BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1795—1800 (1966)

The Syntheses of Polypyromellitimide-amides*

By Motoo SAGA, Toshiyuki SHONO and Koichiro SHINRA

Department of Chemical Technology, Faculty of Engineering, Osaka University, Miyakojima-ku, Osaka

(Received December 6, 1965)

Dibasic acids containing a pyromellitimide ring were synthesized by the reaction of pyromellitic dianhydride with such ω-aminoacids as glycine, ε-amino-caproic acid and *p*-amino-benzoic acid. By the condensation polymerization of the dibasic acids obtained above with diamines, polypyromellitimide-amides were synthesized. The polymers were soluble in *m*-cresol and sulfuric acid, and the inherent viscosities of the polymers ranged from 0.21 to 0.42 (in *m*-cresol). The polymers were found to be considerably heat-stable.

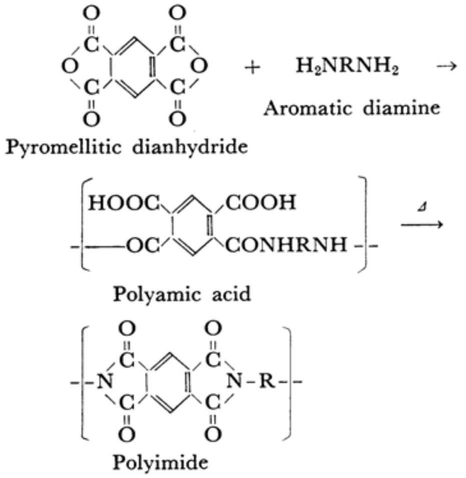
It is generally recognized that the polymers with recurring aromatic units have a high thermal stability, and several synthetic studies of various polymers have been conducted. For example, the polypyromellitimide developed by the duPont Company and already commercialized as "H-film"[1] possesses an excellent heat-resistant property, a cold-proof property, a corrosion-resistant property for various chemicals, and a pronounced film-forming capability.

The method of synthesizing such material is shown as Formula 1 below:

---

* Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

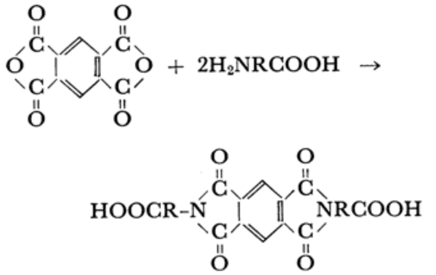
[1] L. E. Amborski, *Ind. Eng. Chem.*, **2**, 189 (1963).



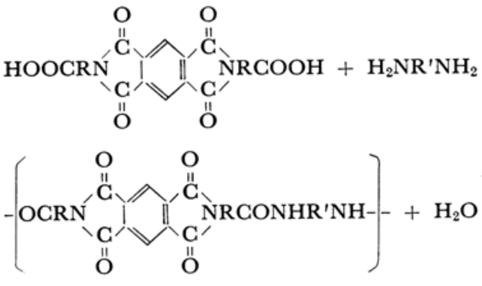
(1)

However, the polypyromellitimide has the disadvantage that it has no solubility in many organic solvents. One method of correcting this defect may be the introduction of the amide-linkages or straight-chain methylene groups into the polymer backbone, in addition to the imide-linkage.

In the present study, dibasic acids, as is generally shown by the Formula 2 were synthesized by the reaction of pyromellitic dianhydride with such ω-aminoacids as glycine, ε-amino-caproic acid and *p*-amino-benzoic acid. The polypyromellitimide-amides, generally shown by the Formula 3, were synthesized by the condensation polymerization of these dibasic acids with diamines.



(2)



(3)

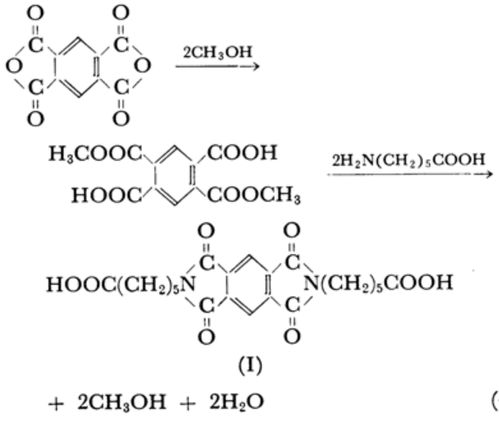
Polypyromellitimide-amide

The structures of these compounds were confirmed through elementary analyses and a study of the infrared absorption spectra.

