THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Science (Chemistry)
DEGREE

Chemistry
FIELD

Chemistry
DEPARTMENT

TITLE: Synthesis and Characterization of Polyamide-4

NAME: Miss Patcharin Pinthong

THIS THESIS HAS BEEN ACCEPTED BY

THESIS ADVISOR
(Associate Professor Cholticha Noomhorm, Ph.D.)

THESIS CO-ADVISOR
(Assistant Professor Wirunya Keawwattana, Ph.D.)

DEPARTMENT HEAD
(Assistant Professor Noojaree Prasitpan, Ph.D.)

APPROVED BY THE GRADUATE SCHOOL ON

DEAN
(Associate Professor Gunjana Theeragool, D.Agr.)

THESIS

SYNTHESIS AND CHARACTERIZATION OF POLYAMIDE-4

PATCHARIN PINTHONG

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Science (Chemistry)
Graduate School, Kasetsart University
2009

Patcharin Pinthong 2009: Synthesis and Characterization of Polyamide-4. Master of Science (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Associate Professor Cholticha Noomhorm, Ph.D. 88 pages.

Synthesis and characterization of polyamide-4 (PA-4) were investigated. Synthesis of polyamide-4 from γ-aminobutyric acid (GABA) by melt polymerization was unsuccessful. PA-4 was successfully synthesized by anionic ring-opening polymerization of 2-pyrrolidone (Py) by using N-sodium-2-pyrrolidone (Na) as initiator and N-benzoyl-2-pyrrolidone (BPy) as activator in the presence of 15-crown-5 at 30 to 60^{o}C from12 to 24 h under alternating between under nitrogen atmosphere for 3 h and reduced pressure for 1 h. Weight average molecular weight ($\overline{M}_{W}$) from 398 to 9233 and quite low yield from 2.94 to 25.43% of PA-4 having T_{m} ~ 241-256^{o}C and T_{c} ~ 168-210^{o}C was obtained. The effect of the sodium and 15-crown-5 was studied at 40^{o}C. It was found that $\overline{M}_{W}$ and yield of PA-4 slightly increased with increasing the amount of Na and 15-crown-5. PA-4 was also obtained from copolymerization of Py and GABA using mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 and varying the mmol of GABA from 10 to 30 at 105^{o}C for 8 h and at 40^{o}C for 24 h. Polymer yield obtained was extremely low (highest was 6.5%). $\overline{M}_{W}$ of PA-4 obtained by the copolymerization of Py and GABA at 105°C was higher than at 40°C. The highest $\overline{M}_{W}$ PA-4 obtained in this study was 9233 which can be obtained either from Py:BPy:Na:Crown = 100:1:3:2 at 40^{o}C for 24 h or from copolymerization of Py:BPy:Na:Crown:GABA = 100:1:3:2:20 at 105^{o}C. Polyamide-4,4 was synthesized by both solution and interfacial polycondensation at room temperature for biodegradation comparison with PA-4. PA-4 begun to degrade after incubating in composted soil for 120 h but was not degraded after incubating 14 h in all the enzymes used.

____________________________ ____________________________ ___ / ___ / ___

Student’s signature Thesis Advisor’s signature

ACKNOWLEDGEMENTS

First and foremost, I would like to express my gratitude to my advisor, Associate Professor Cholticha Noomhorm, for her valuable guidance, helpful discussions, encouragement and kindness throughout the course of my graduate study at Kasetsart University. I would like to sincerely thank Assistant Professor Wirunya Keawwattana, my co-advisor, Dr. Potjanart Suwanruji and Assistant Professor Nantana Jiratumnukul for her technical knowledge and helpful assistance. This thesis cannot be accomplished without their help.

Grateful acknowledgement is expressed to Dr. Pensri Bunsawansong, Department of Chemistry, Faculty of Science, Kasetsart University for providing the nuclear magnetic resonance spectroscopy analyses.

Special acknowledgement is extended to Dr. Yutaka Tokiwa and Mr. Raku Takao from Institute for Biological Resources and Functions, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibraraki, Japan for differential scanning calorimetry analyses and measurements of BOD and TOC in degradation analyses.

Thanks for my lovely friends and staffs at the Department of Chemistry, Faculty of Science, Kasetsart University for their help during this study.

Finally, I am sincere grateful to my dearly father and mother for their encouragement and support throughout this thesis. Their unconditional love is the source of my strength.

Patcharin Pinthong
April 2009

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

Figure **Page**

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

Appendix Figure **Page**

LIST OF ABBREVIATIONS

BOD = Biochemical oxygen demand

BPy = N-benzoyl-2-pyrrolidone

dl = Deciliters

DSC = Differential scanning calorimetry

FAU = Finkel-Biskis-Reilly murine sarcoma virus (FBR-MuSV) ubiquitously expressed

GABA = γ-Aminobutyric acid

IR = Infrared spectrometry

ISO = International Organization for Standardization

JIS = Japanese Industrial Standards

$\overline{M}_n$ = Number average molecular weight

$\overline{M}_w$ = Weight average molecular weight

Na = Sodium

NMP = 1-Methyl-2-pyrrolidone

NMR = Nuclear magnetic resonance spectroscopy

PA-4 = Polyamide-4

PA-4,4 = Polyamide-4,4

PHB = Poly(D-3-hydroxybutyrate)

Py = 2-Pyrrolidone

rh = Relative Humidity

T_c = Crystallization temperature

T_g = Glass transition temperature

T_m = Melt temperature

TOC = Total organic carbon

δ = Chemical shift values

$[\eta]$ = Intrinsic viscosity

η_{rel} = Relative viscosity

η_{sp} = Specific viscosity

SYNTHESIS AND CHARACTERIZATION OF POLYAMIDE-4

INTRODUCTION

Synthetic polymers derived from petroleum based have displaced metals, glasses, ceramics and wood in many products, especially in the area of packaging such as, bags, films, flexible pouches and rigid container. According to recent statistics on worldwide use of plastic bags, Americans are the top user with more than 380 billion bags a year, followed by Taiwaneses (20 billion bags), Britons (12 billion bags) and Australians (6.9 billion bags). Thailand produces nearly 22 million tons of solid waste annually in 2003 (Pollution Control Department, 2003). Municipal solid waste from everyday waste produced by households and businesses made up to ~67% of the total solid waste generation, while non-hazardous waste produced by industries accounted for ~27%. The remainder of the waste includes infection waste from hospitals and hazardous waste produced by industries and communities. Although there is no record on how many plastic bags Thai use each year, it had been roughly estimated that plastic waste accounts for 19.5% (2.8 million tons) of country’s total municipal solid waste 14.4 million tons a year (Figure 1) and only 25.0% (0.7 million tons) of this plastic waste (mostly soft drink and other bottles) was recovered and recycled. Thus the remaining 75.0% (2.1 million tons) of plastic wastes was required to be disposed. With the current rate of growth in population and consumption, 17 million tons of solid waste will be needed to be disposed in 2010. Conventional disposal method by incineration of these plastic wastes is associated with many environmental problems, such as production of dioxins. As a result, most of these plastic wastes have been accumulating in landfills because they are very stable and cannot be degraded easily in the natural environment due to their long polymer molecules which are too large and too tightly bound. In order to reduce the impact of plastic waste on the environment from the incineration and from the continued depletion of landfill space, development of biodegradable polymers having comparable properties to replace the existing non-biodegradable polymers is becoming increasing important at present. These polymers need to be biodegradable and non-toxic, on the other hand, should have good chemical, mechanical, thermal and rheological properties and the raw materials for obtaining these polymers should be annually renewable so as the end products should be composted to reduce the use of fossil resources.

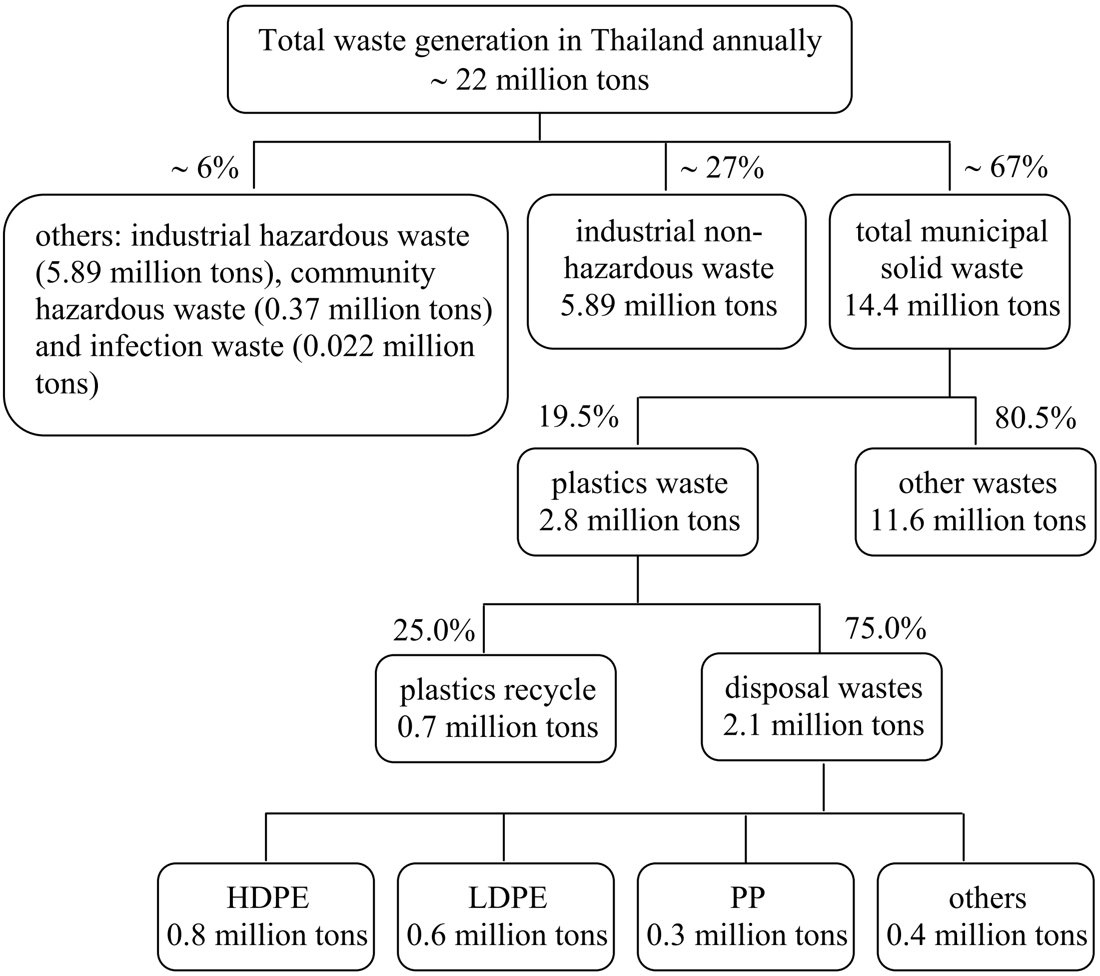
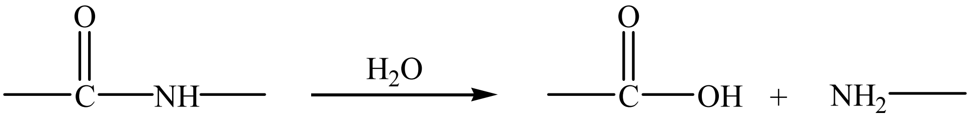


Figure 1 Waste generation in Thailand in 2003.

Source: Pollution Control Department (2003)

The possibilities of microbiological attack to various polymers had been studying to clarify the relationship between biodegradation and chemical structure of the polymer. A variety of biodegradable polymers had been synthesized and investigated. It had been pointed out and summarized in various reviews that one of the important factors in biodegradation is the presence of hydrolysable linkage such as ester, amide, urethane and urea linkages in the main chains (Hocking, 1992; Satyanarayana and Chatterji, 1993). So far, most of the investigations on the biodegradable synthetic polymers had been emphasized mainly on the polymers containing ester linkage in the main chain, such as poly(ε-caprolactone), poly(3-hydroxybutyrate), poly(lactic acid), and poly(butylene succinate), however, use of these polymers is still limited due to their high costs compared to those of petroleum based polymers and properties (Noomhorm and Tokiwa, 2006). Although polyamides are high performance polymers due to their unique combination of thermal, physical and mechanical properties, little attention has been focused on biodegradable polymers containing only amide linkage in the main chain (Kawasaki *et al*., 2005). Generally, it has been known that the degradation of synthetic polyamides is slower than that of the corresponding synthetic polyesters through both biological and hydrolytic processes under neutral conditions. The higher resistance to the degradation of polyamide may be caused mainly by highly ordered crystalline morphology and strong intermolecular hydrogen bonds between neighboring chains of the amide linkages (Hashimoto *et al*., 2002). On the contrary, all polyamides are susceptible to hydrolysis by strong acids, a reaction essentially the reverse of the synthetic reaction (Figure 2). The molecular weight of polyamide products thus drops fast and cracks form quickly at the affected zones.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH- \xrightarrow{H_2O} -\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_2-$$

Figure 2 Hydrolysis of polyamide under strong acid condition.

In addition, proteins that contain amide linkages (-CO-NH-) from α-amino acids are found readily degraded by proteolytic enzymes, however, very little is actually known about the biodegradation of amide linkages present in the main polymer chain of polyamides or nylon. Recently, some microorganisms that can degrade polyamide had been reported. *Flavobacterium* sp.K172 was able to hydrolytically degrade nylon-6 oligomers, but cannot degrade nylon-6 polymers (Negoro *et al.*, 1980, 1983; Kakudo *et al.*, 1993). White rot fungi strain IZU-154, *Phanerochaete chrysosporium* and *Trametes versicolor* were able to degrade nylon-6,6 under ligninolytic conditions (Deguchi *et al.*, 1997, 1998). Polyamide-4 (nylon-4) was found to biodegrade in composted soil (Hashimoto *et al.*, 1994, 2002, 2004) and in an activated sludge (Kawasaki *et al.*, 2005; Yamano *et al.*, 2008). It could be assumed, at this point, that only polyamide-4 was readily biodegraded in nature according to these findings. Hence, it is possible that polyamide-4 or nylon-4 could become an attractive biodegradable polymer because not only that polyamide-4 has excellent physical and mechanical properties, but it can also be obtained from renewable γ-aminobutyric acid (GABA) (Figure 3), that can directly be produced from some kinds of bacteria such as *Lactobacillus* sp. and by marine Psedomonad from glutamate (Mountfort and Pybus, 1992; Higuchi *et al.,* 1997; Yamano *et al.*, 2008).

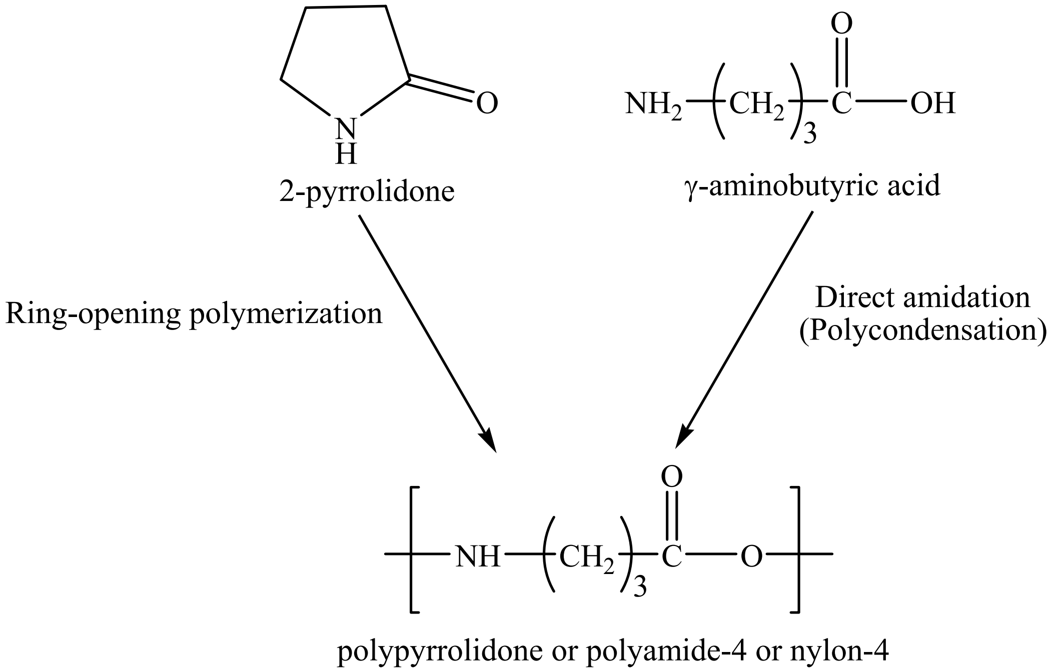


Figure 3 Direct amidation or polycondensation and ring-opening polymerization for polypyrrolidone or polyamide-4 or nylon-4 synthesis.

Polyamide-4 or nylon-4 was first invented in 1953 (Ney *et al.*, 1953) by anionic ring-opening polymerization of 2-pyrrolidone (Figure 3). The great interest in nylon-4 is due to the fact that nylon-4 textile fibers combine the good strength properties of nylon-6 or nylon-6,6 (Table 1) and a much higher moisture adsorption similar to cotton in its absorbance over the whole relative humidity (rh) range than its higher homologues (Table 2) (Sweeny, 1972). It undergoes a fast thermal degradation just below its melting point (260°C). This difficulty has caused some limitations to obtain the nylon-4 fibers by melt spinning, but, it can be made into shaped and film by melt-molding or extrusion. Thus it decreased the original interest for application of nylon-4 as possible synthetic fibers.

Table 1 Tensile properties of polypyrrolidone or polyamide-4 and related polylactam fibers.

Fiber	Dry tenacity, g/den	Elongation, %	Denier	Wet tenacity, g/den	Elongation, %	Denier	Tenacity retained when wet, %	Modulus retained when wet, %
Poly(pyrrolidone)	4.1	31	3.0	3.1	32	3.0	70-80	45-65
Poly(caprolactam)	8.3	30	6.0	7.1	29	6.0	85-90	55-70
Nylon-6,6	7.8	20	6.0	6.7	17	5.9	85-90	55-70
Poly(capryllactam)	7.5	24	5.6	7.1	22	5.6	93-97	90-95
Poly(laurolactam)	7.2	24	5.1	7.3	24	5.1	100	90-95

Source: Sweeny (1972)

Table 2 Water absorption of polyamides.

Polyamide made from	Number of CH_2 groups	Water absorption of polymers	
		65% rh	99% rh
Pyrrolidone	3	9.1	28
Caprolactam	5	4.3	9.5
Enantholactam	6	2.8	5.0
Capryllactam	7	1.7	3.9
ω-Aminopelargonic acid	8	1.5	3.3
Azaundecan-2-one	9	1.4	1.9
ω-Aminoundecanoic acid	10	1.3	2.8
Azacyclotridecan-2-one	11	1.3	2.7

Source: Sweeny (1972)

Since then intense research activities to improve the polymerization process and to enhance the thermal stability of polyamide-4 were studied. The literature concerning synthesis of polyamide-4 was essentially patents (Barnes *et al*., 1957; Barnes, 1973; Bacskai, 1977, 1978a, 1978b, 1979; Barnes, 1981; Barnes and Barnes, 1981a, 1981b) and was mainly focused on increasing the rate of polymerization by adding N-acyl initiator (e.g. N-acetylpyrrolidone or N-benzoylpyrrolidone) or compounds which can form N-acylpyrrolidone (e.g. acid anhydride, acid chlorides, esters, or amides) to the 2-pyrrolidone/alkaline initiator system (Budin and Kralicek, 1976; Roda *et al*., 1977a, 1977b, 1980, 1981a, 1981b, 1983). It was found that polyamide-4 produced with the aid of N-acyl initiators is relatively low in molecular weight and had a very board molecular weight distribution. Higher molecular weight and narrower molecular weight distribution had been reported using 2-pyrrolidone/alkaline/carbon dioxide as initiator, but the polymerization rate was lower than polymerization without carbon dioxide. Studies showed that higher conversion and molecular weight polyamide-4 were obtained using certain onium salt and crown ether than using pyrrolidone/potassium/carbon dioxide alone due to the tight complexation of the potassium cation which led to a free more reactive pyrrolidone anion (Collman, 1978; Bacskai, 1979, 1982). Technological knowledge in the production of polyamide-4 therefore be developed in order for polyamide-4 being used as biodegradable polymer. Thus, in this study, an attempt was made to investigate used the effect of crown ether for finding the conditions for synthesis of polyamide-4 by anionic ring-opening polymerization of 2-pyrrolidone using sodium as an alkali metal initiator and N-benzoylpyrrolidone as an N-acyl activator.

OBJECTIVES

1. To investigate factors and conditions for synthesis of polyamide-4 by ring-opening polymerization.

2. To characterize the synthesized polyamide-4.

3. To evaluate the biodegradability of the synthesized polyamide-4.

LITERATURE REVIEW

Today, polymers are used in nearly all areas of daily life and their production and fabrication are the major worldwide industries. Nowadays, a wide variety of synthetic polymers are produced worldwide to the extent of approximately 140 million tons per year. The birth of polymer may be traced back to the mid-nineteenth century. In 1839, Charles Goodyear developed the vulcanization process that transformed the sticky latex of natural rubber to a useful elastomer (Sekiguchi and Coutin, 1992). Polyamides are polymers containing amide groups (-CO-NH-) in the main polymer chains and they are the largest and most important group of linear-acyclic nitrogen polymers. Polyamides are widely represented in nature as various proteins and numerous other substances of biological importance, which are found among the constituents of animal and plant organisms. The first synthetic polyamide, poly(3-benzoamide), an aromatic polyamide, was obtained by Harbordt in 1862. The first aliphatic polyamide reported in the literature is polyhexanoamide, obtained in 1899 by Gabriel and Maas. However, the synthesis of polyamide having high molecular weight had to wait for half a century, when Carothers prepared polyhexanediamide or nylon-6,6 based on aliphatic diamine and diacid in 1933, and its industrial manufacture was begun in 1937. A variety of polyamides that provide a wide range of materials was then synthesized from various combinations of amino acids, bibasic acids and diamines. The extensive research in this area was due to the success of the aliphatic and later aromatic systems, which have been developed into commercial products by fiber producers like Monsanto, DuPont, and Celanese etc. The first synthetic fibers of practical importance were obtained from polyamides and were conspicuous by their extremely high strength and occupied the first place among all synthetic fibers. In 1974, the aliphatic and aromatic polyamides were given separate generic nomenclature by the Federal Trade Commission. Polyamides are generally classified as aliphatic polyamides or nylons, and aromatic polyamides or aramids.

Polyamide or nylon is a thermoplastic silky material, first used commercially in a nylon-bristled toothbrush (1938), followed more famously women’s stocking

(1940). It was intended to be a synthetic replacement for silk in many different products after silk became scarce during World War II. It replaced silk in military applications such as parachutes and flake vests, and was used in many types of vehicle tires. Solid nylon is used for mechanical parts such as screws, gears and other low to medium stress components previously cast in metal. Engineering grade nylon is processed by extrusion, casting, and injection molding.

Polyamide-4 or nylon-4 or polypyrrolidone is an attractive polymer for use in fibers. A summary of the other fiber properties compared with those of some currently produced fibers was shown in Table 3. The comfort was found to be equal to that of cotton when in staple form and much better than polyesters or conventional polyamides when in filament form. There was no static cling because of the normal moisture content which prevented the build-up of static electricity. The fabrics were found to have good soil release and not to pick up body odors. The abrasion resistance was outstanding and recovery from strain was 100% after 24 hours. It was also found that fabrics made from this fiber could be ironed at cotton setting because of the moisture present and there was no danger of melting a hole in the garment or for the fabric to stick to the iron as with a polyester fabric. Of course, the lack of incentive to commercialize this fiber was certainly not due to its properties, the difficult was still in the polymer area. The polymer of necessity must be made by the bulk method; suspension polymerization is not possible because the suspending liquid is encapsulated in the polymer. Because of the slow polymerization rate a continuous method was not practical and the batch method resulted in the usual batch-to-batch variations. These variations were serious because it was necessary to change the spinning conditions to suit each batch thus making continuous spinning impossible. An additional problem was that the tough polymer cake (from bulk process) had to be ground which was difficult and accompanied by high losses due to the formation of too small particles to be fed into an extruder. A method to speed up the bulk polymerization was needed to a point where a continuous process would be feasible.

Table 3 Comparison of polyamide-4 or nylon-4 properties with those of some currently produced fibers.

