzer. The heating rate was 10°C/min.

## RESULTS AND DISCUSSION

The synthesis of PMDA with glycine, D,L-alanine, and β-alanine leads to monomers with two acid chloride end groups (1, 2, 3). This enabled us to obtain the polymers shown in Table I.

**Table II Physicochemical Properties of Polyimides Studied**

Polymer	Melting Point (°C)	Viscosity ( $\eta_{inh}$ )	PDT (°C) <sup>a</sup>	R (%) <sup>b</sup>
8	37	0.29	408	0
9	41	0.37	397	0
10	45	0.31	405	0
11	—	—	430	30
12	—	—	410	32
13	—	—	425	35
14	—	0.48	410	46
15	—	—	395	48

<sup>a</sup> Temperature of maximum rate of polymer degradation from TG experiments.

<sup>b</sup> Wt % residue at 600°C from TG experiments.

Poly(imide ester)s synthesized from monomers (1) and (2) and poly(ethylene glycol)-2000 are soluble in organic solvents and even in water. The detailed studies of structures and properties of two copolyimides (8) and (9) were done previously.<sup>2,3</sup> Their physicochemical parameters are shown in Table II.

The condensation of poly(imide amide)s (8, 9) give similar polymers to those described earlier.<sup>1</sup> These resins are insoluble. The temperatures of maximum degradation rate of copolyimides are in the range of 420°C (see Table II). The polymers synthesized from monomer (3) are obviously similar to those obtained from monomers (1) and (2) described previously.

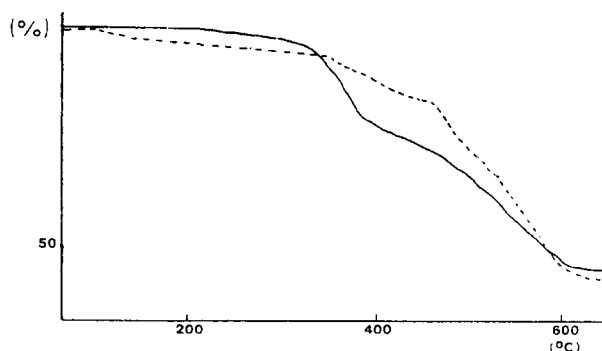
The dianhydride (4) was condensed with benzidine which was used as a representative of aromatic diamines. The obtained polymer (14) shows interesting physical properties such as solubility, and adhesion to metals and glass. A structure containing the constituent unit of this resin was studied as a model compound (6) to avoid difficulties connected with the complex polymeric structure. The elemental analysis is given in the Experimental part. <sup>1</sup>H-NMR spectrum shows a very wide signal of amide hydrogen =NH at  $\delta = 4.44$  ppm and the carboxylic hydrogen—COOH signal at  $\delta = 9.06$  ppm. There are also characteristic frequencies of amide and carboxylic groups in the IR spectrum (—NH 3360 cm<sup>-1</sup> and —OH 2500–3700 cm<sup>-1</sup>).

The data presented prove the under the conditions studied imide rings are not formed, although compounds (6) and (14) were heated up to 250°C or treated by known, strong dehydrating agents such as acetyl chloride, thionyl chloride, or acetic anhydride. The model compound (6) and polymer (14) are soluble in 2M NaOH solution which additionally proves the presence of free carboxylic groups. These

facts allow us to propose the structure of polymer (14) given in Table I. It is interesting that in the condensation of anhydride (5) with the same amines and at the same conditions, the imide rings form without difficulty. It was proved by studying <sup>1</sup>H-NMR and IR spectra of the model compound (7) that there are no characteristic peaks of amide or carboxylic groups. Polymer (15) and model compound (7) are insoluble and infusible.

Temperatures of maximum rate of polymer degradation from TG experiments are shown in Table II. The thermal resistance of copolyimides (8), (9), and (10) makes them useful as phases in gas-liquid chromatography working at high temperature.<sup>4</sup>

The TG studies show that thermal degradation of polymers (8–13) is a one-step process.<sup>2–4</sup> TG plots for polymers (14) and (15) are shown in Figure 1. These curves are multistage. For polymer (14), the first stage, up to 350°C, is probably connected with cyclization and decarboxylation. [The resin (14) heated at 320°C for 20 min becomes insoluble in DMF and NaOH resolution.] The next stage of the



**Figure 1** TG curves of copolyimides [(---) polymer (14); (—) polymer (15)].

TG curve is connected with the degradation of glutarimide. The last high temperature section is due to the pyrolysis of pyromellitimide ring.<sup>5,6</sup> For polymer (15) there are only two stages in the TG curve. They are connected with the degradation of succinimide and pyromellitimide rings, respectively.

## CONCLUSION

The application of glycine, D,L-alanine, and  $\beta$ -alanine in monomer synthesis leads to bisacid chlorides. They can be condensed with glycols or diamines in order to obtain a series of new copolyimides. Some of these resins are soluble and fusible. The properties mentioned make them very promising compounds.

Amino acids of two carboxylic groups such as D,L-glutaric acid and D,L-aspartic acid form, in reaction with PMDA, similar dianhydrides (4) and (5). However, the condensation of these anhydrides with aromatic amines leads to two different compounds. Bis(*N*-2-glutaric anhydride)pyromellitimide (4) gives monoamides with free carboxylic groups. It appears that, under the conditions studied, the formation of a hexamembered imide ring is impossible. The cyclization process takes place only above 250°C

with a very slow rate with simultaneous gradual decomposition.

On the other hand, bis(*N*-2succinic anhydride)pyromellitimide (5) gives penta-membered imide rings easily. The mentioned differences in polymer structures are the reason for quite different physicochemical properties of these compounds. Polymer (14) seems to be the most interesting. Its solubility and strong adhesion to many surfaces make future studies on condensation of dianhydride (4) with other diamines very promising.

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