On compounds similar to those reported here, some descriptions have appeared in the Japanese patents,[2] and there has been a brief report by K. Mienes.[3]

Experimental

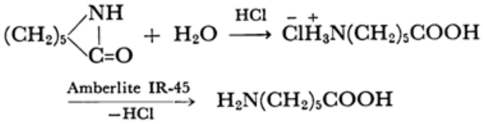
The Synthesis of Pyromellitimide Caproic Acid (I).



(4)

Pyromellitic Dianhydride. — Commercial pyromellitic dianhydride was recrystallized twice from acetic anhydride. This material was confirmed to be anhydride by study of its infrared absorption spectrum ($\nu_{C=O}$ 1775, and 1859 cm^{-1}). m. p. 285.5°C (lit.[4] m. p. 286°C).

ε-Amino-caproic Acid.—Synthesized from ε-caprolactam by the method described in Org. Synth.[5]:



m. p. 202°C (lit.[5] m. p. 202°C)

Pyromellitic dianhydride (6.08 g. (0.0279 mol.)) and 30 ml. of anhydrous methanol were placed in a 100-ml. three-necked flask equipped with a drying tube. This mixture was then shaken by hand and gently warmed on a water bath until the solution became clear. After the reaction mixture had become transparent (in about 1 hour), 7.32 g. (0.0558 mol.) of ε-amino-caproic acid was added. The ε-amino-caproic acid immediately dissolved, and the solution became transparent again after it had been heated on a water bath for an hour. After this procedure the solvent was distilled off, and the product thus obtained was dried under reduced pressure for about 24 hr. The white product obtained was then recrystallized from acetic acid. The infrared absorption spectrum of the dibasic acid (I) is shown in Fig. 1. The characteristic absorption bands of the imide ring[6,7] were recognized at 730, 1380, and 1780 cm^{-1}.

---

[2] Japanese Pat. 21500 (1963).
[3] K. Mienes, *Kunststoffe*, **53**, 493 (1963).
[4] J. Braun and G. Lemke, *Ber.*, **57**, 682 (1924).
[5] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, 28 (1963).
[6] S. Nishizaki and A. Fukami *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 382 (1963).
[7] S. D. Bruck, *J. Chem. Educ.*, **42**, 18 (1965).

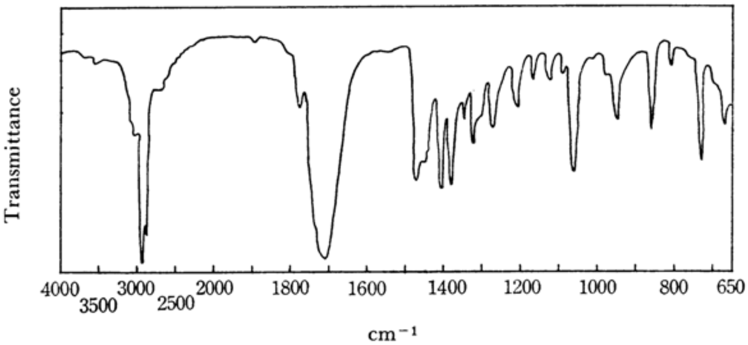


Fig. 1. Infrared spectrum of pyromellitimide caproic acid (I) (Nujol).

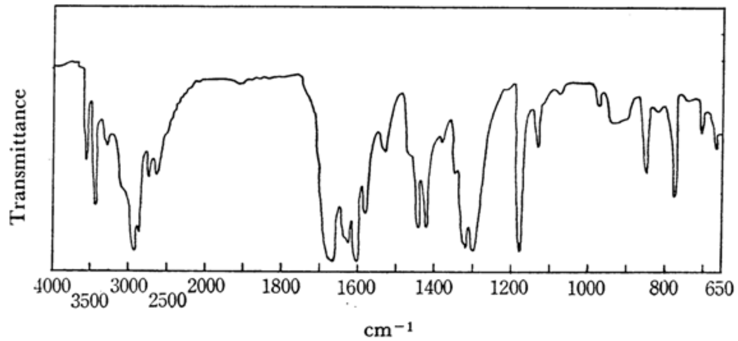
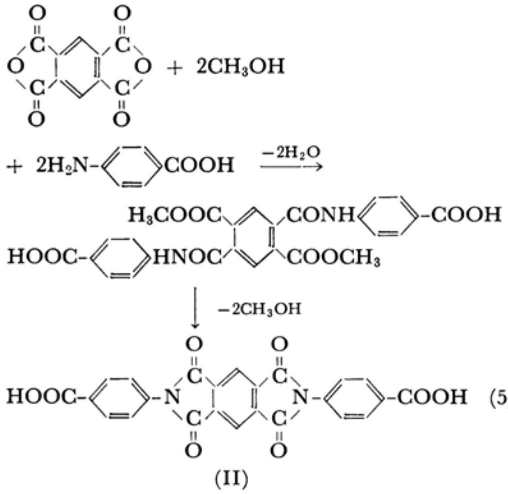