Property	Cotton	Nylon-6,6	Nylon-6	Polyester	Nylon-4
Melting point (^{o}C)	300 dec.	265	220	265	265
Specific gravity	1.54	1.14	1.14	1.38	1.25
Dry tenacity (g/den)	3.0-4.9	2.3-6.0	4.0-7.2	2.8-5.6	3.0-6.0
Tenacity retained when wet (%)	100-110	86-92	86-92	100	70-80
Elongation (%)	3-10	25-65	17-45	24-42	20-50
Loop strength (g/den)	-	2.0-5.1	3.8-5.6	2.5-5.2	3.6-5.4
Knot strength (g/den)	-	2.0-5.1	3.8-5.5	2.5-5.1	3.6-5.4
Initial modulus (g/den)	60	5-24	18-23	10-30	15-20
Elastic recovery (% recovery from 5% strain)	45	88 (at 3%)	99.5	60	100
Energy to rupture (g-cm/den-cm)	0.06-0.17	0.8-1.25	0.67-0.9	0.4-1.1	0.60-0.93
Moisture regain (%)	7.0-8.5	4.0-4.5	4.5	0.4	6.0-9.0
Ironing characteristics	Recommended ironing temp.:400-450^{o}F	Melts at cotton setting	Melts at cotton setting	Melts and sticks to iron at cotton setting	Can be ironed at cotton setting

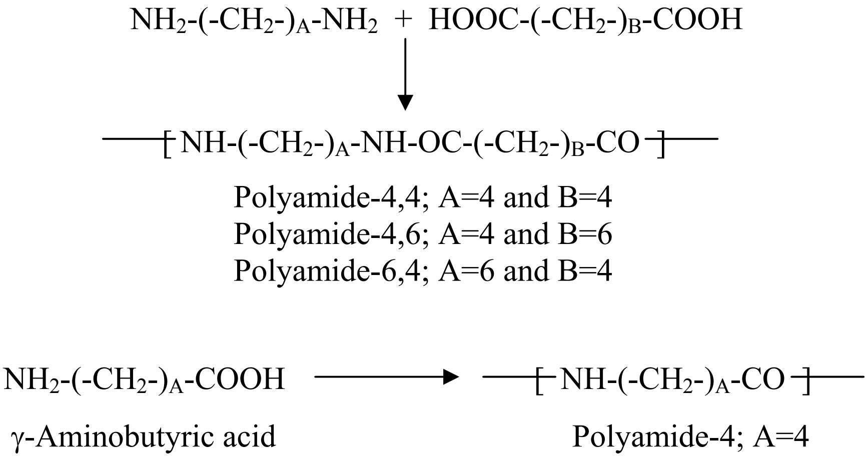
Source: Barnes (1987)

1. Synthesis methods of polyamide-4

Generally, polyamide or nylon including polyamide-4 can be synthesized by two currently available pathways: directly condensation polymerization of diamine and diacid or directly condensation polymerization of amino acid compounds and by ring-opening polymerization of cylic amides or lactams.

1.1 Directly amidation condensation polymerization

The polycondensation reaction in polyamide synthesis is the polyamidation. In direct amidation by melt polymerization, a diamine reacts directly with a dicarboxylic acid, or an acid at one end reacts with an amine at the other end of a single molecule, to form a polymer with elimination of water (Figure 4).



$$NH_2\text{-}(\text{-}CH_2\text{-})_A\text{-}NH_2 + HOOC\text{-}(\text{-}CH_2\text{-})_B\text{-}COOH \longrightarrow \text{—}[NH\text{-}(\text{-}CH_2\text{-})_A\text{-}NH\text{-}OC\text{-}(\text{-}CH_2\text{-})_B\text{-}CO]\text{—}$$

Polyamide-4,4; A=4 and B=4
Polyamide-4,6; A=4 and B=6
Polyamide-6,4; A=6 and B=4

$$NH_2\text{-}(\text{-}CH_2\text{-})_A\text{-}COOH \longrightarrow \text{—}[NH\text{-}(\text{-}CH_2\text{-})_A\text{-}CO]\text{—}$$

γ-Aminobutyric acid   Polyamide-4; A=4

Figure 4 Directly amidation condensation polymerization.

The nylons are named by the number of carbon atoms in the repeat units. It is customary for the first number to represent the number of carbons in the diamine and the second number to represent the number of carbons in the diacid.

Nothing had been reported in the literature for synthesis of nylon-4 from direct amidation of gamma-aminobutyric acid until now. However, a number of direct amidation of diamine and diacid had been reported.

Low molecular weight end-capped dimers, trimers, and tetramers of nylon-4 were prepared by stepwise synthesis using the p-nitrophenyl active ester coupling method. By thermal gravimetric analysis and gas chromatography, it was found that all of the oligomers studied are thermally unstable and decompose upon heating into pyrrolidone. The rate of oligomer decomposition was found to vary with the nature of the end group; maximum thermal stability was observed for a tetramer having acetoxy and *n*-propylamido end groups. The results indicated that linear sequences of γ-aminobutyryl units are inherently thermally unstable and had a strong tendency to revert into the thermodynamically more stable pyrrolidone ring (Bacskai, 1983 and 1984).

A series of aliphatic 1, 4-diaminobutane based polyamides 4.*y* with $y = 8, 9, 10$ and 12 was synthesized and characterized. For comparison, some 1, 6-diaminohexane based counterparts were also studied. PA 4.12, and in particular PA 4.10, proved to have a very beneficial combination of T_m, crystallization rate and physical properties. First indications were obtained, that for a series of aliphatic polyamide isomers, containing 16 carbon atoms in the repeating unit, the melting points are related to the number of ways to make an energetically favorable chain fold upon crystallization: isomers having two possible ways of chain folding have T_m which are 13–15 °C lower than isomers having only one possible way of chain folding upon crystallization (Koning *et al*., 1999).

A polyamide containing a short and a long alkane segment such as polyamide-4,14 was synthesized and characterized (Li and Yan, 2001). The polymer was prepared by melt polycondensation, which yielded materials of molecular weight about 15,000 g/mol. The product was characterized and it was found that well-melt-crystallized nylon-4,14 underwent brill transition at 170°C on heating. When it crystallized at high temperature from the melt, nylon-4,14 crystallized directly into a kind of α phase with two peaks in its XRD patterns, which is very different from nylon-6,6 and nylon-10,12 and similar to nylon-10,10. Upon further cooling to room temperature, nylon-4,14 preserved the triclinic structure (α phase).

Polyamides from the polycondensation of a diamine component comprising 70 mol% or more of *m*-xylylenediamine and a dicarboxylic acid component comprising 70 mol% or more of a C4-C20 α, ω-straight-chain aliphatic dicarboxylic acid in the such as a polyamide produced from *m*-xylylenediamine and adipic acid of α, ω-straight-chain aliphatic dicarboxylic acid in the presence of at least one phosphorus compound from the group consisting of phosphinic acid compounds and phosphonous acid compounds in an amount of 3 to 400 ppm in terms of phosphonous acid compounds and in the presence of an alkali metal compound of a weak acid were produced (Maruo *et al*., 2005). The weak acid has dissociation constant lower than the first dissociation constant of a dicarboxylic acid mainly constituting the polyamide resin in an amount of 0.5 to1.0 mol per one mol of the phosphorus compound. The polyamide produced has been used as a gas barrier material for films and bottles in the application fields of resin-reinforced injection materials and packaging materials because of its high strength, high elastic modulus, low permeability to gaseous substance such as oxygen and carbon dioxide. The polyamide has a terminal amino group and a terminal carboxyl group at its molecular chain ends. The terminal amino group and the terminal carboxylic group were subjected to amidation reaction to increase the molecular weight (increase in melt viscosity) when melted for producing filaments, films, sheets, moldings, etc. The increase in the melt viscosity may result in a low flowing speed and a long-term retention of a molten polymer in a molding machine. A polymer thus heated for an excessively long period of time is subjected to not only further amidation but also cross-linking reaction to become three-dimensional, thereby likely to produce gelated mass that is different from a normal polymer in their properties. The formation of gelated mass is accelerated if a molding machine has a portion stagnating a molten resin.

A process for the manufacture of homopolyamide-4,6 fibers by melt spinning of homopolyamide-4,6 to fibers and multifilament yarns obtainable by the process and the use thereof for the reinforcement of rubber like in tire cords, V-belts etc, was reported (Van Ruiten *et al*., 2005). Polyamide-4,6 was obtained by polycondensation of tetramethylenediamine and adipic acid. Due to the very high melting temperature, the production of polyamide-4,6 was very difficult. It can be produced basically by two-step processes comprising a precondensation step followed by a solid state post-condensation step below the melting temperature at temperature between 225 and 275°C. Homopolyamide-4,6 produced can be used for the manufacture of fibers, films and injection molded articles. The homopolyamide-4,6 fiber is manufactured by melt spinning of homopolyamide-4,6 having nascent morphology with a melting enthalpy of at least 140 J/g and a main melting temperature between 290 and 305°C.

2. Ring-opening polymerization of 2-pyrrolidone

For a long time, it was considered impossible to polymerize the C_4 lactam, pyrrolidone. However, Ney *et al.* found that an insoluble polymer powder was separated when a solution of pyrrolidone was stood for 223 weeks in the presence of alkali and a patent was granted in 1953 (Ney *et al.*, 1953).

The polyamides formed by ring-opening polymerization of lactams carry only one number in their names, for instance, nylon-4 that is formed from 2-pyrrolidone. Approximate melting points of polyamides obtained by ring-opening polymerization were summarized in Table 4.

The lactam ring is strongly resonance stabilized and the carbonyl activity is low. Nevertheless, the ring-opening polymerizations start with small amounts of initiators through trans-acylation reactions. Fairly high temperatures, however, are needed, often above 200°C. In all such reactions, one molecule acts as an acylating agent or as an electrophile while the other one act as a nucleophile and undergoes the acylation. Generally, the initiators activate amide groups causing them to react with other lactams through successive transamidations that results in formations of polyamides. Both acids and bases catalyze the transamidation reactions. The additions of electrophiles affect increases in the elctrophilicity of the carbonyl carbon of the acylating lactam. The nucleophiles, on the other hand, increase the nucleophilicity of the lactam substrate.

Table 4 Approximate melting points of polyamides: -[-NH-(-CH_2-)$_n$-CO-]-.

Polyamide	Repeating unit, n	Melting points (^oC)
3	2	320-330
4	3	260-265
5	4	260
6	5	215-220
7	6	225-230
8	7	195
9	8	197-200
10	9	173
11	10	185-187
12	11	180
13	12	173

Source: Raave (2000)

The common feature of ring-opening polymerization is relief of ring strain to produce linear polymer. Ring-opening and polymerizability of cyclic amides or lactam vary greatly with ring size and substituents. Ease of polymerization varies with ring strain. Polymerization of lactams is a thermally controlled equilibrium process between polymer and cyclic monomer, and in some cases, there are ceiling temperatures above which lactam only is favored. For comparison, caprolactam, a seven-membered ring, polymerizes readily at high temperatures with anionic initiators. On the other hand, butyrolactam, a five-membered ring, and valerolactam, a six-membered ring, polymerize only at relatively low temperatures and reconvert to monomer in the presence of the polymerizing catalyst at higher temperatures, e.g. 60 to 80^{o}C.

Polymerization of lactams produces important commercial polymers and currently, the most important ring-opening polymerization is that of capropactam to produce nylon-6. Lactam molecules can polymerize by three different mechanisms: cationic, anionic and hydrolytic polymerization.

It is known that 2-pyrrolidone can be polymerized to produce a useful high molecular weight thermoplastic product that has become known as polypyrrolidone or polyamide-4 (Figure 3). Most of the ring-opening polymerization of 2-pyrrolidone reported in the literatures were carried out under the anionic condition in the presence of alkaline polymerization catalysts such as potassium hydroxide, potassium pyrrolidone.

3. Anionic polymerization of lactams

The anionic polymerizations of lactams are initiated by strong bases capable of forming lactam anions (Figure 5). Such bases can be alkali metals, metal hydrides, organometallic compounds and metal amides. The initiation step of ring opening amidation can be shown in Figure 6. The primary amine anions abstract protons very rapidly from other molecules of lactams to form amino-acryllactams.

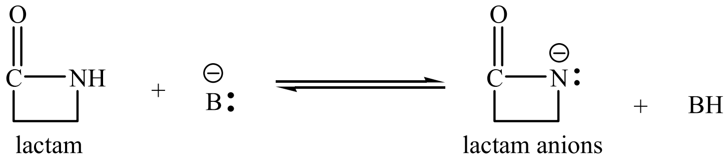


Figure 5 The anionic polymerizations of lactams are initiated by strong bases.

Source: Raave (2000)

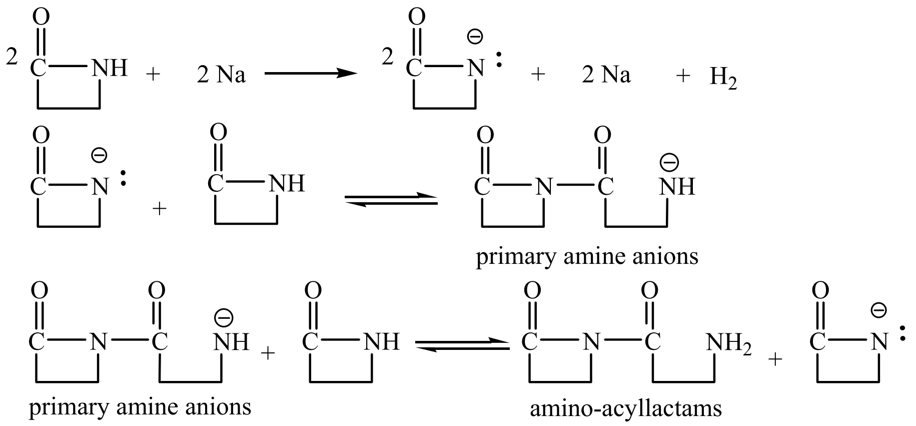


Figure 6 The initiation step of ring opening amidation.

Source: Raave (2000)

In these reactions, the propagation centers are the cyclic amide linkages of the N-acylated terminal lactam rings (Figure 7). Acylation of the amide nitrogens has the effect of increasing the electron deficiencies of these groups. This in turn increases the reactivities of the cyclic amide carbonyls toward attacks by the nucleophilic lactam anions. Very rapid proton exchange follows. This results in equilibrium between the lactam and the polymeric amide anions.

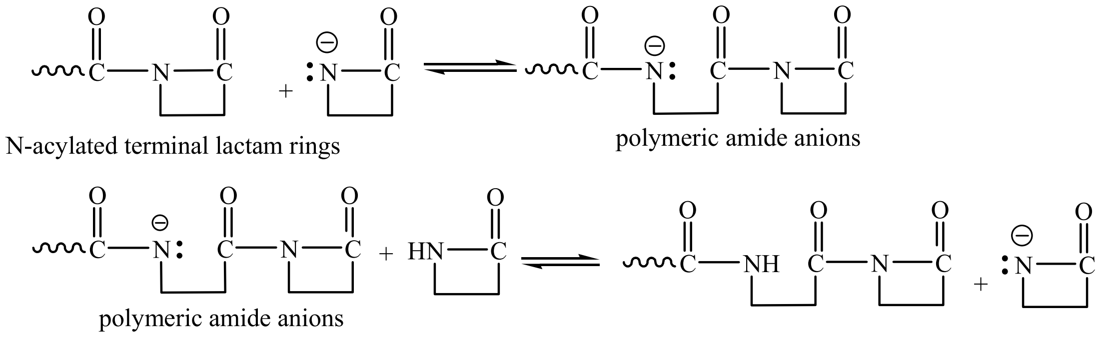


Figure 7 The propagation centers are the cyclic amide linkages of the N-acylated terminal lactam rings.

Source: Raave (2000)

The polymer amide anions can undergo acylation by acyllactam groups with accompanying ring opening or with formation of lactam anions (Figure 8). In the first instance, it is an alternate path of propagation with formation of imide groups. The acylation reactions shown above are much faster than the initiation reactions. As a result, increases in molecular weights take place at the beginning of the polymerizations. Bimolecular aminolyses may contribute to that, through their contributions to the total conversions are negligible.

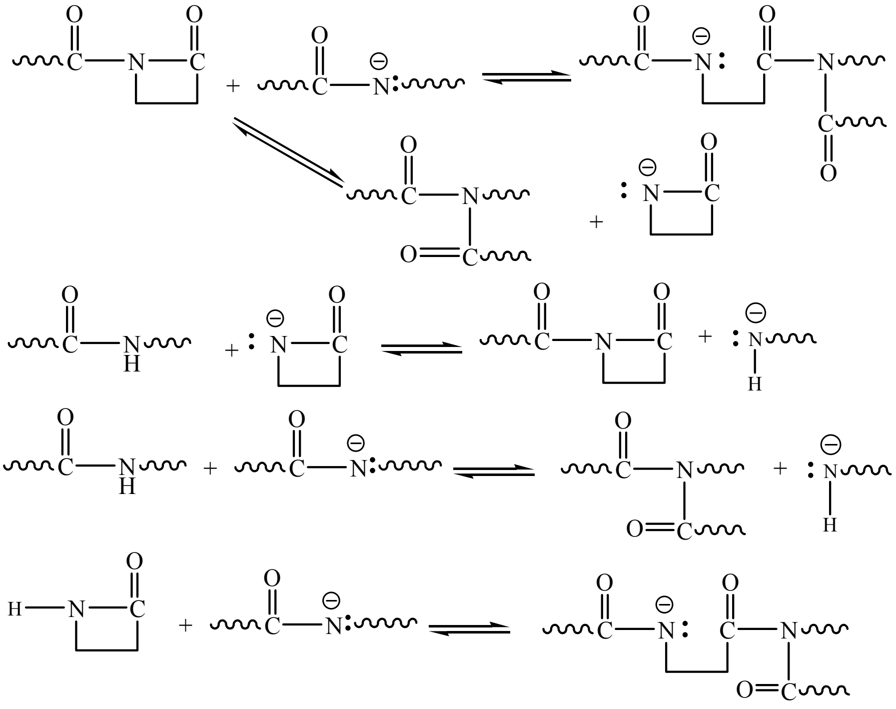


Figure 8 The alternate path of propagation with formation of imide groups.

Source: Raave (2000)

The overall rates of polymerizations depend on the concentrations of acyllactams and diacylamine groups as well as on the lactam anions. The latter result form dissociations of the lactam salts, depending upon the nature of the metal as shown in Figure 9, where Me means metal. The alkali metals can be rated in the following order with respect to the rates of initiations and propagations: Li<Na<K<Ca. Additions of activators or cocatalysts, such as acyl halides, anhydrides

or isocyanates, can result in elimination of the induction period. These additives insure formations of stabilized adducts (Figure 10). The structures of the activators can determine the rates of addition to the first lactam anion. If, for instance, the acyl group is large, as in pivaloylcaprolactam, the decrease in the rate can be merely due to steric hindrance. On the other hand, substituents like the benzoyl group increase the rates of additions to the first lactam anions. In addition, the structures of the activators can also affect the course of the polymerization. This is because they become incorporated at the end of the polymeric molecules and may influence the basicity during the polymerization reactions. Polymerizations in the presence of acylating agents are often called activated polymerization. If the acylating agents are absent from the reaction mixture the reactions may be called nonactivated. Sometimes the terms assisted and nonassisted are used instead (Raave, 2000).

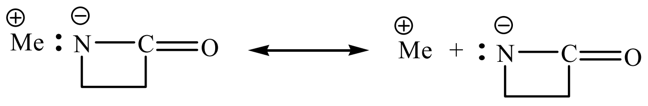


Figure 9 Dissociations of the lactam salts.

Source: Raave (2000)

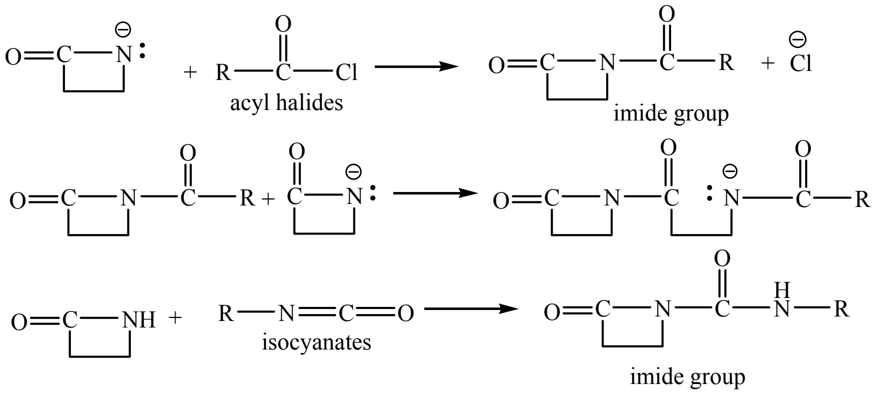


Figure 10 The structural of the activators.

Source: Raave (2000)

The property of 2-pyrrolidone, polymerized in the presence of alkaline salts at low temperature, was first reported by Ney *et al.* (1953). Barnes *et al.* (1957) studied the polymerization of 2-pyrrolidone without the addition of activators. In a vessel equipped for vacuum distillation and mechanical stirring, 2-pyrrolidone was placed and potassium hydroxide pellet was then added. The water was removed by distillation at temperature of 90-120 °C and under pressure of 0.5-10 mmHg. After in 1958, Hall proposed a mechanism for the alkali catalyzed polymerization which has as its key step the attack of a lactam anion on an N-acyllactam chain end. It was suggested that the most important factor determining lactam polymerizability was the rate of cyclization of intermediates to reform the lactam. The intermediate may be amino acid or acylamino acid in the water-catalyzed polymerization or a ω-aminoacyllactam in the alkali-catalyzed polymerization.

It was found that polyamide-4 produced with the aid of N-acyl initiators was relatively low in molecular weight and had a very broad molecular weight distribution. Higher molecular weight and narrower molecular weight distribution had been reported using 2-pyrrolidone/alkaline/carbon dioxide as initiator. The CO_2 activated potassium pyrrolidonate catalyst system for the polymerization of 2-pyrrolidone was first reported in patent by Ney (1961).

Clark and Black (1962) studied the polymerization of 2-pyrrolidone under polymerization condition in the presence of a polymerization catalyst (e.g. alkali metals, hydroxides) and polymerization activator selected from the group consisting of nitrogen dioxide and certain organic nitrites (e.g. n-butyl nitrite, 2-methylbenzyl nitrite).

Increasing the rate of polymerization of polyamide-4 was focused by adding N-acyl initiator (e.g. N-acetylpyrrolidone or N-benzoylpyrrolidone) or compounds which can form N-acylpyrrolidone (e.g. acid anhydride, acid chlorides, esters, or amides) to the 2-pyrrolidone/alkaline initiator system. Furthermore it was attempted to improve the thermal stability of the polymer formed by variations in the catalyst system used. Typical examples were the use of N-acetylpyrrolidone/$MAlEt_4$, diphenyl ketene/$MAlEt_4$ (where M is Li, Na or K) and diphenyl ketene/K by Tani and Konomi (1966).

Schirawski (1972) studied polymerization of 2-pyrrolidone by three different types of catalytic systems: Na/N-acetylpyrrolidone, KOH/CO_2 or KOH/SO_2. The corresponding polymers were compared with each other and tried to be spun by melt extrusion. Polymers obtained by KOH/CO_2- and KOH/SO_2-catalysis can be spun from the melt without difficulties. Products obtained by Na/N-acetylpyrrolidone-catalysis were, however, not stable enough.

Barnes (1973) subsequently discovered that polyamide-4 prepared with carbonated potassium pyrrolidonate (py-K/CO_2) was higher in molecular weight and had a narrower molecular weight distribution than polymer prepared without CO_2.

Sekiguchi *et al.* (1973) studied anionic polymerization of α-pyrrolidone and α-piperidone using their quaternary ammonium salts, which prepared extra situ, as catalysts. Pyrrolidone and piperidone salts gave the corresponding lactam polymers of increased molecular weight, with an improved yield, as compared to those obtained using classical alkaline catalysts.

In 1976, Budin and Kralicek studied the effect of the purity of monomers and of potassium salt 2-pyrrolidone used as an initiator and the effect of reaction conditions on the course of anionic polymerization of 2-pyrrolidone. Fundamental differences in the course of activated and nonactivated polymerization had been found. The optimum polymerization rate of the nonactivated polymerization was obtained at 50°C and that of the activated one at 40°C. An increase of the particle number in course of nonactivated polymerization could be ascribed to the formation of new growing center which were formed due to a simultaneously proceeding disproportionation reaction of 2-pyrrolidone anion with amide group of the monomer or of the polymer. To the contrary, with the N-benzoyl-2-pyrrolidone activated polymerization of 2-pyrrolidone, a decrease of the number of macromolecules with time had been observed. This was evidently due to condensation reactions of terminated by N-acyllactam groups.