Fig. 2. Infrared spectrum of pyromellitimide benzoic acid (II) (Nujol). (unimidized)

Yield 88%; m. p. 231°C.

Found: C, 59.44; H, 5.41; N, 6.33. Calcd. for $C_{22}H_{24}O_8N_2$: C, 58.91; H, 5.49; N, 6.30%.

The Synthesis of Pyromellitimide Benzoic Acid (II).



(5)

(II)

p-Amino-benzoic Acid.—Purified by recrystallization of the commercial-grade product from ethanol. White needles were thus obtained. m. p. 187°C (lit.[8] m. p. 187—187.5°C), II was prepared by a method similar to that used for pyromellitimide caproic acid I.

In this case, however, the imidization reaction could occur only with difficulty. A completely imidized substance was not obtained, even after drying under reduced pressure for several days at 60—70°C. By drying under reduced pressure at 250°C, a completely imidized substance was, however, obtained.

The pyromellitimide benzoic acid (II) obtained being insoluble in all organic solvents, the unreacted starting material was removed by extraction with glacial acetic acid and ethanol.

Yield 92%; m. p. 350°C.

Found: C, 62.73 H, 2.93. Calcd. for $C_{24}H_{12}O_8N_2$: C, 63.15 H, 2.65%.

The infrared absorption spectra of the dibasic acid (II) before and after the imidization reaction are shown in Fig. 2 and Fig. 3 respectively. The characteristic absorption bands due to amide CO and NH stretching vibration existing in the 1600—1650 and 3400—3500 cm^{-1} ranges before the imidization (Fig. 2) disappeared after imidization.

After imidization (Fig. 3), those which appear to have come from the characteristic absorption bands of the imide ring were recognized at 720, 1380, and 1780 cm^{-1}.

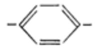
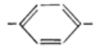
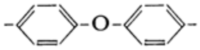
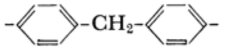
The material before the imidization reaction was a yellow powder and was soluble in many organic solvents, but after the imidization reaction it became a brown powder and was insoluble in an organic solvent.

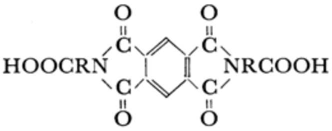
The Synthesis of Pyromellitimide Acetic Acid (III).

---

[8] N. A. Lange, "Hand Book of Chemistry," Ninth Edition, Hand Book Publishers, Inc. Sandusky, Ohio (1956), p. 399.

TABLE I. PREPARATION OF POLYPYROMELLITIMIDE-AMIDE

Polymer No.	Dibasic acid R*1	Diamine R′*2	Preparation method*3	Reaction condition		Yield %	Decomp. temp. °C	η_{inh}*4
				Temp. °C	Time hr.			
I	$-(CH_2)_5-$	$-(CH_2)_6-$	A	180	12	67.4	350	0.42
II	$-(CH_2)_5-$	$-(CH_2)_6-$	A	180	16	68.6	350	0.37
III	$-(CH_2)_5-$	$-(CH_2)_6-$	B	180	10	64.5	320	0.33
IV	$-(CH_2)_5-$	$-(CH_2)_{10}-$	A	180	12	64.3	255	0.28
V	$-(CH_2)_5-$	$-(CH_2)_{10}-$	A	180	16	67.7	270	0.36
VI	$-(CH_2)_5-$	$-(CH_2)_{10}-$	B	180	12	62.5	230	0.27
VII		$-(CH_2)_6-$	B	180	12	65.5	235	0.21
VIII		$-(CH_2)_6-$	B	180	12	58.3	220	0.23
IX	$-CH_2-$		A	200	10	68.5	350	—
X	$-CH_2-$		A	200	10	56.2	350	—

*1 R: 

*2 R′: $H_2NR'NH_2$

*3 A: Equimolar reaction between dibasic acid and diamine.
B: Nylon salts were employed.