Choi (1976) studied the polymerization of 2-pyrrolidone in the presence of an alkaline as a polymerization catalyst, a complex of a halogenated lactam (Figure 11) and a Lewis acid of the formula MX_a as activators (wherein m = 2 or 3; n = 5 to 11; M = metal of Group IIIA, IVA, VA, VIA or IVB of the Periodic Table; a = the valence of M; and X and X′ = chlorine or bromine independently).

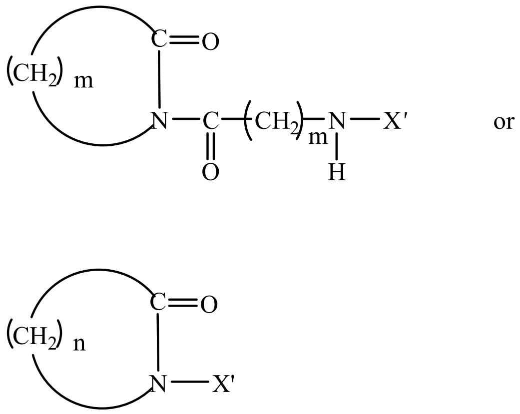


Figure 11 Formula of complexes of a halogenated lactam.

Source: Choi (1976)

Bacskai (1977) studied the process of polymerizing 2-pyrroldione in the presence of an alkaline polymerization catalyst and a polymerization promoted by a derivative of a sulfonic acid selected from among sulfonic acid anhydride, N-sulfonyl-2-pyrroldione and sulfonyl halide.

In addition, Roda *et al.* (1977a) studied effect of activating agents on the anionic polymerization of 2-pyrrolidone using N-potassium -2-pyrrolidone as an initiator in a 1:1 ratio with N-acetyl-, N-benzoyl- and N-pivaloyl-2-pyrrolidone, N-benzoyl-8-octanelactam or N-benzoyl-12-dodecanelactam as activators in the heterogeneous stage of the polymerization process under isothermal conditions and

Roda *et al.*,1977b studied γ-butyrolactone/potassium tertiary butanolate at temperature between 30 and 78ºC.

Copolymers of 2-pyrroldione and C_7-C_{12} lactams were provided in solids form, at relatively high rates and molecular weights by polymerization in the presence of alkaline catalysts and carbon dioxide, by the inclusion of an auxiliary catalyst and a copolymerization promoter comprising certain onium salt and N-acyl lactams, respectively (Bacskai, 1978a). In the preparation of a catalyst for the alkaline catalyzed polymerization of pyrrolidone, an alkali metal alkoxide was contacted with excess 2-pyrrolidone and the product alcohol was removed by passing an inert gas through the reaction mixture at high temperature (Bacskai, 1978b).

The modified anionic polymerization methods of 2-pyrrolidone using crown ether catalyst system were studied. Crown ethers are macrocyclic polyethers which are neutral compounds containing 4-20 oxygen atoms each separated from the next by two or more carbon atoms. Macrocyclic polyethers have been found to form stable complexes with salts of alkali metals, other metals and ammonium salts. The macrocyclic polyethers are believed to form salt-polyether complexes in which the cation is encircled by the oxygen atoms of the polyether ring and is held there by the electrostatic attraction between the cations and the negative ends of the CO dipoles. The complex is believed to be stabilized by encirclement of the catalyst by the oxygen atoms of the polyether ring and other stoichiometric complexes, depending upon the diameter of the cation and the diameter of the macrocyclic polyether ring. The 18-crown-6 and 15-crown-5 are generally preferred for their reported affinity for K^+ and Na^+ respectively. Thus, the choice of a particular polyether as the optimum activator for the anionic polymerization can vary with the particular cationic species of the catalyst, but can be determined by those having ordinary skill in the art by molecular diameter considerations and by routine trial-and-error optimization tests. Activated the anionic polymerization of lactam in the presence of crown ether such as 18-crown-6, dibenzo-18-crown-6, dicyclohexyl-18-crown-6, 15-crown-5 and diglyme having the ability to form stable complexes with salts of 2-pyrrolidone was investigated (Collman, 1978).

In 1979, Bacskai studied processes of copolymerization 2-pyrroldione and caprolactam to yield a copolymer which can be formed into useful filaments. The processes were characterized by using both crown ether and an N-acyl pyrrolidone as activators and using a limited copolymerization temperature range.

Water is one of the most effective and most widely used inhibitors for the absolute majority of polymerizations proceeding by the anionic mechanism. In 1979, Chuchma *et al*. carried out a preliminary investigation of the effects of water on the activated anionic polymerization of 2-pyrrolidone. The results of polymerization at 45°C showed that conversion decreases with increasing content of water causing a decrease in the concentration of initiation due to the equilibrium neutralization between potassium-2-pyrrolidone, water and 2-pyrrolidone to a decrease in the concentration of activator caused by the alkaline hydrolysis of the latter.

A high molecular weight and high yield polymer for the preparation of membranes for separation purposes were obtained by the anionic polymerization of 2-pyrrolidone through the use of CO_2 /potassium pyrrolidonate catalyst system. The effects of the quantity of CO_2, the potassium pyrrolidonate catalyst, the reaction temperature on the yield and molecular weights of the polyamide-4 were studied. At reaction temperature of 50°C and reaction time of 120 hours produced a polymer having the highest yield of 50.9% with intrinsic viscosity of 4.42 dl/g (Huang *et al.*, 1981).

There was a method of forming pure white polymers of 2-pyrroldione when using SO_2 as the activator. The method involved the use of the rubidium or cesium salt of 2-pyrrolidone as the alkaline catalysts in place of the sodium or potassium salt customarily used which caused the formation of yellow polymer (Barnes, 1981; Barnes and Barnes, 1981a).

A process for forming polymers of 2-pyrrolidone in pellet form via bulk polymerization was disclosed. Polymerization accelerators were employed to markedly shorten the polymerization time thus making possible a compact continuous polymerization apparatus which produced pellets of high polymer content requiring no further polymerization. The pellets were formed by forcing the polymerizing mixture through small tubes to form rods of polymer which then cut into short lengths (Barnes and Barnes, 1981b).

Costa *et al.* (1981) studied the anionic polymerization of 2-pyrrolidone in bulk and suspension under isothermal conditions. After a discussion about the disadvantages of the bulk process carried out by using N-potassium-2-pyrrolidone as initiator and N-acetyl-ε-caprolactam as activator, a possible alternative way was proposed on the basis of the suspension polymerization initiated by N-potassium-2-pyrrolidone and activated by silicon tetrachloride.

Vishvanath *et al.* (1981) studied the effect of transient cooling of the polymerization mixture on the anionic polymerization of 2-pyrrolidone initiated with potassium 2-pyrrolidone prepared in situ and activated with N-acetyl-2-pyrrolidone. It was found that an increase in conversion and molecular weight was controlled by the time interval between the inset of polymerization and transient cooling of the mixture, unlike an isothermal arrangement of the experiment.

In 1982, Bacskai studied the effect of onium salts and crown ethers on the pyrroliodne-K/CO_2 (py-K/CO_2) catalyzed polymerization of 2-pyrrolidone. The reaction sequence leading to the active polymerization catalyst, formed from 2-pyrrolidone, KOH, CO_2 and tetramethylammonium chloride (TMAC), was shown in Figure 12.

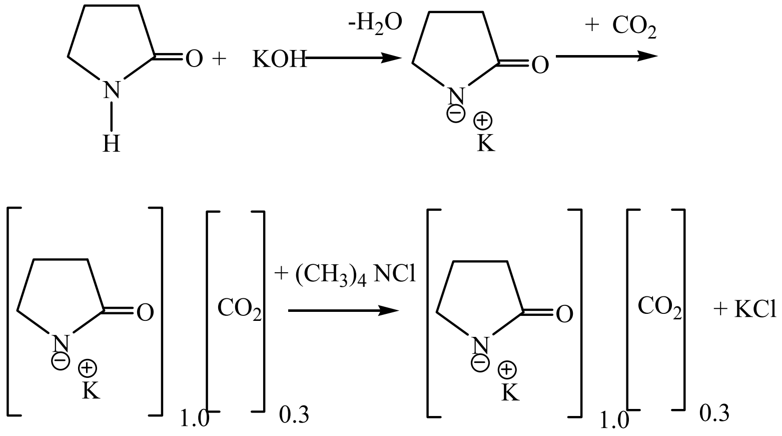


Figure 12 Mechanism of anionic polymerization of 2-pyrrolidone, KOH, CO_2 and tetramethylammonium chloride (TMAC).

Source: Bacskai (1982)

It was found that using py-K/CO_2 + TMAC catalyst, higher conversions and molecular weight were obtained than with py-K/CO_2 alone. The polymerization catalyzed by py-K/CO_2 and various crown ethers was also studied. The results showed that certain crown ethers have a large rate accelerating and molecular weight increasing effect on the polymerization. The effect was similar to that observed with the onium salts and was consistent with the tight complexation of the potassium cation by crown ether which leaded to a free more reactive pyrrolidone anion. This work, 18-crown-6 gave the largest rate acceleration with maximum conversion and molecular weight at crown ether to py-K/CO_2 ratio of approximately 0.7.

Daniel *et al.* (1982) studied the polymerization of 2-pyrrolidone initiated with potassium salt (2-oxo-1-pyrrolidinylpotassium) and accelerated by the presence of CO_2. For the optimal concentration of ≈ 5 mol% potassium salt and 0.5 mol% of CO_2, the most suitable polymerization temperature was found to range between 45 and 55°C.

Roda *et al.* (1983) studied the effect of addition of quaternary ammonium halides in the nonactivated polymerization of 2-pyrrolidone initiated with the potassium salt of 2-pyrrolidone. The polymerization was accelerated upon small additions of Me_4NCl, whereas addition of Et_4NBr and Bu_4NBr had a retardation effect and reduced the molecular weight of polymer. The formation of the corresponding quaternary ammonium salts of 2-pyrrolidone in situ was analogous to the formation of the pure salts in their synthesis from the ammonium halides. The nonactivated polymerization of 2-pyrrolidone initiated with the pure tetramethylammonium salt of 2-pyrrolidone showed all kinetic features of other nonactivated polymerizations of 2-pyrrolidone. High yields and molecular weights of poly (2-pyrrolidone) and a higher number of growth centers during polymerization were evidence of a higher dissociation of tetramethylammonium salt of 2-pyrrolidone dissolved in 2-pyrrolidone in comparison with potassium salt of 2-pyrrolidone as the initiator. The activation energy of polymerization activated with tetramethylammonium salt of 2-pyrrolidone ($47.9\ kJ \cdot mol^{-1}$ in the range 35 to 55°C) and the reaction order with respect to tetramethylammonium salt of 2-pyrrolidone (1.3 at 45°C) were determined.

Polymerization of 2-pyrrolidone with potassium salt of 2-pyrrolidone as an initiator at temperature 25-70°C was investigated using 1-(1-pyrrolin-2-yl)-2-pyrrolidone (Sysel *et al.*,1983) and studied the polymerization of 2-pyrrolidone using N-iminolactam such as 1-(1-pyrrolin-2-yl)-2-pyrrolidone, 1-(1-azacyclohept-1-en-2-yl)-2-pyrrolidone, 1-(1-azacyclonon-1-en-2-yl)-2-pyrrolidone, 1-(1-azacyclohept-en-2-yl)-1-azacycloheptan-2-one and 1-(phenyliminomethyl)-2-pyrrolidone (Brozek *et al.*, 1988) as accelerators respectively.

In 1989, Huang and Rhim investigated in detail the synthesis of polyamide-4 by the anionic polymerization of 2-pyrrolidone at 40°C via CO_2/KOH and CO_2 /KOH/18-crown-6 ether catalyst for membrane separation purposes. Under the reaction conditions of reaction temperature of 40°C, reaction time of 24 hours, CO_2 quantity of 60 sec at a constant flow rate of 3.5 L/min and 1.98 mol% crown ether, a maximum yield of 95.36% of polyamide-4 polymer with intrinsic viscosity of 3.28 dl/g was obtained.

An amino acid of 4-aminobutyric acid was added to the polymerization system of 2-pyrrolidone by the action of the anionic polymerization catalyst of calcium hydroxide and polymerization initiating carbon dioxide. In this way, it is possible to obtain a high molecular weight of 2-pyrrolidone polymer which was useful as fibers and plastic materials. (Masao and Yoshiyuki, 1993)

4. Biodegradation Studies

All nylons are susceptible to hydrolysis, especially by strong acid. When being molded, nylon must be dried to prevent hydrolysis in the molding machine barrel since water at high temperatures can also degrade the nylon.

In addition, proteins that contain amide linkages (-CO-NH-) from α-amino acids are found readily degraded by proteolytic enzymes, however, very little is actually known about the biodegradation of amide linkages present in the main polymer chain of polyamides or nylons. Recently, some microorganisms that can degrade polyamide had been reported. *Flavobacterium* sp.K172 was able to hydrolytically degrade 6-aminohexanoic acid cyclic dimmer, but cannot degrade nylon-6 polymers. The wild strain K172 harbors three kinds of plasmid, pOAD1 (26.2 megadaltons), pOAD2 (28.8 megadaltons) and pOAD3 (37.2 megadaltons) were studied by Negoro *et al.* (1980, 1983) and Kakudo *et al.* (1993).

The polyamide-4 can be a bio-based biodegradable polymer produced from renewable resources using biomass, as are polylactic acids, because polyamide-4 is a linear polymer of 4-aminobutyric acid and because 4-aminobutyric acid is produced by some bacteria such as marine Pseudomonad from biomass (Mountfort *et al.,* 1992).

In 1994, it was found that a film of polyamide-4, obtained easily through the ring-opening polymerization of 2-pyrrolidone, was decomposed in the composted soil gathered from the Nagoya University Farm and disappeared within 4 months (Hashimoto *et al.*, 1994).

Lactobacillus sp. strain E1 catalyzed the decarboxylation of glutamate (Glu), resulting in a nearly stoichiometric release of the products gamma-aminobutyrate (GABA) and CO_2 (Higuchi *et al*, 1997).

White rot fungi strain IZU-154, *Phanerochaete chrysosporium* and *Trametes versicolor* were able to degrade nylon-6,6 under ligninolytic conditions (Deguchi *et al.*, 1997, 1998). In 2002, Hashimoto *et al.* proposed that the polyamide-4 portion in the blend films composed of polyamide-4 and polyamide-6 was degraded and completely disappeared within 4 months in two kinds of composted soils gathered from different university farms as well as pure polyamide-4 film reported previously. While the polyamide-6 portion remained unchanged even after the burial test for 15 months. Three species of microorganisms (i.e., ascomytous fungi) were isolated through the inoculation from the polyamide-4 film partially degraded in the soil on a medium containing polyamide-4 powder as a carbon source.

Different novel copolymers, ABA-type block copolymers composed of polyamide-4 as outer segments and polyoxyethylene as an inner segment and AB- and ABA-type block copolyamides containing polyamide-4 and another hydrophilic polyamide derived from a bicyclic lactam, were synthesized by the anionic ring-opening polymerization of 2-pyrrolidone using the corresponding acyllactam-type macromolecular activators. The degradation rate of both block copolymers containing polyamide-4 segments in a composted soil was found to decrease with increasing content of the second segments, although they were also hydrophilic and biodegradable (Hashimoto *et al*, 2004).

Linear and branched polyamide-4 were prepared by the ring-opening polymerization of 2-pyrrolidone. The polymerizations were carried out using benzoyl chloride, terephthaloyl dichloride, isophthaloyl dichloride, benzene-1,3,5-tricarbonyl trichloride and biphenyl-3,3',5,5'-tetracarbonyl tetrachloride as the initiators at various concentrations. The melting points of the polyamide-4 settled into the vicinity of 265°C with increasing molecular weight, however, obvious difference owing to branching could not be found. The tensile strength and tensile strain showed positive molecular weight dependence over the range measured. With the same degree of molecular weight, the tensile strength of the branched polyamide-4 tended to be larger than that of the linear polyamide-4. From these results, it made possible to improve the tensile strength by introducing branched structure into the polymerization-4 chains. Turning now to biodegradation test by an activated sludge, the polyamide-4 easily degraded regardless branched structure or linear structure. It was confirmed that the polyamide-4 was metabolized into carbon dioxide and nitrate by microbes in the activated sludge (Kawasaki *et al*, 2005).

Yamano *et al*. (2008) identified a biodegradation microorganism of polyamide-4, a linear polymer of 4-aminobutyric acid (GABA). They isolated polyamide-4 degrading bacteria, *Pseudomonas sp*. strains ND-10 and ND-11, from activated sludge. They found that polyamide-4 alone was readily biodegraded in activated sludge. These results suggested that the degrading bacteria produced extracellular hydrolytic enzymes that can degrade polyamide-4 to 4-aminobutyric acid.

MATERIALS AND METHODS

Materials

1. Chemicals

The following chemicals were obtained from commercial sources and used directly without further purification unless noted:

1.1 Acetone (Analytical reagent grade, Merck)

1.2 4-Aminobutyric acid or γ-aminobutyric acid, GABA (Analytical reagent grade, Fluka)

1.3 Chloroform (Analytical reagent grade, Merck)

1.4 1,4-Diaminobutane (Analytical reagent grade, Aldrich)

1.5 Benzoyl chloride (Analytical reagent grade, Aldrich)

1.6 Ethanol (Analytical reagent grade, Merck)

1.7 Ethyl ether, anhydrous (Analytical reagent grade, Mallinckrodt)

1.8 Enzymes; aspergillus oryzae (≥800 FAU/g), bacillus thermoproteolyticus rokko (50-100 units/mg protein), bromelain (3-7 units/mg protein), α-chymotrypsin (≥40 units/mg protein), proteinase K (≥30 units/mg protein), pepsin (3,200-4,500 units/mg protein), subtilisin carslberg (7-15 units/mg solid) and streptomyces griseus (≥3.5 units/mg solid, Sigma) and ficin (300-500 milk clotting units/mg, MP Biomedic)

1.9 Formic acid (Analytical reagent grade, APS Ajax Finechem)

1.10 Hydrochloric acid (Analytical reagent grade, APS Ajax Finechem)

1.11 *m*-Cresol (Analytical reagent grade, Aldrich) was filtered through qualitative no. 1 Whatman filter paper.

1.12 Methanol (Analytical reagent grade, Merck)

1.13 1-Methyl-2-pyrrolidone (Analytical reagent grade, Fluka)

1.14 Molecular sieves (4A beads, Aldrich)

1.15 1,4,7,10,13-Pentaoxacyclopentadecane, 15-crown-5 (Analytical reagent grade, Aldrich)

1.16 2-Pyrrolidone, Py (Analytical reagent grade, Aldrich) was dried overnight over molecular sieves 4A, and then distilled under reduced pressure (15 mmHg) at 180°C to remove the excess water before used.

1.17 Sodium (Aldrich) was used after removing impurities on the surface.

1.18 Succinyl chloride (Analytical reagent grade, Aldrich)

1.19 Toluene (Analytical reagent grade, Fisher)

1.20 Triethylamine (Analytical reagent grade, Fluka)

1.21 Poly-D-3-hydroxybutyrate, PHB, powder with a number-average molecular weight ($\overline{M}_n$) of 2.1×10^5 (Mitsubishi Gas Chemical) was passed through a 250 µm wire screen to have uniform particle size.

2. Instruments

2.1 Melting points

Melting points were taken using a Fisher Johns apparatus at the Department of Chemistry, Kasetsart University.

2.2 Polymer molecular weight determination

Weight average molecular weight ($\overline{M}_w$) of polyamide-4 or nylon-4 was calculated as followed: $[\eta] = 3.98 \times 10^{-4} \overline{M}_w^{0.77}$, where $[\eta]$ is the intrinsic viscosity (Bacskai, 1982). Viscosity of polyamide-4 was measured in an Ubbelohde type viscometer, Cannon No. 1B L279 at 30°C ± 0.05°C in a constant temperature bath, Polyscience Model 70. The relative viscosity (η_{rel}) and specific viscosity (η_{sp}) were determined in *m*-cresol at concentration of polyamide-4 (c) = 0.5 g/dl from $\eta_{rel} = t/t_o$ and $\eta_{sp} = (t/t_o)/t_o$, respectively, where t = efflux time of polyamide-4 solution and t_o = efflux time of *m*-cresol. Then intrinsic viscosity ($[\eta]$) was calculated from: $[\eta] = \left(2\left(\eta_{sp} - \ln \eta_{rel}\right)/c^2\right)^{1/2}$.

2.3 Spectroscopy

2.3.1 Infrared (IR): Infrared (IR) spectra were recorded in cm^{-1} as KBr pellets using FTIR Perkin-Elmer System 2000 instrument at Department of Chemistry, Kasetsart University, Bangkok, Thailand.

2.3.2 Nuclear Magnetic Resonance (NMR): All nuclear magnetic resonance (NMR) spectra were recorded on Varian Unity model Innova 400 MHz spectrometer with formic acid (HCOOH) and deuterated water (D_2O) as solvents at the Department of Chemistry, Kasetsart University. ^{1}H MNR chemical shift values (δ scale) were reported in parts per million (ppm) and the appearance peak at δ 8.00 ppm of <u>H-</u>CO in formic acid (HCOOH) is used as an internal standard. Spin multiplicity assignments are indicated using the following abbreviations: s for singlet, d for doublet, t for triplet, q for quartet, p for pentet and m for multiplet. ^{13}C NMR chemical shift values (δ scale) were also reported in parts per million (ppm) and the appearance peak at δ 170.00 ppm of <u>C</u>=O in formic acid is used as an internal standard.

2.4 Thermal analysis

The glass transition temperature (T_g) and the melt temperature (T_m) were measured with a differential scanning calorimeter (DSC) 220 (Seiki Scientific Instruments) using heating rate of 10°C/min. Indium was used as standard for temperature calibration and the measurements were made under a constant stream of nitrogen.

2.5 Degradation analysis

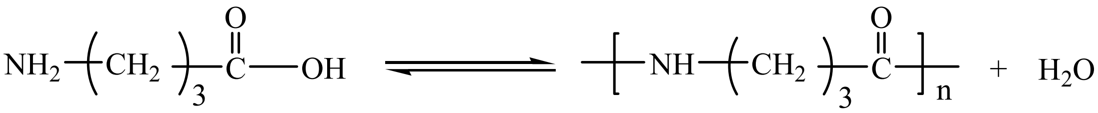
2.5.1 Biochemical oxygen demand (BOD): BOD test was determined with a BOD tester (OM8001A, Ohkura Denki Co, Tokyo, Japan) by the oxygen consumption method according to the JIS K 6950 at 25°C using a soil freshly obtained from a wooded area in Tsukuba city, Japan.

2.5.2 Total organic carbon (TOC): The enzymatic degradability by measuring the water soluble total organic carbon (TOC) was detected with a TOC-5000 Analyzer (Shimadzu, Japan).

Methods

1. Synthesis of polyamide-4

1.1 Direct polycondensation of γ-aminobutyric acid



$$NH_2\text{-}(CH_2)_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \rightleftharpoons \text{-}\!\left[NH\text{-}(CH_2)_3\text{-}\overset{O}{\overset{\|}{C}}\right]_n\!\text{-} + H_2O$$

γ -Aminobutyric acid, GABA

Polyamide-4

1.1.1 Melt polycondensation

A total of 5.15 g (50 mmol) γ-aminobutyric acid was added to a 100 ml two-necked flask equipped with stirrer. The reaction vessel was fitted with a distillation head carrying a thermometer and a short condenser. The condenser was positioned so that the lip of the delivery end directed the drip into the bent adapter which led the distillate into a receiver flask as shown in Figure 13. The polymerization was heated to 165, 175 and 185°C for 12 h by alternately between under continuous flow of nitrogen for 3 h and under reduced pressure for 1 h. At the end of the reaction period chosen, the reaction vessel was cooled down, and the white powder product of the original γ-aminobutyric acid which is still soluble in water was obtained.

400 MHz ^{1}H NMR (D_2O): δ 1.79 (pentet, $-CH_2-C\underline{H}_2-CH_2-$), 2.19 (triplet, $-C\underline{H}_2-CO-$), 2.91 (triplet, $-C\underline{H}_2-NH-$) and 4.67 ppm (D_2O).

Figure 13 Apparatus for melt polycondensation of γ-aminobutyric acid and anionic ring-opening polymerization of dehydrated 2-pyrrolidone.