*4 Measured at a concentration of 0.5 g./100 ml. *m*-cresol at 30°C.

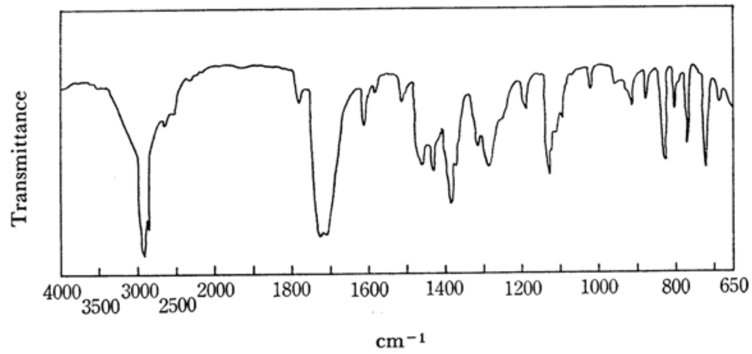


Fig. 3. Infrared spectrum of pyromellitimide benzoic acid II (Nujol). (imidized)

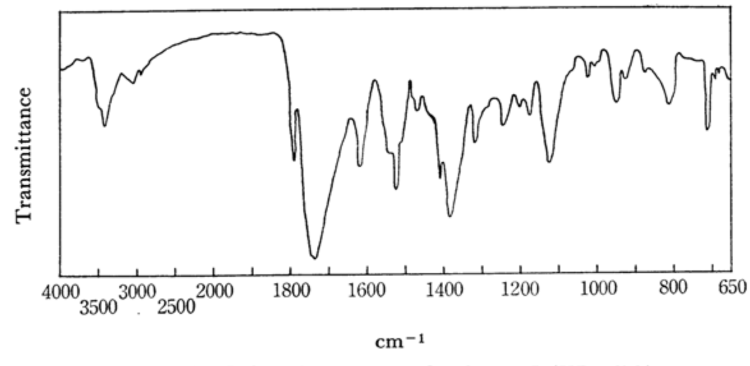
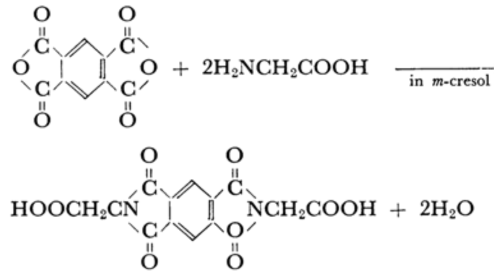


Fig. 4. Infrared spectrum of polymer I (KBr disk).



(6)

(III)

Glycine. — A commercial product was purified by recrystallization from methanol. *m*-Cresol (50 ml.) was taken into a 100-ml. three-necked flask, to which was then added 7.5 g. (0.1 mol.) of glycine. This mixture was heated to 100°C while being stirred. After the reaction had been completed, the product was recrystallized from dioxane, yielding light yellowish crystals.

The product obtained in this way was found by a study of its infrared absorption spectrum to be completely imidized.

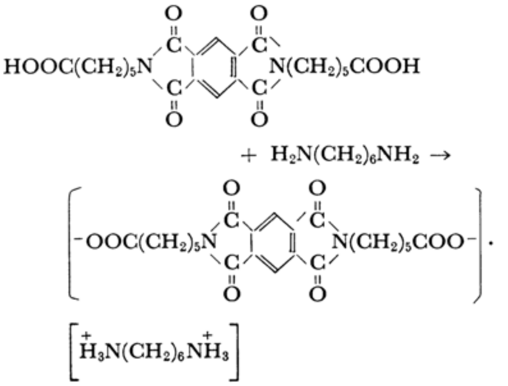
Yield 81.3%; m. p.>320°C

Found: C, 50.72 H, 2.82. Calcd. for $C_{14}H_8O_8N_2$: C, 50.60 H, 2.55%.

The Synthesis of Nylon Salt.—In order to increase the degree of polymerization, and also in order to utilize the insoluble dibasic acid (II) as the polymer component, nylon salt was prepared by the following method.