1.1.2 Melt polycondensation in solution

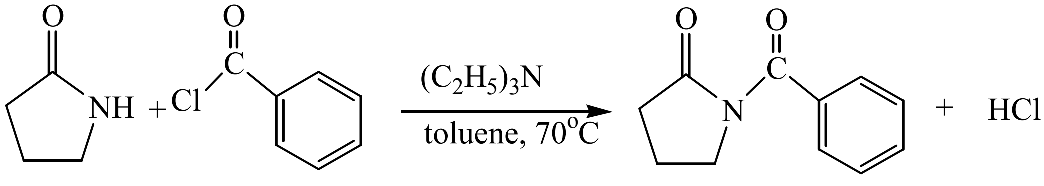
Modification of method reported by Han *et al.* (2003) was used to prepare polyamide-4. The mixture of 5.15 g (50 mmol) of γ-aminobutyric acid, 11.5 ml (120 mmol) of 1-methyl-2-pyrrolidone (NMP) and 5.4 ml (50 mmol) toluene were transferred into a round bottom flask fitted with a nitrogen inlet, a Dean-Stark trap fitted with a condenser, a thermometer and a magnetic stirrer as shown in Figure 14. The nitrogen sparkled reaction mixture was heated under reflux until the water was removed completely from the system by toluene-water azeotropic distillation. When it appeared that no addition water was being collected, toluene was quantitatively removed from the reaction system by distillation. Then the reaction mixture was kept at 165, 175 and 185°C under continuous flow of dry nitrogen for 6 h. At the end of the reaction period chosen, the reaction vessel was cooled down. The brown product of the original γ-aminobutyric acid dissolved in 1-methyl-2-pyrrolidone (NMP) was obtained.

400 MHz ^{1}H NMR (D_2O): δ 1.56 (pentet, -CH_2-$C\underline{H}_2$-CH_2-), 2.05 (triplet, -$C\underline{H}_2$-CO-) and 2.98 ppm (triplet, -$C\underline{H}_2$-NH-).

Figure 14 Azeotropic distillation apparatus with a Dean-Stark trap.

1.2 Ring-opening polymerization

1.2.1 Synthesis of N-benzoyl-2-pyrrolidone (BPy)



2-pyrrolidone

N-benzoyl-2-pyrrolidone (BPy)

N-benzoyl-2-pyrrolidone was synthesized using the procedure reported by Budin and Kralicek (1976). Into a 100 ml one-neck round bottom flask connected with a reflux condenser and magnetic stirrer was placed 7.8 ml (100 mmol) 2-pyrrolidone, 13.9 ml (100 mmol) triethylamine, 11.6 ml (100 mmol) benzoyl chloride and 30 ml toluene (Figure 15). The mixture was stirred and heated at 70°C for 3 h, cooled to room temperature and poured into a solution of 2.0 ml of 2.5 N HCl in 100 ml of water. At the end of the reaction, the yellow crystal was filtered and washed several time with water and dried in vacuum. After washing with diethyl ether and drying in vacuum at 30°C for 24 h, 12.06 g (63.81 %) of N-benzoyl-2-pyrrolidone**,** melting point (m.p.) = 85°C, was obtained.

400 MHz ^{1}H NMR ($CDCl_3$): δ 2.13 (p, 2H, $-CH_2-C\underline{H}_2-CH_2-$), 2.59 (t, 2H, $-C\underline{H}_2-CO-$), 3.95 (t, 2H, $-C\underline{H}_2-NH-$), 7.40 (t, 2H, Ar-$\underline{H}$ meta to CO), 7.51 (t, 2H, Ar-$\underline{H}$ para to CO) and 7.61 ppm (d, 2H, Ar-$\underline{H}$ ortho to CO). 400 MHz ^{13}C NMR ($CDCl_3$): δ 17.59 ($-CH_2-\underline{C}H_2-CH_2-$), 33.23 ($-\underline{C}H_2-NH-$), 46.47 ($-\underline{C}H_2-CO-$), 127.72 (2-$\underline{C}$-Ar ortho to CO), 128.84 (2-$\underline{C}$-Ar meta to CO), 131.84 (-$\underline{C}$-Ar para to CO), 134.30 (-CO-$\underline{C}$-Ar), 170.64 (-NH-$\underline{C}$O-Ar) and 174.48 ppm ($-NH-\underline{C}O-CH_2-$). FT-IR (KBr): ν_{max} 3054 ($\underline{C-H}$ stretch, aromatic), 2965, 2898 ($\underline{C-H}$ strectch, methylene $-CH_2-$), 1743 (-N-$\underline{C=O}$), 1663 (Ar-$\underline{C=O}$) and 1474 cm^{-1} ($\underline{C=C}$ ring strect).

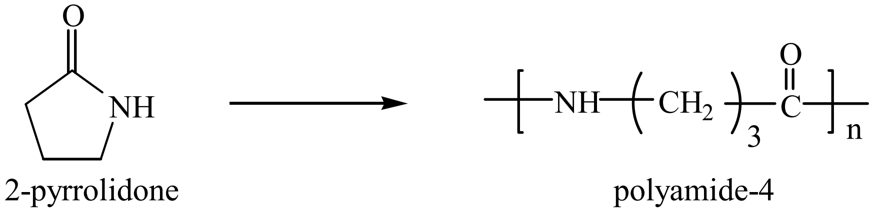
Figure 15 Apparatus for N-benzoyl-2-pyrrolidone synthesis.

1.2.2 Dehydration of 2-pyrrolidone

2-Pyrrolidone was dehydrated prior to polymerize as follows. 2-Pyrrolidone (Py) was dried overnight over molecular sieve 4A, filtered and transferred into an two-neck round bottom flask fitted with a two plug value with one outlet connected to a nitrogen supply and the other outlet connected to the vacuum pump as shown in Figure 16. The reaction vessel was kept at 100°C for 2 h under reduced pressure and dehydrated 2-pyrrolidone was obtained.

Figure 16 Apparatus for dehydration of 2-pyrrolidone.

1.2.3 Anionic ring-opening polymerization



A modification of the method reported by Budin and Kralicek (1976) was used to prepare polyamide-4 from 2-pyrrolidone. All anionic ring-opening polymerizations were carried out by changing the apparatus from Figure 16 to Figure 13. The 100 ml two-neck round bottom flask was equipped with a magnetic stirrer, a thermometer, a nitrogen inlet and a short condenser. The condenser was fitted into a vacuum adapter, which is connected to receiver flask and, via heavy-walled rubber tubing, to a mercury manometer and hence to the trap and vacuum pump.

Anionic ring-opening polymerization of 2-pyrrolidone (Py) was carried out using N-sodium-2-pyrrolidone as an initiator and N-benzoyl-2-pyrrolidone (BPy) as an activator in the presence of 15-crown-5 by varying the mmol ratio of 2-pyrrolidone(Py): N-benzoyl-2-pyrrolidone (BPy): sodium (Na): 15-crown-5 as shown in Table 5. The polymerization was initiated by N-sodium-2-pyrrolidone which is prepared in situ by directed dissolution of the desired amount of 2-pyrrolidone (Py) and sodium (Na) at 60˚C under N_2 atmosphere (Figure 17). For example, 8.5 g of Py and 0.023 g of Na were weighed into the flask for Py:Na = 100:1 mmol ratio. After sodium was reacted completely, the mixture was cooled down to room temperature. Then, the desired amount of N-benzoyl -2-pyrrolidone and 15-crown-5 were added and the content was kept at the desired temperature and conditions. At the end of the polymerization, the mixture was washed with ethanol, filtered through a sintered glass funnel (F 4-5.5 µm) and dried under vacuum oven for 24 h. The white powder was dissolved in formic acid and precipitated in acetone followed by washing with water and methanol respectively. Finally, after drying under vacuum at 30^{o}C for 24 h, white powdered products were obtained and characterized.

400 MHz ^{1}H NMR ($HCOOH/D_2O$): δ 1.56 (pentet, $-CH_2-C\underline{H}_2-CH_2-$), 2.05 (triplet, $-C\underline{H}_2-CO-$) and 2.98 ppm (triplet, $-C\underline{H}_2-NH-$) and 400 MHz ^{13}C NMR ($HCOOH/D_2O$): δ 29.06 ($-CH_2-\underline{C}H_2-CH_2-$), 37.25 ($-\underline{C}H_2-CO-$), 42.94 ($-\underline{C}H_2-NH-$) and 179.90 ppm ($-CH_2-\underline{C}O-$). The FT-IR (KBr): ν_{max} 3297 ($\underline{H-N}-C=O$), 3066 (overtone of $\underline{H-N}-C=O$ at 1541 cm^{-1}), 2958, 2874 ($-\underline{CH_2}-$), 1636 ($H-N-\underline{C=O}$), 1541 ($\underline{H-N}-C=O$) and 1414 cm^{-1} ($-\underline{C-N}-CH_2-$).

Table 5 Conditions for synthesis of polyamide-4 from 2-pyrrolidone by anionic ring-opening polymerization.

Sample code	2-Py (mmol)	BPy (mmol)	Na (mmol)	15-crown-5 (mmol)	Temp (˚C)	Condition
$N_1C_{0.5}T_6$	100	1	1	0.5	60	12 h by alternating between N_2 atmosphere for 3 h and under reduced pressure for 30 min
$N_2C_{0.5}T_6$			2			
$N_3C_{0.5}T_6$			3			
$N_3C_1T_3$	100	1	3	1	30	24 h by alternating between N_2 atmosphere for 3 h and under reduced pressure for 1 h
$N_1C_0T_4$	100	1	1	0	40	
$N_1C_1T_4$				1		
$N_1C_2T_4$				2		
$N_1C_3T_4$				3		
$N_2C_0T_4$	100	1	2	0	40	
$N_2C_1T_4$				1		
$N_2C_2T_4$				2		
$N_2C_3T_4$				3		
$N_3C_0T_4$	100	1	3	0	40	
$N_3C_1T_4$				1		
$N_3C_2T_4$				2		
$N_3C_3T_4$				3		
$N_3C_1T_5$	100	1	3	1	50	

N_x = x mmol of sodium

C_y = y mmol of 15-crown-5

T_z = temperature at z

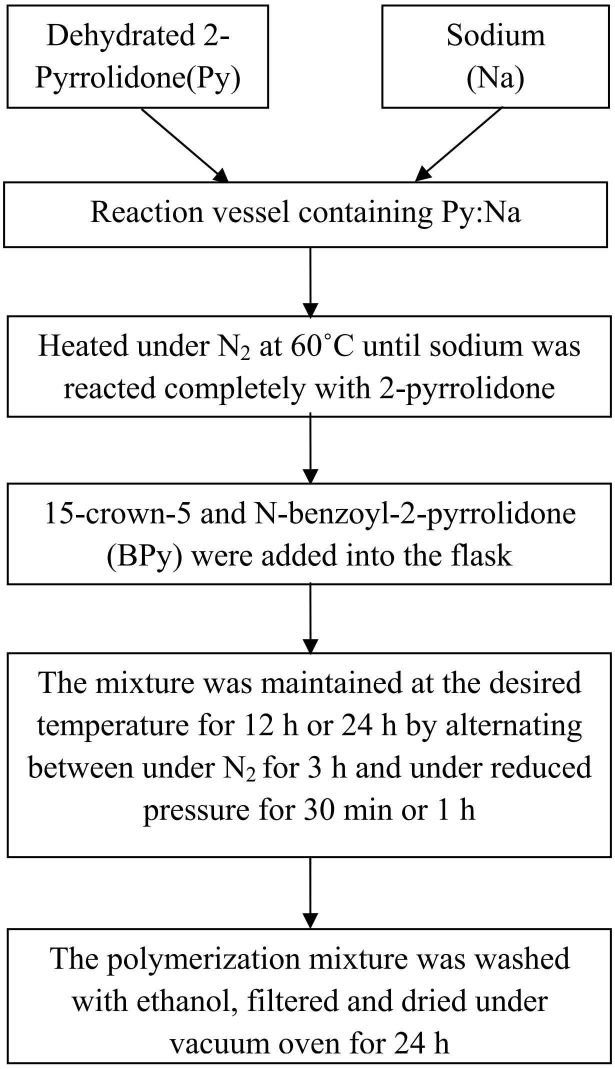
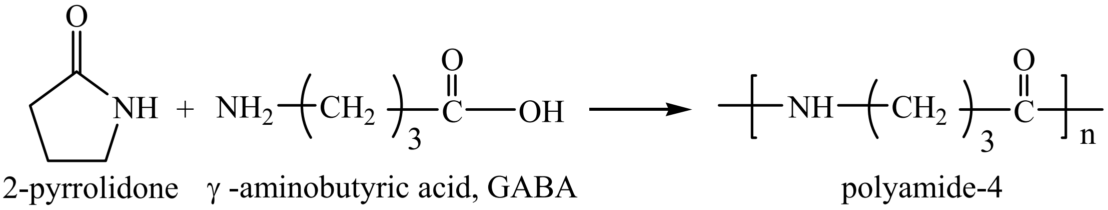


Figure 17 Anionic ring-opening polymerization of 2-pyrrolidone.

1.2.4 Copolymerization of 2-pyrrolidone and γ-aminobutyric acid



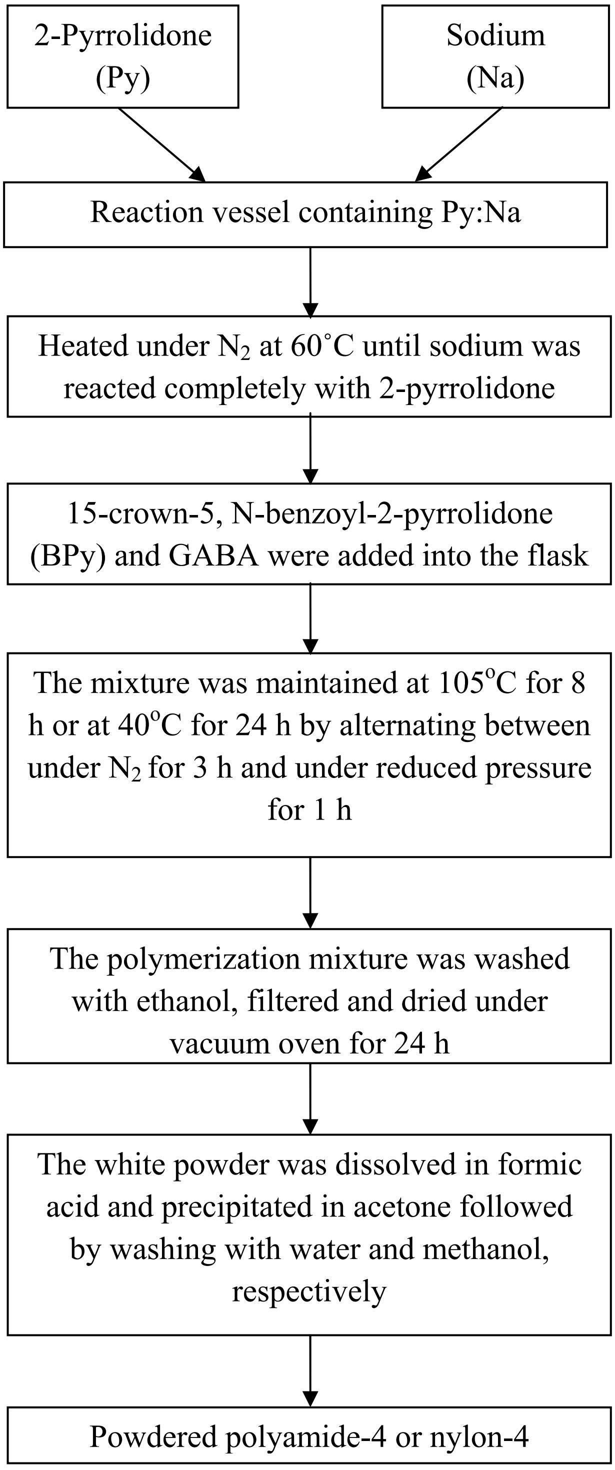
The procedure was essentially the same as previously described for anionic ring-opening polymerization of 2-pyrrolidone with the additional amount of γ-aminobutyric acid as shown in Figure 18. Copolymerization of 2-pyrrolidone (Py) and γ-aminobutyric acid were carried out using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone (BPy) as activator in the presence of 15-crown-5 by varying the mmol ratio of 2-pyrrolidone(Py): γ-aminobutyric acid: N-benzoyl-2-pyrrolidone (BPy): sodium (Na): 15-crown-5 as shown in Table 6.

400 MHz ^{1}H NMR (HCOOH in D_2O): δ 1.56 (pentet, $-CH_2-C\underline{H}_2-CH_2-$), 2.05 (triplet, $-C\underline{H}_2-CO-$) and 2.98 ppm (triplet, $-C\underline{H}_2-NH-$) and 400 MHz ^{13}C NMR (HCOOH in D_2O): δ 29.25 ($-CH_2-\underline{C}H_2-CH_2-$), 37.47 ($-\underline{C}H_2-CO-$), 43.14 ($-\underline{C}H_2-NH-$) and 180.10 ppm ($-CH_2-\underline{C}O-$). The FT-IR (KBr): ν_{max} 3297 ($\underline{H-N}-C=O$), 3066 (overtone of $\underline{H-N}-C=O$ at 1541 cm^{-1}), 2958, 2874 ($-\underline{CH_2}-$), 1636 ($H-N-\underline{C=O}$), 1541 ($\underline{H-N}-C=O$) and 1414 cm^{-1} ($-\underline{C-N}-CH_2-$).

Table 6 Copolymerization of 2-pyrrolidone and γ-aminobutyric acid having mmol ratio of Py:BPy:Na:Crown = 100:1:3:2.

Sample code	GABA (mmol)	Temp (˚C)	Condition
$N_3C_2G_1T_4$	10	40	24 h by alternating between N_2 atmosphere for 3 h and under reduced pressure for 1 h
$N_3C_2G_2T_4$	20		
$N_3C_2G_3T_4$	30		
$N_3C_2G_1T_{10}$	10	105	8 h by alternating between N_2 atmosphere for 3 h and under reduced pressure for 1 h
$N_3C_2G_2T_{10}$	20		
$N_3C_2G_3T_{10}$	30		

N_x = x mmol of sodium
C_y = y mmol of 15-crown-5
G_h = h mmol of γ-aminobutyric acid
T_z = temperature at z



Heated under N_2 at 60˚C until sodium was reacted completely with 2-pyrrolidone

15-crown-5, N-benzoyl-2-pyrrolidone (BPy) and GABA were added into the flask

The mixture was maintained at $105^{o}C$ for 8 h or at $40^{o}C$ for 24 h by alternating between under N_2 for 3 h and under reduced pressure for 1 h

The polymerization mixture was washed with ethanol, filtered and dried under vacuum oven for 24 h

The white powder was dissolved in formic acid and precipitated in acetone followed by washing with water and methanol, respectively

Figure 18 Copolymerization of 2-pyrrolidone and γ-aminobutyric acid.

2. Synthesis of polyamide-4,4

2.1 Solution polycondensation

Modification of method reported by Holland and Hay (2001) was used to prepare polyamide-4,4 by solution polymerization. A solution of 2 ml (20 mmol) of 1,4-diaminobutane in 25 ml of water was placed into an explosion-proof blender (Waring Commercial Laboratory Blender Model 32BL79). After turning the blender on to the maximum speed, a solution of 2.2 ml (20 mmol) of succinyl chloride in 50 ml of chloroform was added rapidly (within 15 sec) and kept at the same speed for another 2 min. The blender was turned off. The yellow powder was filtered, washed with 1:1 v/v of methanol: water and dried in vacuum at 30^{o}C for 24 h. 1.94 g (57.0%) of polyamide-4,4, $\overline{M}_w = 6436$ was obtained.

The FT-IR (KBr): ν_{max} 3297 ($\underline{\text{H-N}}$-C=O), 3066 (overtone of $\underline{\text{H-N}}$-C=O at 1541 cm^{-1}), 2958, 2874 (-$\underline{CH_2}$-), 1636 (H-N-$\underline{\text{C=O}}$), 1541 ($\underline{\text{H-N}}$-C=O) and 1414 cm^{-1} (-$\underline{\text{C-N}}$-CH_2-).

2.2 Interfacial polymerization

Modification of method reported by Holland and Hay (2001) was used to prepare polyamide-4,4 by interfacial polymerization. A solution of 2.2 ml (20 mmol) of succinyl chloride in 50 ml of chloroform was placed into a 100 ml beaker and a solution of 2 ml (20 mmol) of 1,4-diaminobutane in 25 ml of water was carefully run on to the top of the succinyl chloride solution. A polyamide-4,4 film is immediately formed at the interface and can be pulled out from the center with a tweezers and wound on a glass rod. The product was washed with 1:1 v/v of methanol: water and dried in vacuum at 30^{o}C for 24 h., 0.01 g (0.29%) of polyamide-4,4 was obtained.

3. Degradation of polyamide-4 and polyamide-4,4

3.1 Biochemical Oxygen Demand (BOD) Test

Degradation of polyamide-4 and polyamide-4,4 was determined by the oxygen consumption method according to the JIS K 6950 (ISO 14851) at 25°C using a soil freshly obtained from a wooded area in Tsukuba City. The incubation medium contained the following (mg/L): K_2HPO_4, 217.5; KH_2PO_4, 85.0; Na_2HPO_4, 260.5; NH_4Cl, 25.0; $CaCl_2.2H_2O$, 36.4; $MgSO_4.7H_2O$, 22.5; $FeCl_3.6H_2O$, 0.25 (pH = 7.4). The concentration of polymers: powdered poly-D-3-hydroxybutyrate (PHB), powdered polyamide-4 ($N_3C_1T_4$, $\overline{M}_w = 6910$ and $N_3C_2T_4$, $\overline{M}_w = 9233$) and powered polyamide-4,4 ($\overline{M}_w = 6436$) in the incubation medium was 100 mg/L.

3.2 Enzymatic degradation analysis

The enzymatic degradation of polyamide-4 ($N_3C_1T_4$, $\overline{M}_w = 6910$ and $N_3C_2T_4$, $\overline{M}_w = 9233$) was determined by measuring the water soluble total organic carbon (TOC) from the following enzymes: aspergillus oryzae, bacillus thermoproteolyticus rokko, bromelain, α-chymotrypsin, proteinase K, pepsin, subtilisin carslberg, streptomyces griseus and ficin. The reaction mixture (duplicate) was composed of 10 mg of polymer samples, 4.0 ml of 0.1 M phosphate buffer (pH 7), 0.1 ml of 0.5% (w/v) of octyl glucopyranoside and 1 ml of 1 mg/ml of enzymes. The mixture was incubated in a rotary shaker (180 rpm) at 37°C for 14 h. Samples were taken by withdrawing a 5.0 ml aliquot from the mixture at the start and after the mixture were kept at $37^{o}C$ for 14 h. The aliquot was then filtered through a Millipore filter (0.45 µm pore size). The TOC value of polyamide-4 after degradation was obtained after subtraction from the sample and enzyme control.

RESULTS AND DISCUSSION

Synthesis of polyamide-4 was chosen depending on both available monomers: γ-aminobutyric acid (GABA) and 2-pyrrolidone (Py). Although melt polycondensation is the most important means for polyamide synthesis and most polyamides are synthesized by this method, it does not receive much of attention for synthesis of polyamide-4. Attempts were made to synthesize polyamide-4 by melt polycondensation from γ-aminobutyric acid at temperature ranging from 165 to 185°C for 12 h by alternately between under continuous flow of nitrogen for 3 h and under reduced pressure for 1 h without catalysts or activator. Mostly, melt polycondensation is reasonably rapid and does not require catalysts or activator. The polycondensation reaction in polyamide synthesis is the polyamidation which involves the nucleophilic attack of an amino group on the carbonyl carbon atom as shown in Figure 19. Temperatures at 165 to 185°C were chosen because, in general, it is necessary to control melt polycondensation at the temperature range close to the melt temperature of the monomer (melt temperature of GABA =198°C) over a prolonged period. This external heating of melt polycondensation is needed to provide the activation energy of the reaction of condensation, the heat of fusion of monomer and that of the resulting polymer, and the heat of vaporization of the condensation by-product, water.

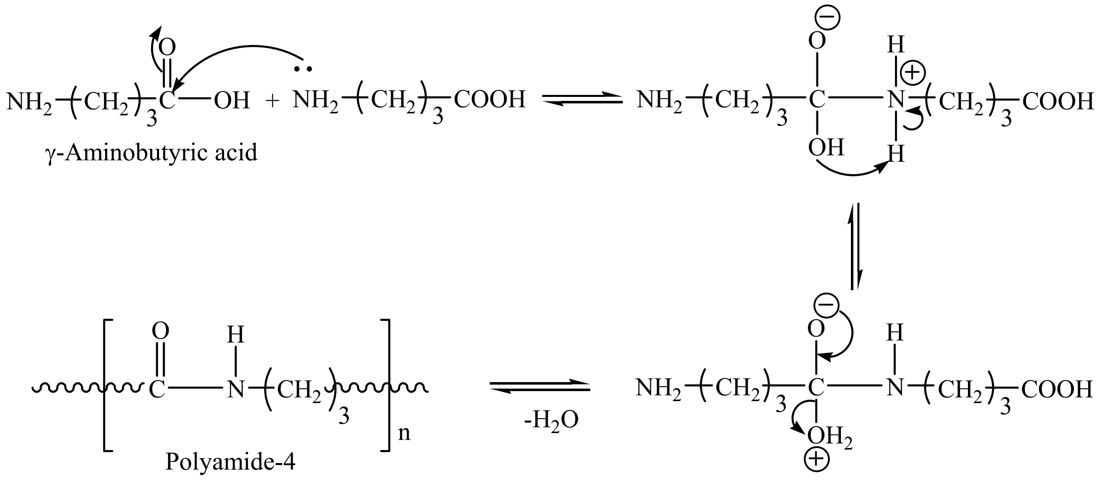


Figure 19 Mechanism of noncatalyzed melt polycondensation of γ-aminobutyric acid.

Characterization of the product obtained by ^{1}H NMR (Figure 20), solubility and biuret test showed that polyamide-4 synthesized from γ-aminobutyric acid by melt polymerization was unsuccessful. The results are in agreement with previously reported stating that melt polycondensation of γ-aminobutyric acid exclusively yield the cyclization products: butanolactam or 2-pyrrolidone (Sekiguchi and Coutin, 1992). This may be due to the prolonged exposure to heat of amide groups in the polymer, as a consequence, reverse reactions (hydrolysis) and side reactions (thermal and oxidative decompositions, monomer and oligomer cyclization, and large ring formation) are significantly predominant. Cyclization is thermodynamically controlled and, consequently, is favored at high temperature. The problem of cyclization lactam formation versus linear polycondensation becomes less important with the increased number of carbon atoms separating two amide groups.

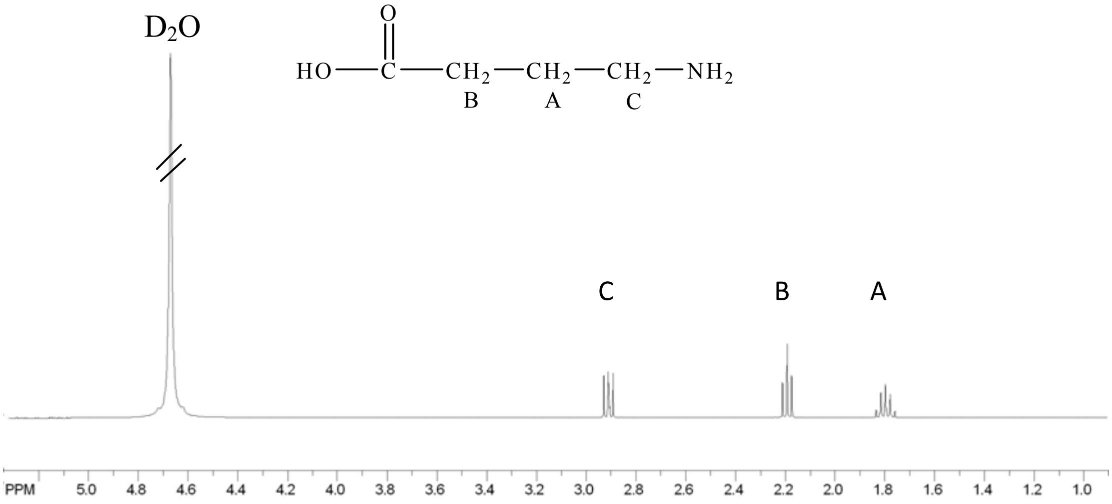


Figure 20 400 MHz ^{1}H NMR spectrum of γ-aminobutyric acid (D_2O).

Melt polycondensation was also carried out in solution. The use of solvent in melt polycondensation is beneficial because the polycondensation may be conducted under milder condition. Because high boiling, polar solvents such as amide solvents (dimethylformamide, DMF; dimethylacetamide, DMAc; and 1-methyl-2-pyrrolidone, NMP) are commonly used, the polarity of the polycondensation mixture can be raised which is an additional factor for lowering the working temperature. Synthesis of polyamide-4 from γ-aminobutyric acid by melt polycondensation in solution was carried out at temperature ranging from 165, 175 to 185°C under continuous flow of dry nitrogen for 6 h in toluene and NMP. Toluene (boiling point = 110°C) was chosen as solvent because azeotropic distillation of water can be easily removed together with toluene. It had been reported that polycondensation rate was accelerated in polar aprotic solvents with boiling points above 130°C which formed azeotropic with water. The rate increases as the boiling point increases due to the efficient removal of water. NMP having the boiling point = 202°C was used in order to accelerate of azeotropic water removal. Characterization of the product obtained by solubility and biuret test showed that polyamide-4 synthesized from γ-aminobutyric acid by melt polymerization in solution was unsuccessful. This may be due to condensation by product, water, could not be completely removed; NMP, an amide solvent, also tended to enter into amide exchange reactions with γ-aminobutyric acid; and polymer chain ends and others were subject to partial oxidation or decomposition (Sekiguchi and Coutin, 1992).

Thus ring-opening polymerization of lactams is in general preferred whenever the corresponding lactams are available. Ring-opening polymerization of lactams is a thermally controlled equilibrium process depending on the lactam-polyamide equilibrium and there is ceiling temperature which is varied with ring strain. Above the ceiling temperature only lactam is favored. Normally, the lactam ring is strongly resonance stabilized and the carbonyl activity is low. Fairly high temperature is needed, often above 200°C, although the ring-opening polymerization starts with a small amount of initiator through trans-acylation. One molecule acts as the acylating agent or as an electrophile while the other one acts as a nucleophile and undergoes the acylation (Figure 21).

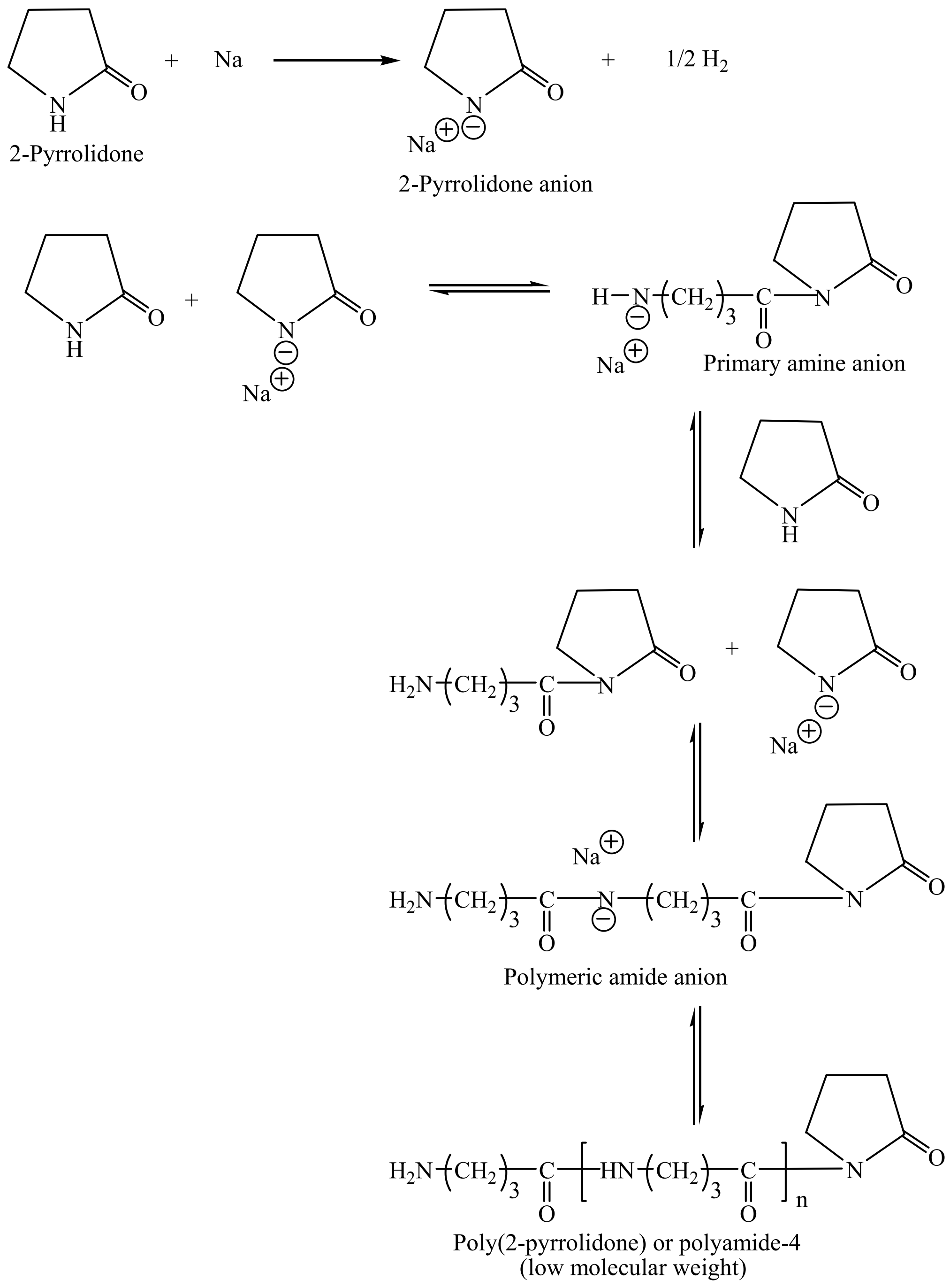


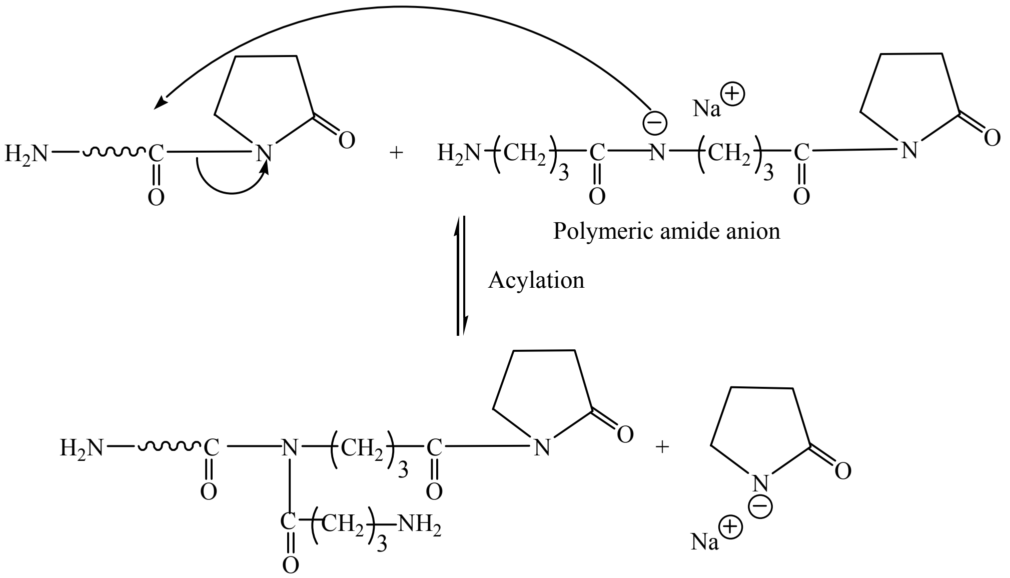
Figure 21 Anionic ring-opening polymerization of 2-pyrrolidone using sodium of 2-pyrrolidone as initiator.

Pyrrolidone, a five-membered ring lactam, polymerizes only at relatively low temperature and reconverts to monomer in the presence of polymerizing catalyst at higher temperature, e.g., 60 to 80°C (Sorenson *et al.*, 2001). As a result, anionic ring-opening polymerization of 2-pyrrolidone was carried out at the temperature range from 30-60°C in this study.

Polyamide-4 can be prepared by anionic ring-opening polymerization of 2-pyrrolidone using a strong base such as a sodium metal as an initiator as shown in Figure 21, but the polymeric amide anions can undergo acylation by acyllactam groups with ring-opening or with formation of 2-pyrrolidone anions (Figure 22). The acylation reactions are much faster than the initiation step. As a result, there are induction periods in the anionic ring-opening polymerization of 2-pyrrolidone.

In order to eliminate the induction period, an activator formed by lactam substituted on the nitrogen atoms by an electrophilic substituent or by the compounds which are able to form such a growing center in the reaction medium was added. It was found that the initial polymerization rate depends on the substituent of the activator (Roda *et al.*, 1977a). For the intrinsic viscosity (molecular weight of the polyamide obtained) at the beginning of the time interval (5 h) the order was found to be N-benzoyl-2-pyrrolidone < N-acetyl-2-pyrrolidone, but after 70 h N-acetyl-2-pyrrolidone < N-benzoyl-2-pyrrolidone. Therefore, N-benzoyl-2-pyrrolidone (BPy) was chosen as an activator for this study (Figure 23).

Acylation with formation of 2-pyrrolidone anion:



Acylation with ring-opening:

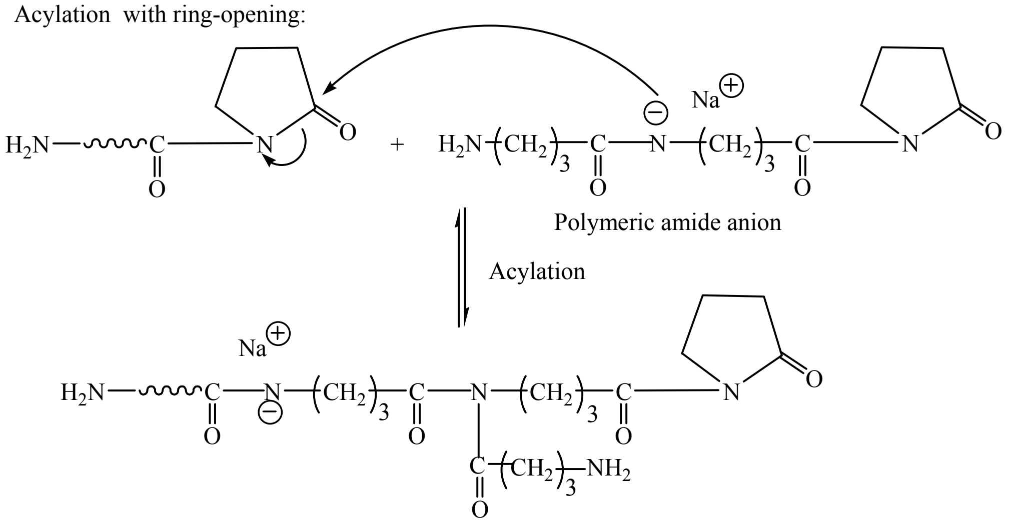


Figure 22 Acylation of polymer amide anions.

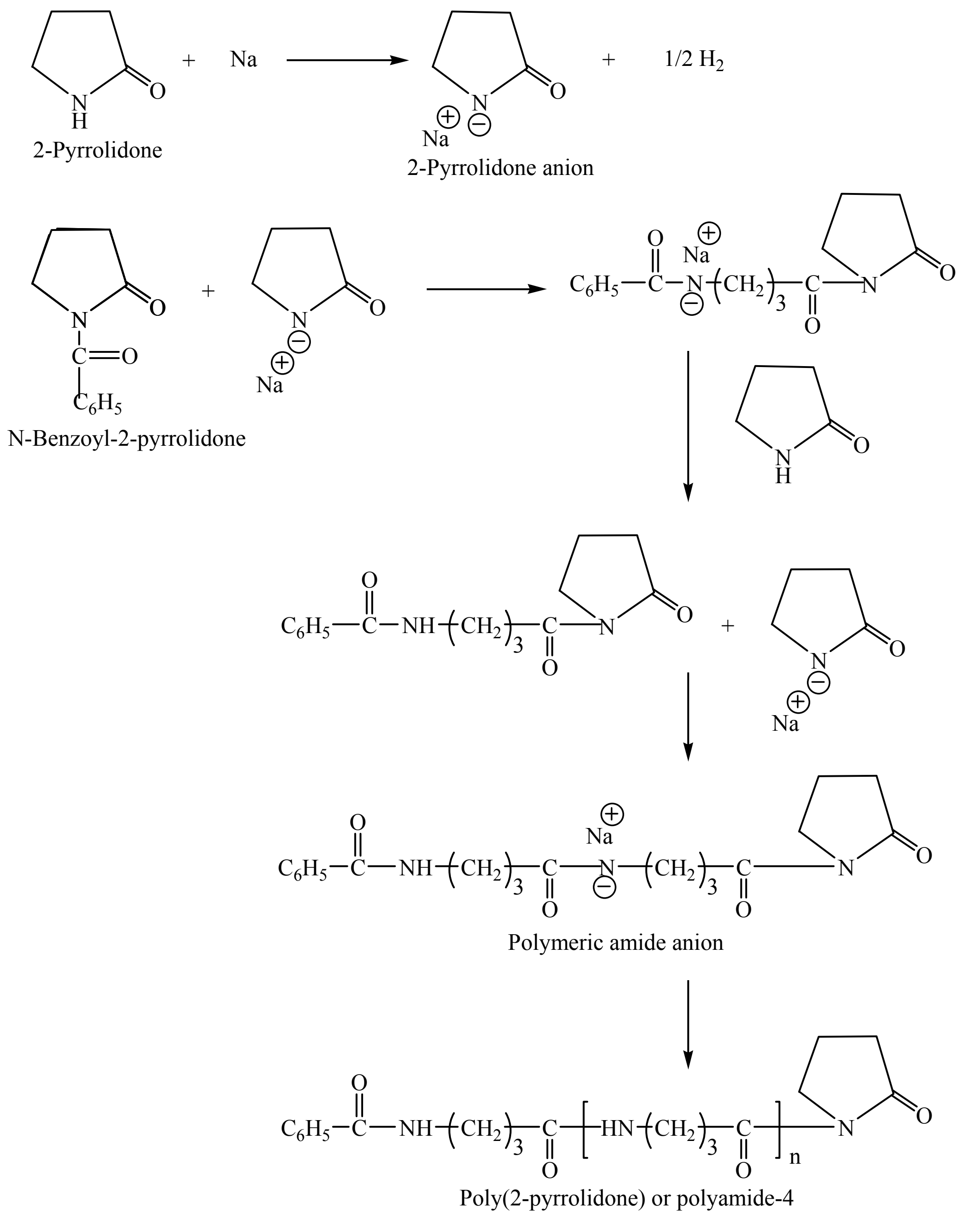


Figure 23 Anionic ring-opening polymerization using sodium of 2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator.

It has been found that free or naked anions cause large rate accelerations in many organic and polymerization reactions. Crown ether is heterocyclic compound that consists of a ring containing several ether groups. The most important property of macrocyclic ether or crown ether is its tendency to form complexes with alkali metal cations and the resulting "free" or "naked" anions cause large rate acceleration in many organic and polymerization. The stability of the polyether complexes depends primarily upon how well the cation fits into the polyether ring. It has been known that 15-membered ring crown ethers such as 15-crown-5 (cavity diameter 1.7-2.2 Å) can form the most stable complex with sodium cation (Na^+, ionic diameter 1.94 Å) (Buchanan *et al.*, 1987) as shown in Figure 24. Since the ring-opening polymerization of Py in this study was catalyzed by the most commonly and available used catalyst, sodium metal, 15-crown-5 was used as a cation complexing agent to complex with the sodium cation and kept it from associating with "free" 2-pyrrolidone anion (II) to enhance the ion separation. The ring strain of 2-pyrrolidone provides the overall thermodynamic driving force for the ring-opening polymerization. The initiation step involves the initial slow attack of sodium initiator to pull off the amide hydrogen from the 2-pyrrolidone to form N-sodium-2-pyrrolidone anion (NaPy)(I) as an initiator. Since "free" 2-pyrrolidone anion (II) is much more reactive than N-sodium-2-pyrrolidone (NaPy) (I). The "free" 2-pyrrolidone anion (II) then reacted with the carbonyl carbon of the activator used, N-benzoyl-2-pyrrolidone (IV) rather than reacted with the 2-pyrrolidone. N-benzoyl-2-pyrrolidone (IV) is much more susceptible to be attack by the "free" 2-pyrrolidone anion (II) because it is an imide, whereas 2-pyrrolidone is an amide. In addition, a much more stable amide anion (V) which is stabilized by the carbonyl group bonded to the nitrogen atom was formed if IV was opened when reacted with II; while a very unstable amide anion (III) which resisted the opening of the ring was formed when IV reacted with 2-pyrrolidone. At this point the initiation step of anionic ring-opening polymerization was complete and the propagation step begun. In this step, the amide anion produced in the initiation step extracted the amide hydrogen from another molecule of 2-pyrrolidone, then the pyrrolidone anion (II) was regenerated and the propagation step repeated to produce the polamide-4 (Figure 24).

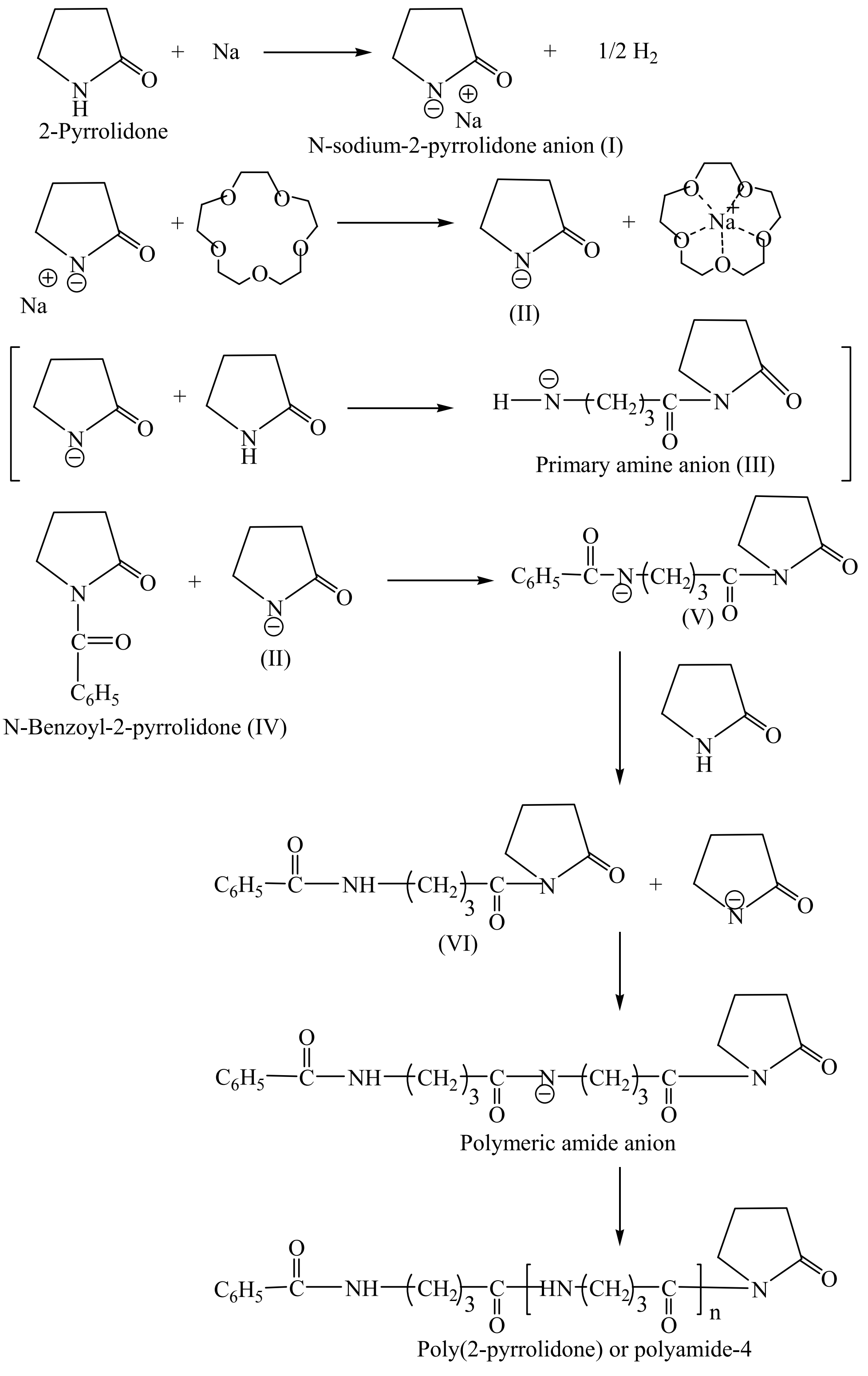


Figure 24 The mechanism of the anionic ring-opening polymerization of 2-pyrrolidone by using sodium of 2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator in the presence of 15-crown-5.