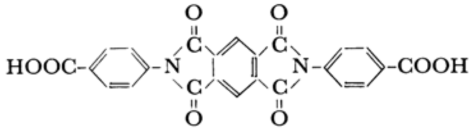
To the dibasic acids suspended in hot water, diamines were added gradually. After the filtration of the transparent solution thus obtained, ethanol was added. Precipitated nylon salts were filtered and dried in a vacuum. The nylon salts obtained in this manner were as follows:

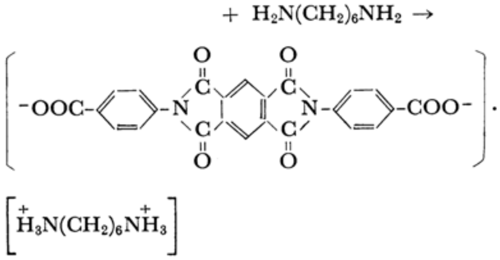
(a) Nylon salt derived from pyromellitimide caproic acid (I) and hexamethylene diamine:



Found: N, 10.21. Calcd. for $C_{28}H_{40}O_8N_4$: N, 10.00%.

(b) Nylon salt derived from pyromellitimide benzoic acid (II) and hexamethylene diamines:





Found: N, 9.85. Calcd. for $C_{30}H_{28}O_8N_4$: N, 9.79%.

Condensation Polymerization between Dibasic Acids and Diamines.—An equimolar reaction between dibasic acid and diamine was carried out. 0.05 mol. of each component dissolved in 15 ml. of purified *m*-cresol was mixed in a thick test bube, the mixture was then heated under dry nitrogen.

When the nylon salts were employed, the condensation polymerization reaction was carried out in a similar way, dissolving 4—5 g. of nylon salts in 30 ml. of *m*-cresol.

The reaction temperature was gradually elevated for about one hour. Thereafter, the reaction was continued at 180°C until the viscosity of the reaction mixture seemed to have reached to the maximum. The polymer solution was then gradually dropped into methanol in order to precipitate the polymer. The precipitated polymer was filtered, and washed with water and acetone. The polymer was refined by repeating the procedure of dissolving the product into *m*-cresol, followed by reprecipitation. The results are shown in Table I.

The infrared absorption spectrum of the polymer I is shown in Fig. 4. In addition to the bands due to imide linkage, the characteristic absorption band for the amide NH stretching vibration was recognized near 3400 cm⁻¹.

The Heat Decomposition of the Polymers.—The thermal gravimetric analysis in atomospheric air of the polymer was undertaken by using a thermanobalance (Hitachi Thermano Balance Electric Furnace). The results of the measurements on the three types of polymers with different unit structures, are shown in Fig. 5.

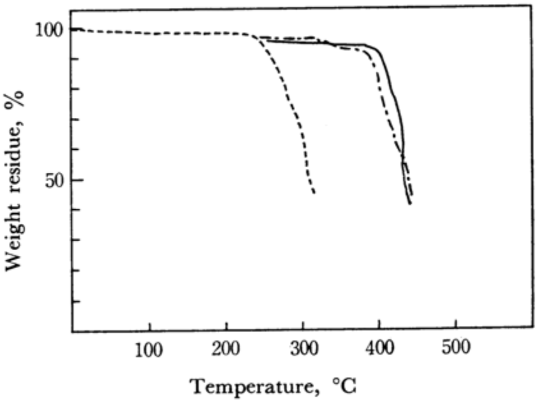


Fig. 5. Thermogravimetric analyses for polymers.
---- polymer I, -·- polymer IX, —— polymer X

Summary

Pyromellitimide caproic acid (I), pyromellitimide benzoic acid (II), and pyromellitimide acetic acid (III) have been synthesized in high yields by the reaction of pyromellitic dianhydride with three types of ω-amino acids, and their structures have been confirmed by elementary analyses and by a study of their infrared absorption spectra.

By the condensation polymerization between the dibasic acids described above and diamines, polypyromellitimide-amides with an imide ring and amide linkage in their molecule have been synthesized. The polymers obtained are generally soluble in *m*-cresol and sulfuric acid, but insoluble in other common organic solvents.

Such structures as the IX and X polymers in which the methylene chain in the molecule is short, and the aromatic unit is rich, were hard to dissolve in all the solvents mentioned above.

The results of the thermal gravimetric analyses indicated that, when the methylene chain is introduced into the polymer backbone, its heat stability appreciably decrease and that the polymer behaves like aliphatic polyamide. Those polymers such as the IX polymer which take a large part of the aromatic unit and a short methylene chain in repeating unit seem to have a good heat stability.

The authors wish to thank Dr. Yoshikazu Hachihama for his many helpful discussions and suggestions during this work.