In this study, synthesis of polyamide-4 by anionic ring-opening polymerization of 2-pyrrolidone (Py) using N-sodium-2-pyrrolidone (NaPy) as initiator and N-benzoyl-2-pyrrolidone (BPy) as activator in the presence of 15-crown-5 was reported. Anionic ring-opening polymerizations of 2-pyrrolidone (Py) were carried out by varying sodium and 15-crown-5 from 1.0-3.0 mmol and 0.5-3.0 mmol respectively, while the mmol ratio of Py:BPy was held constant at 100:1 which are normally used in anionic ring-opening polymerization of cyclic amide or lactam with acyllactam as activator. Polymerizations were kept at 30, 40 or 50°C for 24 h under alternating between nitrogen atmosphere for 3 h and under reduced pressure for 1 h and at 60°C for 12 h under alternating between nitrogen atmosphere for 3 h and under reduced pressure for 30 min.

Since N-benzoyl-2-pyrrolidone (BPy) is not commercially available; it was synthesized in situ by acylation of pyrrolidone with benzoyl chloride in the presence of trimethylamine. Slightly yellow needle crystal of the obtained BPy was confirmed from ^{1}H NMR, ^{13}C NMR and FT-IR spectra as shown in Figures 25-27.

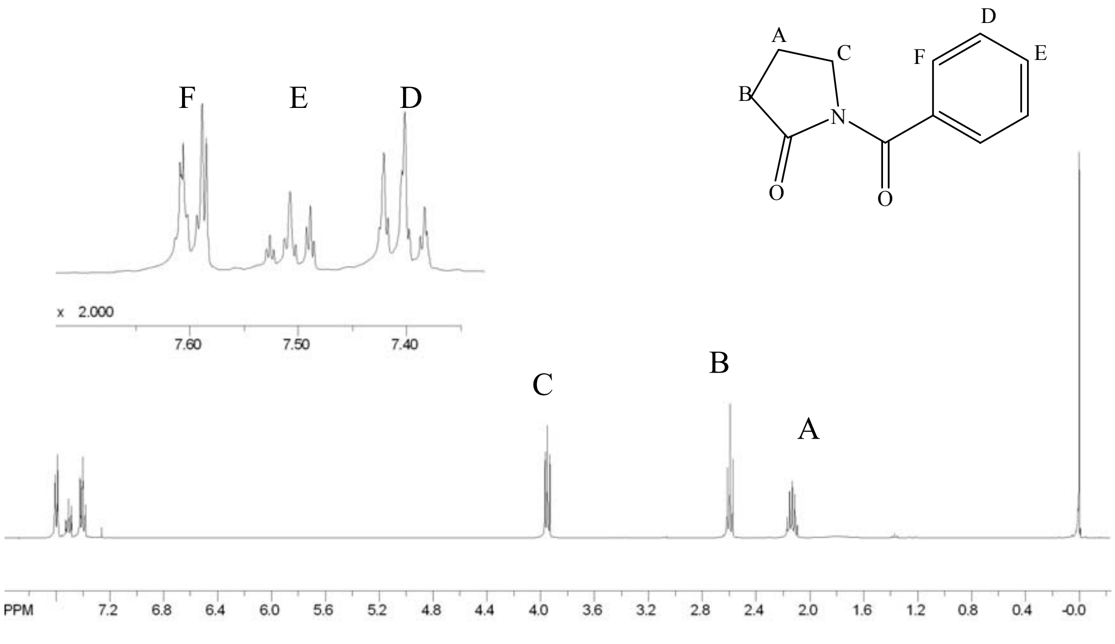


Figure 25 400 MHz ^{1}H NMR spectrum of N-benzoyl-2-pyrrolidone ($CDCl_3$).

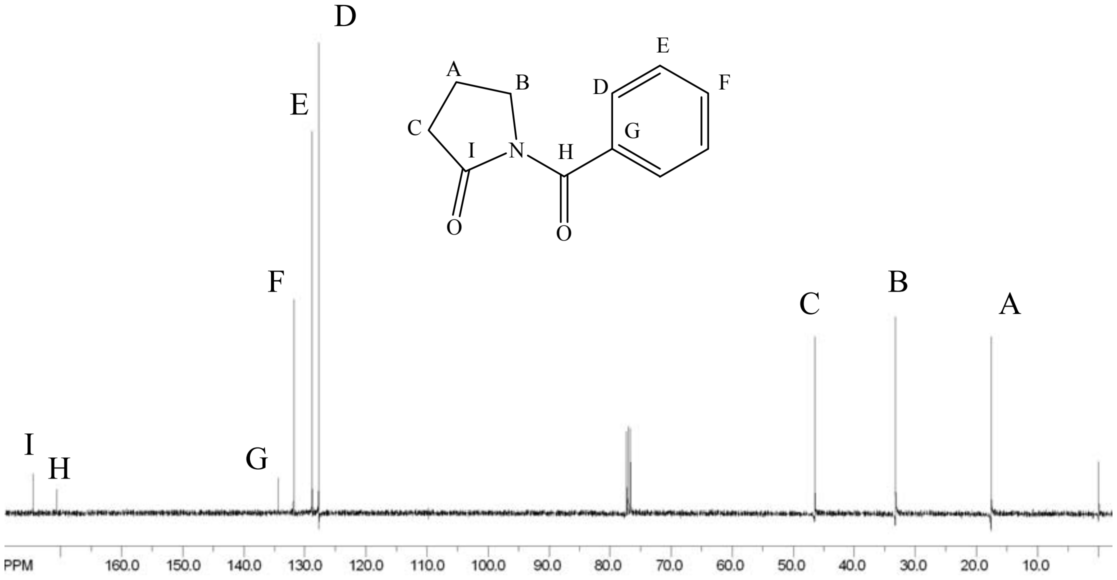


Figure 26 400 MHz ^{13}C NMR spectrum of N-benzoyl-2-pyrrolidone ($CDCl_3$).

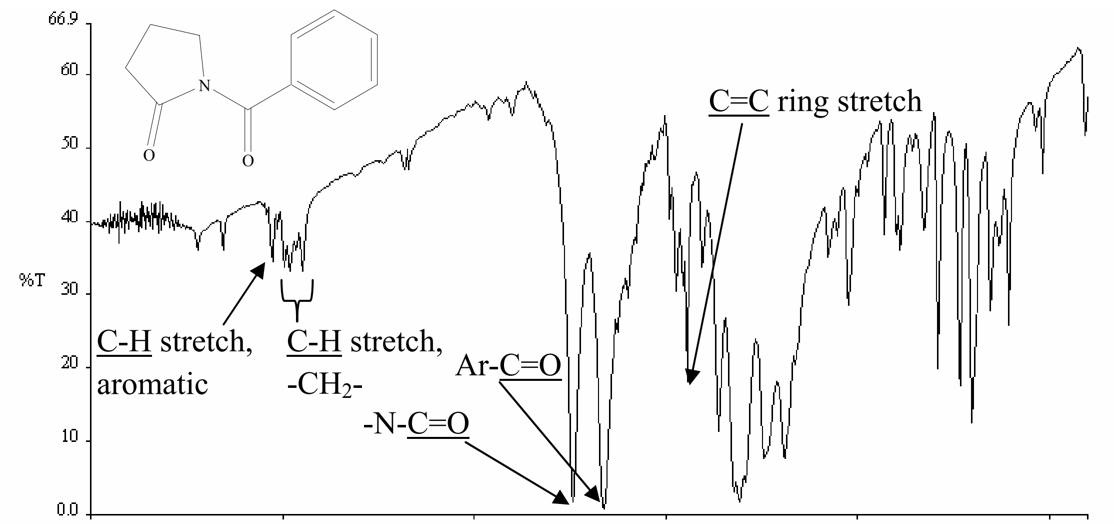


Figure 27 FT-IR spectrum of N-benzoyl-2-pyrrolidone (KBr).

Characterization of the products obtained by ^1H NMR, ^{13}C NMR and FT-IR showed the same spectra as shown in Figures 28-30, thus indicating that polyamide-4 was formed. The weight average molecular weight and polymer yield (%) of all polyamide-4 synthesized in this study were summarized in Table 7. Weight average molecular weight from 398 to 9233 and quite low yield from 2.94 to 25.43% of polyamide-4 were obtained. Thermal properties of polyamide-4 obtained were analyzed by differential scanning calorimetry (DSC) as shown in Figure 31. The results of thermal properties were summarized in Table 8. White powder solids soluble in formic acid having T_m (melt temperature) ~ 241-256°C and T_c (crystallization temperature) ~ 168-210°C were obtained (Appendix Figure 1).

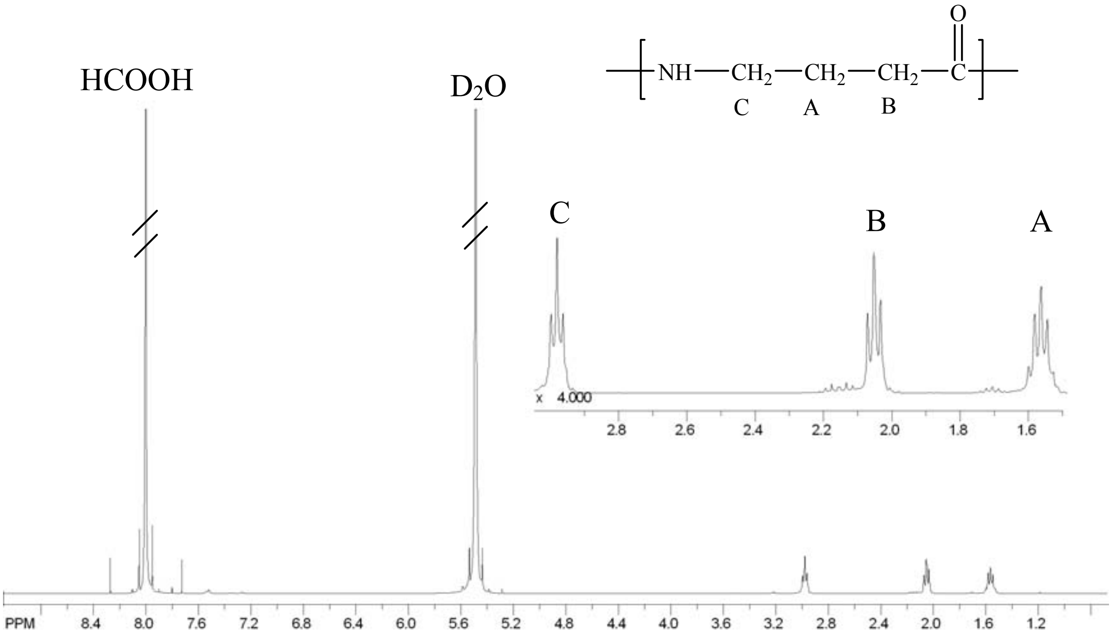


Figure 28 400 MHz ^1H NMR spectrum of polyamide-4 (HCOOH/D_2O) by anionic ring-opening polymerization of 2-pyrrolidone using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator in the presence of 15-crown-5.

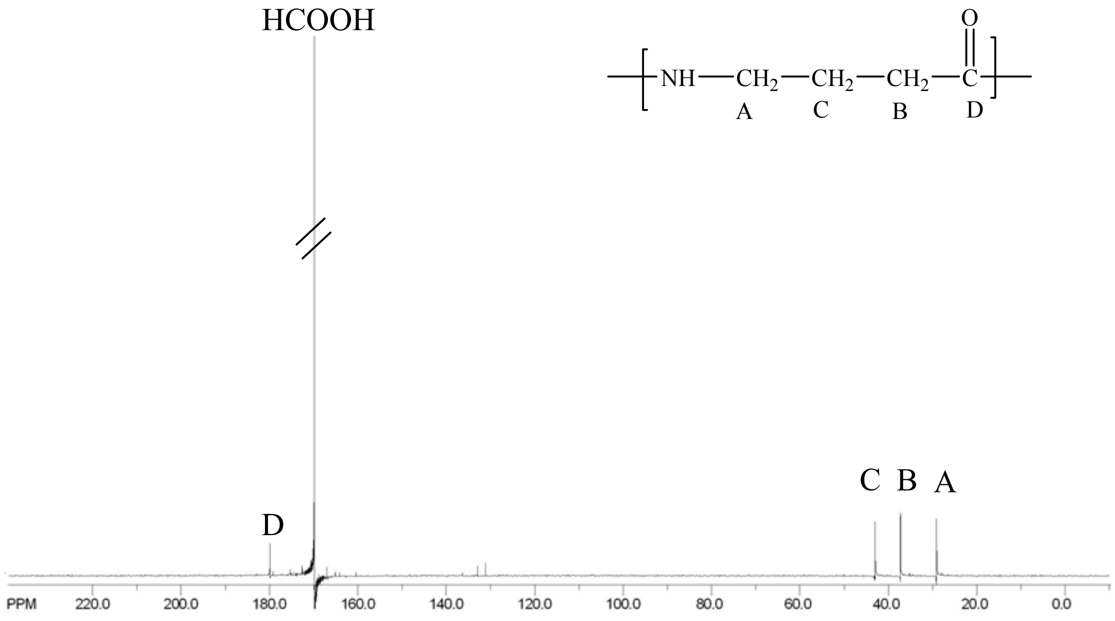


Figure 29 400 MHz ^{13}C NMR spectrum of polyamide-4 (HCOOH/D_2O) by anionic ring-opening polymerization of 2-pyrrolidone using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator in the presence of 15-crown-5.

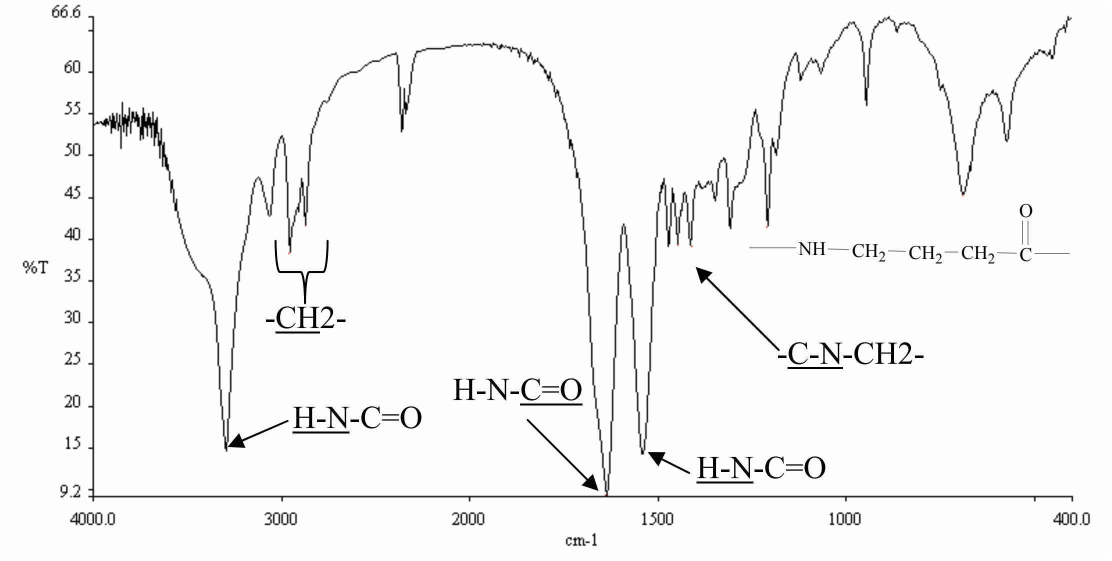


Figure 30 FT-IR spectrum of polyamide-4 (KBr) by anionic ring-opening polymerization of 2-pyrrolidone using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator in the presence of 15-crown-5.

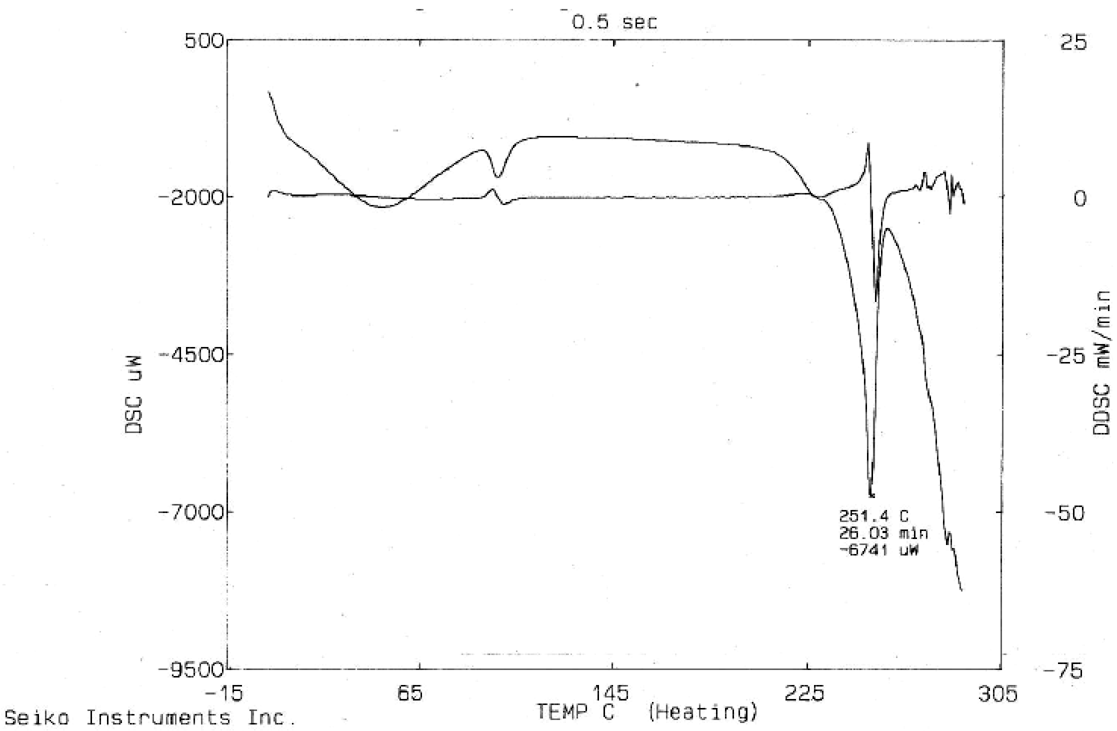


Figure 31 DSC thermogram of polyamide-4 (mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 at 40°C, 24 h).

Table 7 Molecular weight and intrinsic viscosity of polyamide-4 by anionic ring-opening polymerization of 2-pyrrolidone using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator in the presence of 15-crown-5.

Sample code	Yield (%)	[η] (dl.g^{-1})	$\overline{M}_W$
$N_1C_{0.5}T_6$	2.94	0.04	398
$N_2C_{0.5}T_6$	11.06	0.06	674
$N_3C_{0.5}T_6$	7.18	0.10	1309
$N_3C_1T_3$	25.06	0.17	2608
$N_1C_0T_4$	12.34	0.36	6910
$N_1C_1T_4$	13.83	0.16	2410
$N_1C_2T_4$	14.94	0.37	7160
$N_1C_3T_4$	13.09	0.38	7413
$N_2C_0T_4$	15.56	0.27	4756
$N_2C_1T_4$	8.40	0.33	6172
$N_2C_2T_4$	17.28	0.33	6172
$N_2C_3T_4$	14.20	0.37	7160
$N_3C_0T_4$	25.43	0.32	5930
$N_3C_1T_4$	20.74	0.36	6910
$N_3C_2T_4$	16.67	0.45	9233
$N_3C_3T_4$	18.52	0.42	8442
$N_3C_1T_5$	16.67	0.34	6416

Table 8 Thermal properties of polyamide-4 by anionic ring-opening polymerization of 2-pyrrolidone using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator in the presence of 15-crown-5.

Sample code	T_c (°C)	T_m (°C)	Heat of fusion (J/g)
$N_1C_{0.5}T_6$	198.4	249.9	78.18
$N_2C_{0.5}T_6$	183.1	246.2	101.88
$N_3C_{0.5}T_6$	187.8	241.9	74.27
$N_3C_1T_3$	202.5	253.8	85.04
$N_1C_0T_4$	168.4	246.0	78.87
$N_1C_1T_4$	197.0	253.4	170.08
$N_1C_2T_4$	207.8	256.6	89.42
$N_1C_3T_4$	201.6	253.4	96.44
$N_2C_0T_4$	182.9	251.8	103.05
$N_2C_1T_4$	200.4	253.7	96.06
$N_2C_2T_4$	200.4	254.5	94.52
$N_2C_3T_4$	195.2	252.3	92.66
$N_3C_0T_4$	210.6	255.5	78.29
$N_3C_1T_4$	199.4	251.9	71.27
$N_3C_2T_4$	200.8	251.1	79.12
$N_3C_3T_4$	200.5	250.4	86.24
$N_3C_1T_5$	191.1	249.7	69.32

The effect of temperature was studied by keeping the mmol ratio of Py:BPy:Na:Crown = 100:1:3:1 for 24 h under alternating between nitrogen for 3 h and vacuum for 1 h as shown in Figure 32. The addition of N-benzoyl-2-pyrrolidone (IV) eliminates the initial slow step as mentioned earlier and allowed rapid initiation of polymerization. Polymerization temperature was found to have slightly effect on polymer yield (%). Polymer yield (%) was decreased from 25.06, 20.74 and 16.67% when polymerization temperatures were increased from 30, 40 to 50°C respectively. However, weight average molecular weights ($\overline{M}_W$) of polyamide-4 as measured by the intrinsic viscosity were slightly increased from 2608 to 6910 when polymerization temperatures were increased from 30 to 40°C and were almost the same from 40 to 50°C (6910 and 6416). It had been reported previously that the optimum temperature of polymerization is about 40-50°C for all initiation systems and polyamide-4 could not be prepared at above 80°C (Roda *et al.*, 1981a). This temperature can be considered as the limit temperature of the ring-opening polymerization process of 2-pyrrolidone. It is not significant the same as the thermodynamic ceiling temperature because the polymerization of 2-pyrrolidone cannot be characterized as an equilibrium reaction, above all due to the irreversible crystallization of polyamide-4 during polymerization (Fries *et al.*, 1984). Polymerization temperature at 40°C was, therefore, chosen to study the effect of 15-crown-5 and sodium on the anionic ring-opening polymerization.

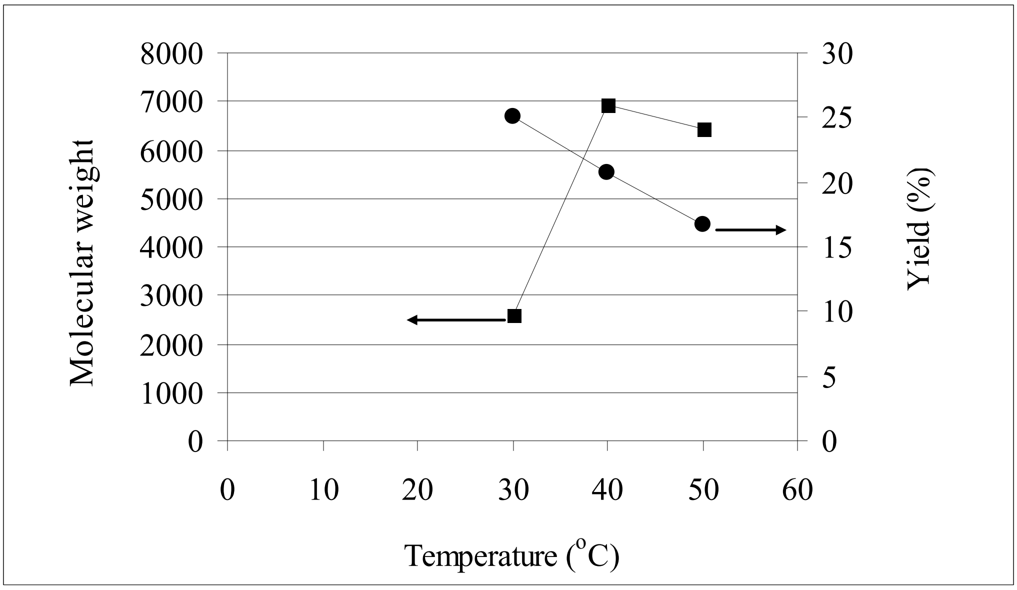


Figure 32 Effect of temperature on the weight average molecular weight and polymer yield (%) of polyamide-4 obtained by keeping the mmol ratio of Py:BPy:Na:Crown = 100:1:3:1 for 24 h.

The "free" 2-pyrrolidone anion should add faster in the rate determining propagation step and, consequently, should lead to higher molecular weight polymers. The effects of sodium and 15-crown-5 on the weight average molecular weight ($\overline{M}_W$) and polymer yield (%) of the anionic ring-opening polymerization of 2-pyrrolidone at 40°C were shown in Figures 33-34. It was found that at the same amount of 15-crown-5, $\overline{M}_W$ of polyamide-4 increased with increasing the mmol of sodium as followed: without addition of 15-crown-5, $\overline{M}_W$ of polyamide-4 decreased from 6910, 4756 to 5930 with increasing of mmol of sodium from 1, 2 to 3 respectively; at 1 mmol of 15-crown-5, $\overline{M}_W$ of polyamide-4 increased from 2410, 6172 to 6910 with increasing the mmol of sodium from 1, 2 to 3 respectively; at 2 mmol of 15-crown-5, $\overline{M}_W$ of polyamide-4 increased from 7160, 6172 and 9233 with increasing the mmol of sodium from 1, 2 to 3 respectively; and at 3 mmol of 15-crown-5, $\overline{M}_W$ of polyamide-4 increased from 7413, 7160 to 8442 with increasing the mmol of sodium from 1, 2 to 3 respectively. It also found that at the same amount of sodium, $\overline{M}_W$ of polyamide-4 increased with increasing the mmol of 15-crown-5 as followed: at 1 mmol of sodium, $\overline{M}_W$ of polyamide-4 increased from 6910, 2410, 7160 and 7413 with increasing the mmol of 15-crown-5 from 0, 1, 2 to 3 respectively; at 2 mmol of sodium, $\overline{M}_W$ of polyamide-4 increased from 4756, 6172, 6172 and 7160 with increasing the mmol of 15-crown-5 from 0, 1, 2 to 3 respectively; and at 3 mmol of sodium, $\overline{M}_W$ of polyamide-4 increased from 5930, 6910, 9233 and 8442 with increasing the mmol of 15-crown-5 from 0, 1, 2 to 3 respectively. It can be concluded that $\overline{M}_W$ of polyamide-4 is slightly increased with increasing the amount of sodium and 15-crown-5 except when 15-crown-5 was omitted which was in agreement with results reported previously. In additional, increasing the amount of sodium and 15-crown -5 also increased the polymer yield (%) of polyamide-4.

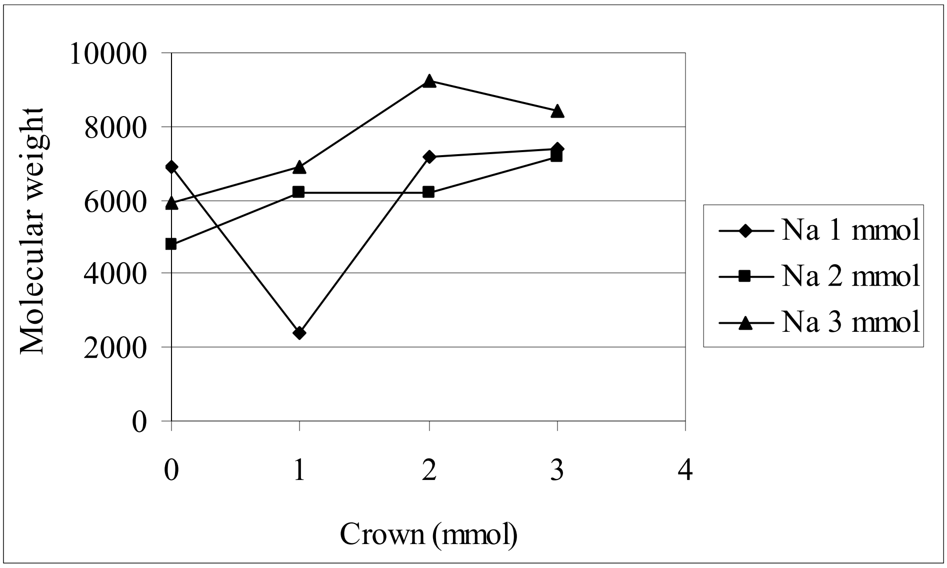


Figure 33 Effect of sodium and 15-crown-5 on weight average molecular weight ($\overline{M}_w$) of polyamide-4 obtained by anionic ring-opening polymerization.

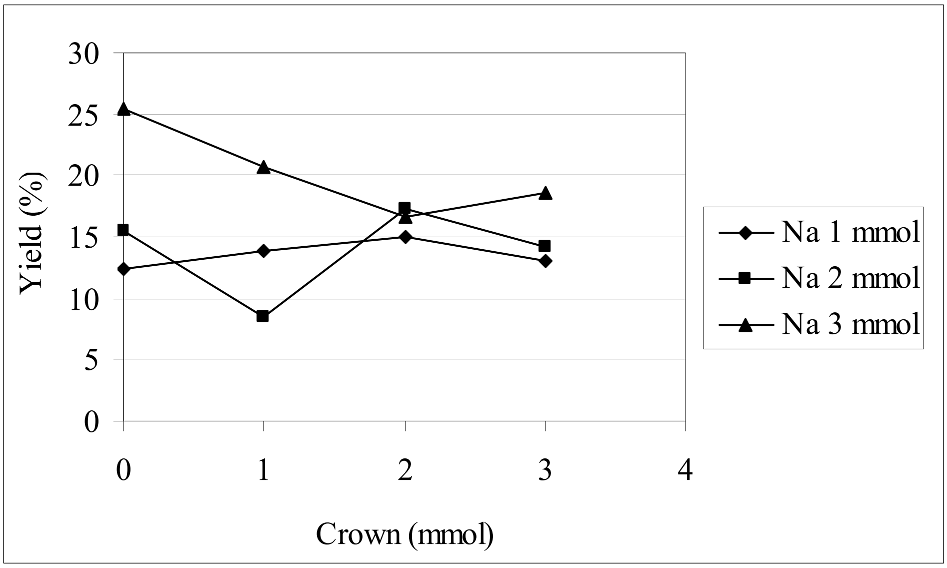


Figure 34 Effect of sodium and 15-crown-5 on polymer yield (%) of polyamide-4 obtained by anionic ring-opening polymerization.

Copolymerization of 2-pyrrolidone (Py) and γ-aminobutyric acid was also investigated using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone (BPy) as activator in the presence of 15-crown-5 by varying the mmol of γ-aminobutyric acid (GABA) from 10, 20 and 30 mmol and kept the mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 at 105°C for 8 h and at 40°C for 24 h under alternating between under nitrogen atmosphere for 3 h and reduced pressure for 1 h. Characterization of the products obtained by ^{1}H NMR, ^{13}C NMR and FT-IR showed the same spectra as shown in Figures 35-37. The spectra were indicated that polyamide-4 was formed. The spectra are similar to spectra of polyamide-4 obtained when polymerizations under the absence of γ-aminobutyric acid. The results of polymer yield, molecular weight and intrinsic viscosity were summarized in Table 9 and Figure 38. Polymer yields (%) were decreased from 6.47, 2.03 to 1.1% at 105°C for 8 h and from 2.24, 1.28 to 1.28% at 40^{o}C for 24 h when γ-aminobutyric acid was increased from 10, 20 and 30, respectively. However, weight average molecular weights ($\overline{M}_W$) of polyamide-4 as measured by the intrinsic viscosity were slightly increased from 7667 to 9233 when γ-aminobutyric acid was increased from 10 to 20 mmol and was slightly decreased from 9233 to 8182 when γ-aminobutyric acid was increased from 20 to 30 mmol at 105°C, and $\overline{M}_W$ of polyamide-4 was slightly decreased from 7160 to 5690 when γ-aminobutyric acid was increased from 10 to 20 mmol and was slightly increased from 5690 to 6662 when γ-aminobutyric acid was increased from 20 and 30 mmol at 40°C. It was also found that polymer yield (%) and $\overline{M}_W$ of polyamide-4 obtained by the copolymerization of 2-pyrrolidone and γ-aminobutyric acid at 105°C for 8 h were higher than at 40°C for 24 h. The results of thermal properties of copolymerization of Py and GABA were summarized in Table 10. The white powders which are soluble in formic acid having T_m (melt temperature) ~ 242-248°C and T_c (crystallization temperature) ~ 168-192°C were obtained.

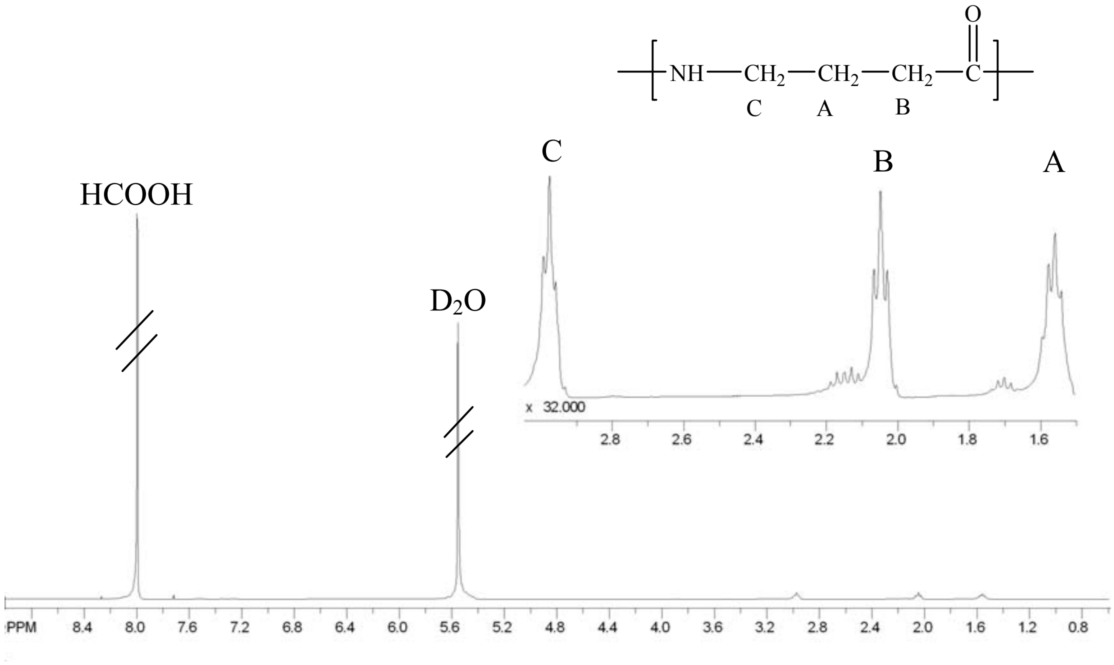


Figure 35 400 MHz ^1H NMR spectrum of polyamide-4 (HCOOH/D_2O) (mmol ratio of Py:BPy:Na:Crown:GABA = 100:1:3:2:10 at 105°C for 8 h).

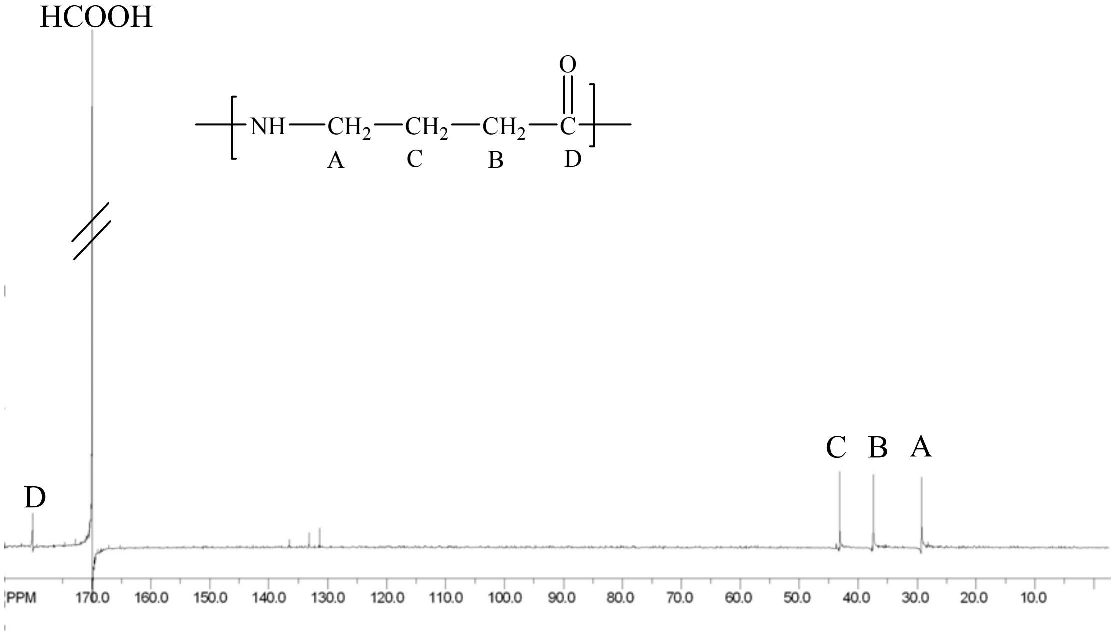


Figure 36 400 MHz ^{13}C NMR spectrum of polyamide-4 (HCOOH/D_2O) (mmol ratio of Py:BPy:Na:Crown:GABA = 100:1:3:2:10 at 105°C for 8 h).

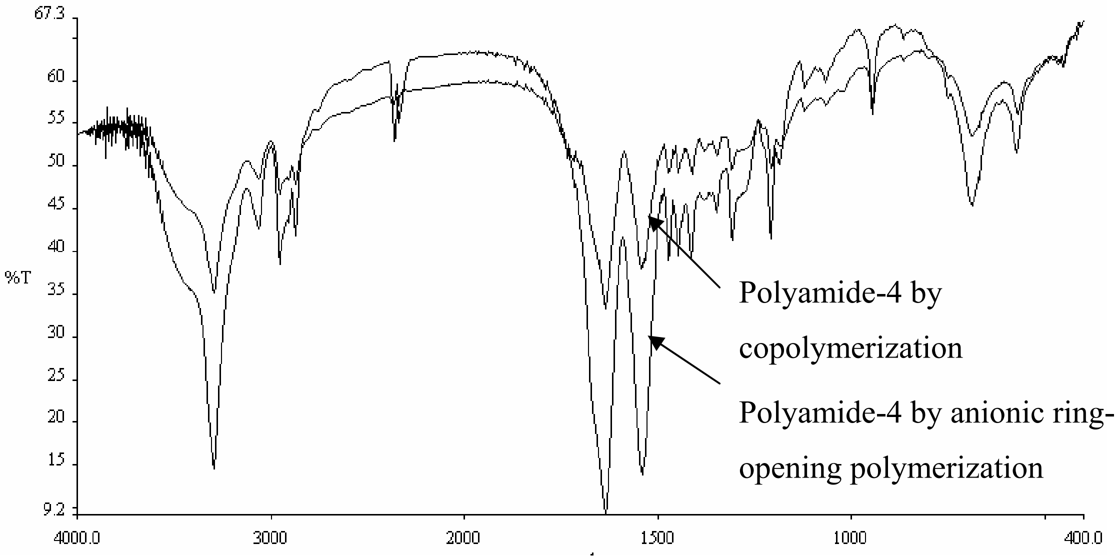


Figure 37 FT-IR spectrum of Py:BPy:Na:Crown:GABA = 100:1:3:2:10 at 40°C for 24 h).

Table 9 Effect of γ-aminobutyric acid (GABA) on polymer yield, weight average molecular weight ($\overline{M}_W$) and intrinsic viscosity in polymerization of 2-pyrrolidone (mmol ratio of Py:BPy:Na:Crown = 100:1:3:2, at 105°C for 8 h and at 40°C for 24 h).

Sample code	GABA (mmol)	Yield (%) (Py+GABA)	[η] (dl.g^{-1})	$\overline{M}_W$
$N_3C_2G_1T_{10}$	10	6.47	0.39	7667
$N_3C_2G_2T_{10}$	20	2.03	0.45	9233
$N_3C_2G_3T_{10}$	30	1.1	0.41	8182
$N_3C_2G_1T_4$	10	2.24	0.37	7160
$N_3C_2G_2T_4$	20	1.28	0.31	5690
$N_3C_2G_3T_4$	30	1.28	0.35	6662

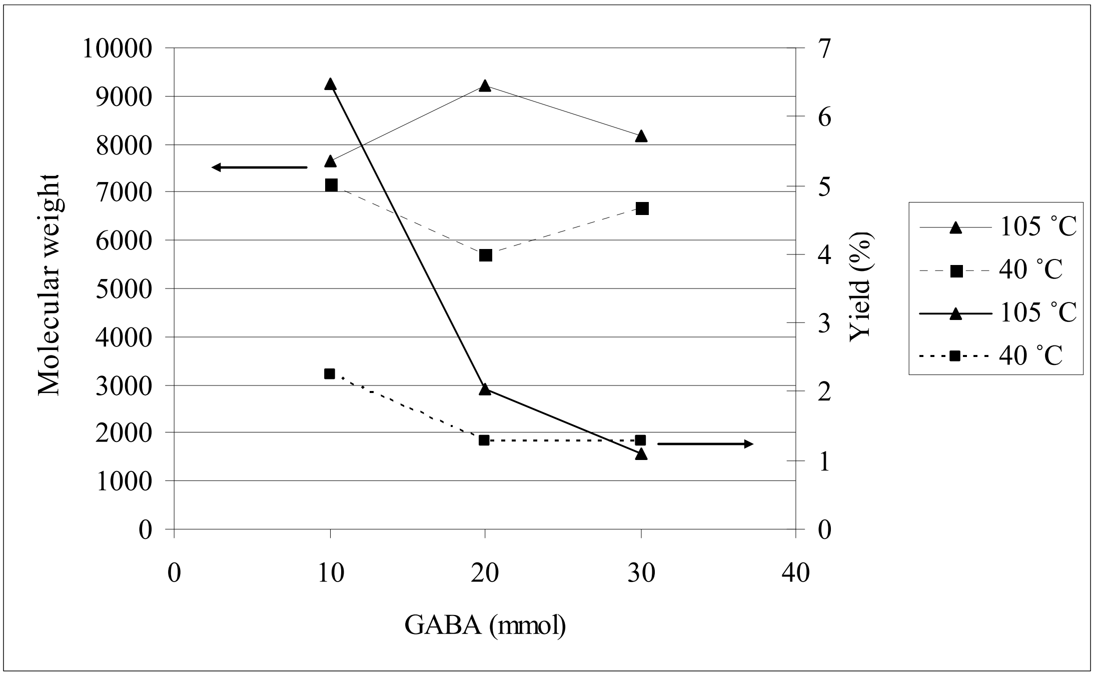


Figure 38 Effect of γ-aminobutyric acid (GABA) on polymer yield (%) and weight average molecular weight of polyamide-4 obtained from the copolymerization of Py:BPy:Na:Crown (mmol ratio = 100:1:3:2, at 40°C for 24 h and 105°C for 8 h).

Table 10 Thermal properties of polyamide-4 by copolymerization of 2-pyrrolidone in the presence of γ-aminobutyric acid (Py:BPy:Na:Crown = 100:1:3:2, at 105°C for 8 h and at 40°C for 24 h).

Sample code	T_c (°C)	T_m (°C)	Heat of fusion (J/g)
$N_3C_2G_1T_{10}$	192.5	248.2	95.95
$N_3C_2G_2T_{10}$	179.7	247.6	100.13
$N_3C_2G_3T_{10}$	183.2	245.5	167.45
$N_3C_2G_1T_4$	168.8	242.4	162.63
$N_3C_2G_2T_4$	176.0	244.0	124.0
$N_3C_2G_3T_4$	174.5	242.5	86.8

In summary, the highest $\overline{M}_W$ polyamide-4 (9233) could be obtained either by anionic ring-opening polymerization of 2-pyrrolidone using the mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 at 40°C for 24 h or by copolymerization of 2-pyrrolidone and γ-aminobutyric acid using the mmol ratio of Py:BPy:Na:Crown:GABA = 100:1:3:2:20 at 105°C for 8 h under alternating between under nitrogen atmosphere for 3 h and reduced pressure for 1 h. It was compared with the high molecular weight of polyamide-4 obtained by anionic ring-opening polymerization with the mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 at temperature 40°C for 24 h under alternating between under nitrogen atmosphere for 3 h and reduced pressure for 1 h which molecular weight has 9233. It was found at 40°C with the same amount of sodium (3 mmol) and 15-crown-5 (2 mmol) that the $\overline{M}_W$ of polyamide-4 obtained by anionic ring-opening polymerization 2-pyrrolidone ($\overline{M}_W$ = 9233) with the mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 are almost comparable with the $\overline{M}_W$ of polyamide-4 obtained by copolymerization of 2-pyrrolidone and γ-aminobutyric acid using the mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 ($\overline{M}_W$ = 7160, 5690 and 6662 varying with the mmol of GABA = 10, 20 and 30 mmol respectively).

Polyamide-4,4 was also synthesized for biodegradation comparison with polyamide-4. Polyamide-4,4 was successfully synthesized by both solution and interfacial polycondensation of 1,4-diaminobutane and succinyl chloride at room temperature. Characterization of the product obtained by FT-IR (Figure 39), solubility and biuret test showed that polyamide-4,4 was obtained.

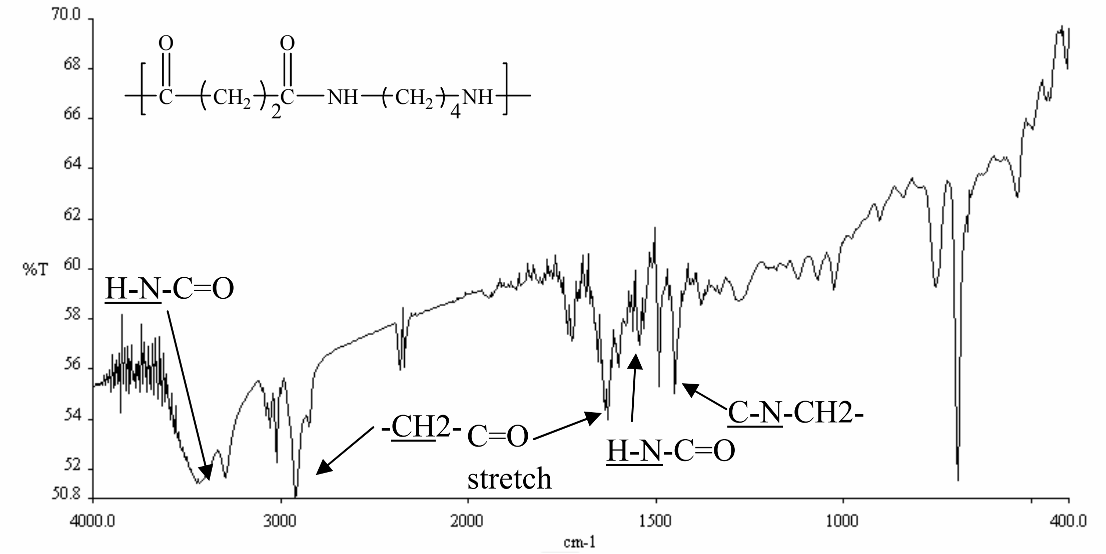


Figure 39 FT-IR of polyamide-4,4 (KBr) by solution and interfacial polycondensation of 1,4-diaminobutane and succinyl chloride at room temperature.

Finally, degradation of polyamide-4 ($N_3C_1T_4$, $\overline{M}_w$= 6910 and $N_3C_2T_4$, $\overline{M}_w$ = 9233) and polyamide-4,4 ($\overline{M}_w$ = 6436) in composted soil was studied by determination of oxygen consumption (biochemical oxygen demand, BOD) according to the JIS K 6950 (ISO 14851) at 25°C as shown in Figure 40. Degradation of the synthesized polyamide-4 and polyamide-4,4 was compared with poly(D-3-hydroxybutyrate) (PHB), the best known member of the group of polyhydroxyalkanoates (PHA) because PHB can be degraded completely in the environment without forming any toxic products (Calabia and Tokiwa, 2004). The degradation of both polyamide-4 ($N_3C_1T_4$ and $N_3C_2T_4$) was higher than that of poly(D-3-hydroxybutyrate) (PHB) but polyamide-4,4 was found nondegradation (Figure 40). Degradation of both polyamide-4 suddenly increased at 120 h cultivation, and then subsequently increased gradually. Therefore, some common microorganisms leading to the decomposition of polyamide-4 may be in the chosen composted soil. It is thought that the nitrogen of the polyamide-4 was metabolized by microbes in the composted soil and was converted into inorganic compounds in the culture media and that the degrading bacteria produce extracellular hydrolytic enzymes that can degrade polyamide-4 to 4-aminobutyric acid or γ-aminobutyric acid. Degradation of both polyamides-4 ($N_3C_1T_4$ and $N_3C_2T_4$) was further studied by enzymatic degradation as summarized in Tables 11 and 12. The degradations were measured from accumulation of water-soluble degradation products (total organic carbon, TOC) by the enzymes. No degradation of both polyamides-4 was observed by all of the enzymes studied within the analyzed period. It can not be concluded completely that the synthesized polyamide-4 are non enzymatic degradation. Longer period of testing may be needed.

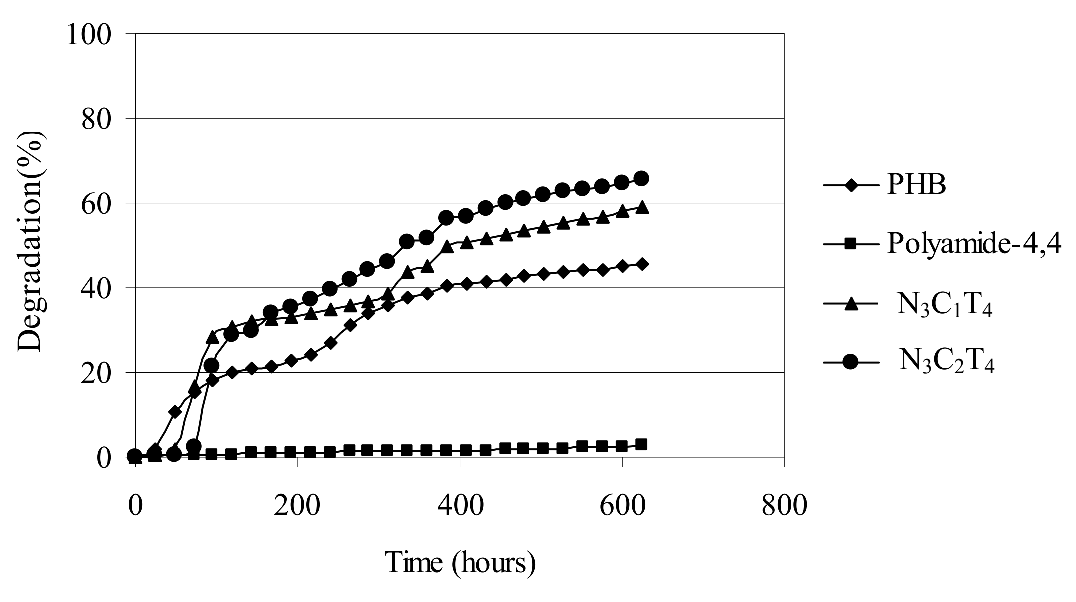


Figure 40 Degradation profiles of polyamides and poly(D-3-hydroxybutyrate) (PHB) in composted soil.

Table 11 Enzymatic degradation of polyamide-4 obtained from anionic ring-opening polymerization of Py:BPy:Na:Crown = 100:1:3:1 ($N_3C_1T_4$, $\overline{M}_w$ = 6910) at 37°C for 14 h.

Enzyme	TOC (ppm)			Biodegradable (ppm)
	Sample + Enzyme	Sample	Enzyme	
Proteinase K	210	147	83	-20
Bacillus thermoproteolyticus rokko	202	147	83	-28
Ficin	194	147	77	-30
Bromelain	197	147	78	-28
Pepsin	219	147	90	-18
Streptomyces griseus	191	147	51	-7
Aspergillus oryzae	198	147	67	-16
Subtilisin carslberg	221	147	95	-21
α-Chymotrypsin	215	147	90	-22

Table 12 Enzymatic degradation of polyamide-4 obtained from anionic ring-opening polymerization of Py:BPy:Na:Crown = 100:1:3:2 ($N_3C_2T_4$, $\overline{M}_w$= 9233) at 37°C for 14 h.

Enzyme	TOC (ppm)			Biodegradable (ppm)
	Sample+ Enzyme	Sample	Enzyme	
Proteinase K	253	171	83	-1
Bacillus thermoproteolyticus rokko	248	171	83	-6
Ficin	229	171	77	-19
Bromelain	226	171	78	-23
Pepsin	234	171	90	-27
Streptomyces griseus	212	171	51	-10
Aspergillus oryzae	236	171	67	-2
Subtilisin carslberg	262	171	95	-4
α-Chymotrypsin	245	171	90	-16

CONCLUSION

Synthesis and characterization of polyamide-4 were investigated.

Melt polymerization at 165 to 185°C for 12 h by alternately between under continuous flow of nitrogen for 3 h and under reduced pressure for 1 h and melt polymerization in solution of toluene and 1-methyl-2-pyrrolidone at 165 to 185°C under continuous flow of nitrogen for 12 h of γ-aminobutyric acid (GABA) were unsuccessful. This may be due to the prolonged exposure to heat of amide groups in the polymer. Reverse reactions such as hydrolysis and side reactions such as thermal and oxidative decompositions, monomer and oligomer cyclization, and large ring formation are significantly predominant.

Polyamide-4 was successfully synthesized by ring-opening polymerization of 2-pyrrolidone. Anionic ring-opening polymerization of 2-pyrrolidone (Py) was carried out by using N-sodium-2-pyrrolidoneas initiator and N-benzoyl-2-pyrrolidone (BPy) as activator in the presence of 15-crown-5 (Crown) at 30 to 50°C for 24 h and at 60°C for 12 h under alternating between nitrogen atmosphere for 3 h and under reduced pressure for 30 min and 1 h respectively. N-sodium-2-pyrrolidoneas initiator and 15-crown -5 were varied from 1.0-3.0 mmol and 0.5-3.0 mmol respectively while mmol ratio of 2-pyrrolidone: N-benzoyl-2-pyrrolidone was kept constant at 100:1. Characterization of the products obtained by ^{1}H NMR, ^{13}C NMR and FT-IR confirmed that polyamide-4 was formed. Weight average molecular weight ($\overline{M}_w$) from 398 to 9233 and quite low yield from 2.94 to 25.43% of polyamide-4 having T_m (melt temperature) ~ 241.9-256.6°C and T_c (crystallization temperature) ~ 168.4-210.6°C were obtained.

Polymerization temperature at 40°C was chosen to study the effect of the sodium and 15-crown-5 because it was found that average molecular weight ($\overline{M}_w$) of polyamide-4 was slightly increased from 2608 to 6910 when polymerization temperature was increased from 30 to 40°C and was almost the same from 40 to 50°C

(6910 and 6416). At the same amount of 15-crown-5, $\overline{M}_W$ of polyamide-4 increased with increasing the mmol of sodium, for example, at 1 mmol of 15-crown-5, $\overline{M}_W$ of polyamide-4 increased from 2410, 6172 to 6910 with increasing the mmol of sodium from 1, 2 to 3 respectively. In addition, at the same amount of sodium, $\overline{M}_W$ of polyamide-4 increased with increasing the mmol of 15-crown-5, for example, at 1 mmol of sodium, $\overline{M}_W$ of polyamide-4 increased from 2410, 7160 to 7413 with increasing the mmol of 15-crown-5 from 1,2 to 3 respectively. It can be concluded that $\overline{M}_W$ and yield of polyamide-4 slightly increased with increasing the amount of sodium and 15-crown-5.

Polyamide-4 was also obtained from copolymerization of 2-pyrrolidone and γ-aminobutyric acid (GABA) using N-sodium-2-pyrrolidone as initiator and N-benzoyl-2-pyrrolidone as activator in the presence of 15-crown-5 by varying the mmol of GABA from 10 to 30 and kept the mmol ratio of Py:BPy:Na:Crown = 100:1:3:2 at 105^{o}C for 8 h and at 40^{o}C for 24 h under alternating between under nitrogen atmosphere for 3 h and reduced pressure for 1 h. Polymer yield obtained was extremely low (the highest was 6.5%), $\overline{M}_W$ of polyamide-4 was increased with increasing GABA from 10 to 20 mmol and slightly decreased with increasing GABA from 20 to 30 mmol at 105^{o}C. On the contrary, $\overline{M}_W$ of polyamide-4 was decreased with increasing GABA from 10 to 20 mmol and slightly increased with increasing GABA from 20 to 30 mmol at 40^{o}C. Polymer yield (%) and $\overline{M}_W$ of polyamide-4 obtained by the copolymerization of 2-pyrrolidone and γ-aminobutyric acid at 105°C for 8 h was higher than at 40°C for 24 h.

The highest $\overline{M}_W$ polyamide-4 obtained in this study was 9233 which can be obtained either from Py:BPy:Na:Crown = 100:1:3:2 at 40^{o}C for 24 h or from copolymerization of Py:BPy:Na:Crown:GABA = 100:1:3:2:20 at 105^{o}C for 8 h under alternating between under nitrogen atmosphere for 3 h and reduced pressure for 1 h.

Polyamide-4,4 (PA-4,4) was synthesis for biodegradation comparison with polyamide-4. It was successfully synthesized by both solution and interfacial polycondensation at room temperature. Polyamide-4,4 having $\overline{M}_w = 6436$ was obtained.

Degradation of polyamide-4 ($N_3C_1T_4$, $\overline{M}_w = 6910$ and $N_3C_2T_4$, $\overline{M}_w = 9233$) and polyamide-4,4 ($\overline{M}_w = 6436$) in composted soil was studied. Degradation of both polyamide-4 was higher than poly(D-3-hydroxybutyrate), a known degradable polymer. Both polyamide-4 started to degrade after incubating in composted soil for 120 h, then increased gradually and reached 60% degradation in 600 h. Enzymatic degradation of both polyamide-4 was conducted but both synthesized polyamide-4 was not degraded after incubating in all the enzymes used for 14 h.

LITERATURE CITED

Bacskai, R. 1977. **Sulfonic Acid Derivatives as Promoters for the Polymerization of 2-Pyrrolidone.** U.S. Patent 4, 042, 573.

_____. 1978a. **Anionic Copolymerization of 2-Pyrrolidone with C_7-C_{12} Lactam.** U.S. Patent 4, 107, 154.

_____. 1978b. **Process for the Preparation of a Catalyst Containing Pyrrolidone Composition.** U.S. Patent 4, 075, 182.

_____. 1979. **Crown Ether and N-acylpyrrolidone Activated Copolymerization of 2-Pyrrolidone and Caprolactam.** U.S. Patent 4, 169, 936.

_____. 1982. Synthesis of Ultrahigh Molecular Weight Nylon 4 with Onium Salt and Crown Ether Containing Catalysis. **Polymer Preprints** 23(2): 162-163.

_____. 1983. Synthesis and Thermal Stability Evaluation of End-capped Nylon-4 Oligomers. **Polymer Preprints** 24 (2): 63-64.

_____. 1984. Synthesis and Thermal Stability Evaluation of End-capped Nylon-4 Oligomers. **Polym. Bull.** 11: 229-236.

Barnes, A.C. 1981. **Polymerization of 2-Pyrrolidone with Alkali Metal Pyrrolidonates and Polymerization Products Thus Obtained**. European Patent 0, 032, 995.

Barnes, C.E. 1973. **Polymers of 2-Pyrrolidone.** U.S. Patent 3, 721, 652.

_____. 1987. Nylon 4 – Development and Commercialization. **Lenzinger Berichte.** 62-65.

Barnes, C.E. and A.C. Barnes. 1981a. **Polymerization of 2-Pyrrolidone with Cesium or Rubidium Catalyst.** U.S. Patent 4, 247, 684.

_____ and _____. 1981b. **Continuous Bulk Polymerization of 2-Pyrrolidone.** U.S. Patent 4, 247, 685.

_____, O.N. William, R.N. William and R.L. Warren. 1957. **Polymerization Procedures for 2-Pyrrolidone.** U.S. Patent 2, 809, 958.

Brozek, J., P. Rehak, M. Marek, J. Roda and J. Kralicek. 1988. Anionic Polymerization of Lactams Accelerated with N-Iminolactams, 1 2-Pyrrlidone. **Makromol. Chem.** 189: 9-16.

Buchanan, G.W., K. Bourque, G.K. Diedrich and M.Z. Khan. 1987. Cis-Cyclohexyl-15-crown-5 Ether: Dynamic Stereochemistry in Solution as Studied By Carbon-^{13}C NMR Techniques. **Magn. Reson. Chem.** 25: 65-68.

Budin, J. and J. Kralicek. 1976. Anionic Polymerization of 2-Pyrrolidone. **Collect. Czech. Chem. Commun.** 41: 220-230.

Calabia, B.P and Y.Tokiwa. 2004. Microbial Degradation of Poly(D-3-hydroxybutyrate) by New Thermoplilic *Streptomyces* Isolate. **Biotechnol. Lett.** 26: 15-19.

Choi, S.K. 1976. **Polymerization of 2-Pyrrolidone.** U.S. Patent 3, 968, 087.

Chuchma, F., A. Bosticka, J. Roda and J. Kralicek. 1979. Influence of Water on the Activated Anionic Polymerization of 2-Pyrrolidone. **Makromol. Chem.** 180: 1849-1851.

Clark, H.G. and W.B. Black. 1962. **Activators for the Polymerization of Pyrrolidone.** U.S. Patent 3, 069, 392.

Collman, J.P. 1978. **Crown Ether Activated Lactam Polymerization.** U.S. Patent 4, 073, 778.

Costa, G., M. Nencioni, S. Russo and G.L. Semeghini. 1981. The Anionic Polymerization of 2-Pyrrolidone in Bulk and in Suspension. **Makromol. Chem.** 182: 1399-1405.

Daniel, L., J. Brozek, J. Roda and J. Kralicek. 1982. Anionic Polymerization of 2-Pyrrolidone Accelerated with CO_2, Part 1. **Makromol. Chem.** 183: 2719-2729.

Deguchi, T., M. Kakezawa and T. Nishida. 1997. Nylon Biodegradation by Lignin-Degrading Fungi. **Appl. Environ. Microbiol.** 63: 329-331.

_____, Y. Kitaoka, M. Kakezawa and T. Nishida. 1998. Purification and Characterization of a Nylon-Degrading Enzyme. **Appl. Environ. Microbiol.** 64: 1366-1371.

Fries, T., J. Belohlavkova, J. Roda and J. Kralicek. 1984. Limit Temperature of the Anionic Polymerization of 2-Pyrrolidone. **Polym. Bull.** 12: 87-91**.**

Hall, H.K. 1958. Structural Effects on the Polymerization of Lactams. **J. Am. Chem. Soc.** 80: 6404-6409.

Han, S., B.S. Kim, S.W. Kang, H. Shirai and S.S. Im. 2003. Cellular Interactions and Degradation of Aliphatic Poly(ester amide)s Derived from Glycine and /or 4-Aminobutyric Acid. **Biomaterials**. 24: 3453-3462.

Hashimoto, K., T. Hamano and M. Okada. 1994. Degradation of Several Polyamides in Soils. **J. Appl. Polym. Sci.** 54: 1579-1583.

Hashimoto, K., M. Sudo, K. Ohta, T. Sugimura, H. Yamada and T. Aoki. 2002. Biodegradation of Nylon 4 and Its Blend with Nylon 6. **J. App. Polym. Sci**. 86: 2307-2311.

_____, _____, T. Sugimura and Y. Inagaki. 2004. Synthesis of Novel Block Copolymers Containing Polyamide 4 Segments and Control of Their Biodegradability. **J. App. Polym. Sci.** 92: 3492-3498.

Higuchi, T., H. Hayashi and K. Abe. 1997. Exchange of Glutamate and Gamma-Aminobutyrate in a *Lactobacillus* Strain. **J. Bacteriol.** 179: 3362-3364.

Hocking, P.J. 1992. The Classification Preparation and Utility of Degradable Polymers. **J. Macromol. Sci.: Rev. Macromol. Chem. Phys**. C32: 35-54.

Holland, B.J. and J.N. Hay. 2001. The Dependence of Non-Volatile Residue Formation in Nylon 6 and Nylon 6,6 during Thermal Degradation on Hydrogen Bonding in the Melt. **Polymer** 42: 4759-4761.

Huang, R.Y.M., U.Y. Kim, J.M. Dickson, D.R. Lioyd and C.Y. Peng. 1981. Investigations on Nylon 4 Membranes. Synthesis and Transport Properties. I. Synthesis of Nylon 4 Polymer. **J. Appl. Polym. Sci.** 26: 1135-1142.

_____ and J.W. Rhim. 1989. Synthesis of Nylon 4 through the Use of the Carbon Dioxide/Potassium Pyrrolydonate Catalyst System with and without Added 18-Crown-6 Ether Activator. **J. Appl. Polym. Sci.** 37: 55-64.

Kakudo, S., S. Negoro, I. Urabe and H. Okada. 1993. Nylon Oligomer Degradation Gene, *nylC*, on Plasmid pOAD2 from a *Flavobacterium* Strain Encodes Endo-Type 6-Aminohexanate Oligomer Hydrolase: Purification and Characterization of the *nylC* Gene Product. **Appl..Environ. Microbiol.** 59: 3978-3980.

Kawasaki, N., A. Nakayama, N. Yamano, S. Takeda, Y. Kawata, N. Yamamoto and S. Aiba. 2005. Synthesis, Thermal and Mechanical Properties and Biodegradation of Branched Polyamide 4. **Polymer** 46: 9987-9993.

Koning, C., L. Teuwen, R. Jong. G. Janssen and B. Coussens. 1999. **Polyamides 4.10 and 4.12 and Their Isomers. High Perform. Polymer.** 11: 387-394.

Li, Y. and D. Yan. 2001. Preparation, Characterization and Crystalline Transition Behavior of Polyamide-4,14. **Polymer** 42:5055-5058.

Maruo, K., T. Kanda and K. Yamamoto. 2005. **Polyamide Resin.** U.S. Patent 6, 841, 651 B2.

Masao, N. and M. Yoshiyuki. 1993. **Production of Powdered 2-Pyrrolidone Polymer**. Japan Patent 05-039355.

Mountfort, D.O. and V. Pybus. 1992. Regulatory Influence on the Production of Gamma-Aminobutyric Acid by a Marine Psedomonad. **Appl. Environ. Microbiol.** 58: 237-242.

Negoro, S., H. Shinagawa, A. Nakata, S. Kinoshita, T. Hatozaki and H. Okada. 1980. Plasmid Control of 6-Aminohazanoic Acid Cyclic Dimer Degradation Enzymes of *Flavobacterium* sp. K172. **J. Bacteriol**. 143: 238-245.

_____, T. Taniguchi, M. Kanaoka, H. Kimura and H. Okada. 1983. Plasmid-Determined Enzymatic Degradation of Nylon Oligomers. **J. Bacteriol**. 155: 22-31.

Ney, W.O. 1961. **Pyrrolidone Polymerization.** U.S. Patent 2, 973, 343.

_____, W.R. Nummy and C.E. Barnes. 1953. **Polymers from Pyrrolidone.** U.S. Patent 2, 638, 463.

Noomhorm, C. and Y.Tokiwa. 2006. Effect of Poly(dioxolane) as Compatibilizer in Poly(ε-caprolactone)/Tapioca Starch Blends. **J. Polym. Environ.** 14: 149-159.

Pollution Control Department. 2003. **Thailand State of Pollution Report. Solid Waste.** 48-56.

Raave, A. 2000. **Principles of Polymer Chemistry.** 2nd ed. Kluwer Academic/Plenum Publishers, New York. pp. 227-230, p. 359.

Roda, J., J. Brozek and J. Kralicek. 1980. Isolation and Characterization of Alkali Carboxylates of 2-Pyrrolidone. **Makromol. Chem., Rapid Commun.** 1: 165-169.

_____, J. Kralicek, V. Subr and J. Stehlicek. 1983. Nonactivated Anionic Polymerization of 2-Pyrrolidone in the Presence of Quaternary Ammonium Cations. **Makromol. Chem.** 184: 1987-1996.

_____, M. Kuskova and J. Kralicek. 1977a. Effect of Activating Agents on the Anionic Polymerization of 2-Pyrrolidone. **Makromol. Chem**. 178: 3203-3209.

_____, _____ and _____. 1977b. Effect of the Preparation Method of the 2-Pyrrolidone Potassium Salt on the Anionic Polymerization of 2-Pyrrolidone. **Makromol. Chem.** 178: 247-251.

_____, P. Sysel and J. Kralicek. 1981a. Anionic Polymerization of 2-Pyrrolidone Accelerated by 1-(1-Pyrrolin-2-yl)-2-pyrrolidone. **Polym. Bull.** 5: 609-614.

_____, Z. Votrubcova, J. Kralicek, J. Stehlicek and S. Pokorny. 1981b. Condensation as Side Reaction in the Anionic Polymerization of 2-Pyrrolidone. **Makromol. Chem.** 182: 2117-2126.

Satyanarayana, D. and P.R.Chatterji. 1993. Biodegradable Polymers: Challenges and Strategies. **J. Macromol. Sci.: Polym. Rev.** C33: 349-368.

Schirawski, G. 1972. Untersuchungen zur Anionischem Polymerisation von Pyrrolidon. **Makromol. Chem.** 161: 57-68.

Sekiguchi, H. and B. Coutin. 1992. Polyamides, pp. 807-939. *In* H.R. Kricheldorf, ed. **Handbook of Polymer Synthesis, Part A.** Marcel Dekker, Inc., New York.

_____, P.R. Tsourkas and B. Coutin. 1973. Anionic Polymerization of α-Pyrrolidone and α-Piperidone Using Their Quaternary Ammonium Salts as Catalysts. **J. Polym. Sci. Polym. Symp.** 42: 51-61.

Sorenson, W.R., F. Sweeny and T.W. Campbell. 2001. **Preparative Methods of Polymer Chemistry.** 3rd ed. Wiley Interscience, New York.

Sweeny, W. 1972. Polyamides (General), pp. 1-46. *In* Kirk, R.E., D.F. Othmer, H.F. Mark and A. Standen, eds. **Encyclopedia of Chemical Technology.** Vol. 16. 2nd ed. Interscience Publishers, New York.

Sysel, P., J. Brozek, J. Roda and J. Kralicek. 1983. Anionic Polymerization of 2-Pyrrolidone Accelerated by 1-(1-Pyrrolin-2-yl)-2-Pyrrolidone. **Acta Polymerica** 34: 715-719.

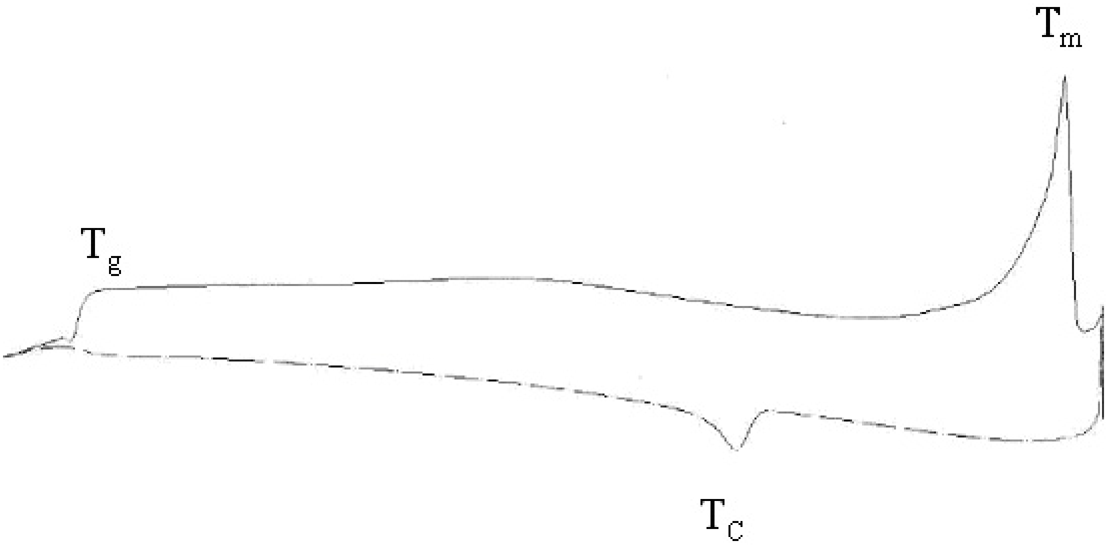
Tani, H. and T. Konomi. 1966. Polymerization of Five-, Six-, and Seven-Membered Ring Lactams by Using Metallic Potassium or Metallic Aluminum Alkylate as Catalyst and Certain N-Acyl Lactams or Diphenyl Ketene as Initiator. **J. Polym. Sci. Part A-1.** 4: 301-318.

Van Ruiten, J., J.A.F. Kunst, R. Rulkens and J.P. Penning. 2005. **Process for the Manufacture of Homopolyamide-4,6 Fibers.** U.S. Patent 3, 911,257.

Vishvanath, S.P., J. Roda and J. Kralicek. 1981. Acceleration of the Anionic Polymerization of 2-Pyrrolidone. **Makromol. Chem.** 182: 3119-3128.

Yamano, N., A. Nakayama, N. Kawasaki, N. Yamamoto and S. Aiba. 2008. Mechanism and Characterization of Polyamide 4 Degradation by *Pseudomonas* sp. **J. Polym. Environ.** 16: 141-146.

APPENDIX



Appendix Figure 1 DSC thermogram of polyamide-4.

CIRRICULUM VITAE

NAME : Miss Patcharin Pinthong

BIRTHDAY : May 21, 1984

BIRTHDAY PLACE : Bangkok, Thailand

EDUCATION :

YEAR	**INSTITUTE**	**DEGREE/DIPLOMA**
2006	King Mongkut's University of Technology Thonburi.	B.Sc. (Chemistry)

SCHOLARSHIP : Kasetsart University Research and Development Institute (KURDI) 2008