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Doctoral Dissertation

Syntheses, Properties, and Biodegradation of Aliphatic Polyamides

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Contents

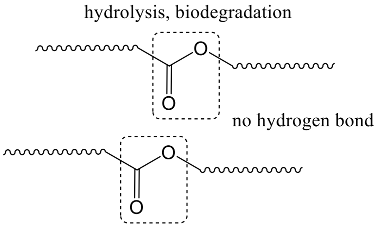
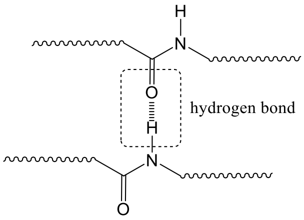
General Introduction

Plastics have been used in almost all parts of the world from the advantages: stability, processability, lightness, and low cost. In recent years, the global production level is about 290 million tons. From the stability for long periods of time, the plastics continue to remain in natural environment. That is to say, environmental load and pollution caused by remaining plastic waste is becoming a serious problem in throwaway society. Specifically, millions of tons of plastics have led to the shortage of the reclaimed land, the possibility of poisonous gas generation by incineration in low performance furnace, the serious influence toward marine life by accidental eating, the spoilage of natural landscape by indiscreet scattering.

During the last four decades, the deleterious influence of the synthetic polymers on the environment has been perceived clearly by researchers.1,2) There are two solutions of the environmental problems caused by plastics. One is the effective use of plastics resources such as reuse or recycling of commodity and as material or chemical or thermal recycling of the used plastics. The other one for solving the environmental problems is the utilization of the substance circulation in the realm of nature. The latter solution is the designing the polymer structure being susceptible to decompose by natural microbe, namely, the research and development of biodegradable polymers causing no harm to the natural environment. Historically, biodegradation of natural polymer (rubber) was observed at least 80 years ago,3) then, possibilities of microbiological attack to various polymers have been studying to clarify the relationship between biodegradation and chemical structure of the polymers.4) As a consequence, a wide variety of biodegradable polymers has been synthesized and investigated.5-17) These biodegradable polymers have been developed by means of chemical modification for natural polymers, microorganism fermentation process and chemical synthesis.18-20) In particular, chemical synthesis of biodegradable polymers is an excellent method in terms of the availability of many kinds of monomers, the possibility of controlling polymer structures and the consequent diversities of chemical and physical properties. Summarizing various reviews, it has been pointed out that one of the important factors in biodegradation is the presence of hydrolysable linkage such as ester, amide, urethane and urea groups in the main chains.21,22) From that knowledge, various kinds of polymers whose hydrolysable linkage: aliphatic polyesters,23) copolyesters,24,25) copolyesterethers,26,27) and copolyesteramides28,29) have been studied in the area of chemical synthesis.

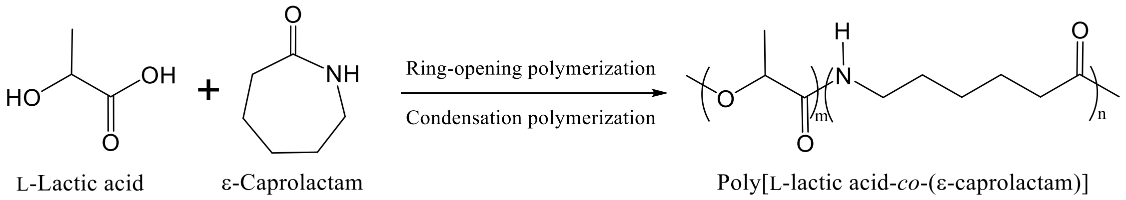
Among those polymers, various aliphatic polyesters have been extensively studied and developed for practical use. The aliphatic polyesters are essentially biodegradable and widely used, whereas their thermal and mechanical properties are insufficient depending on application purpose. On the other hand, aliphatic polyamides, with the strong hydrogen bond between polymer chains, have excellent thermal and mechanical properties, whereas their biodegradability is low in general under the usual environment. In particular case such as enrichment culture30) or special fungus31) treatments, low molecular weight32), naturally occurring polymers33), the aliphatic polyamides are biodegraded. That being the case, it is of technical as well as fundamental interest to study biodegradation of aliphatic polyamides having amide linkage. The features of ester linkage and amide linkage are summarized in Table 1 for comparison. On the basis of the each features, aliphatic polyamides, with their potential biodegradability, have possibility to become attractive biodegradable materials. Specifically, the aliphatic polyamides in this thesis are composed of polyamide 6 or polyamide 3 units in polyester backbone or only polyamide 4 unit. These units are selected on the basis of the features for polyamides which have relative short methylene chains. Polyamide 6 has high melting point without biodegradability. Polyamide 3 has too strong hydrogen bond to melt without biodegradability. As to polyamide 4, the copolyesteramide containing polyamide 4 unit has incomplete properties, whereas the biodegradation of polyamide 4 itself has been found in view of the past study. Thus polyamide 4 has high melting point with biodegradability. The selected polyamides have relative short methylene chains. It is, therefore, of interest in biodegradability as well as physical property to develop novel biodegradable polymers having these amide linkages: amide linkage incorporated into polyester, copolyesteramide (Chapter 1, 2) and only amide linkage, polyamide (Chapter 3, 4, 5).

Table 1 The features of ester linkage and amide linkage

	Aliphatic polyester  		Aliphatic polyamide 
Hydrophilicity	+	<	++
Hydrolysis	++	>	+
Biodegradation	++	>	±
Physical properties	+	<	++

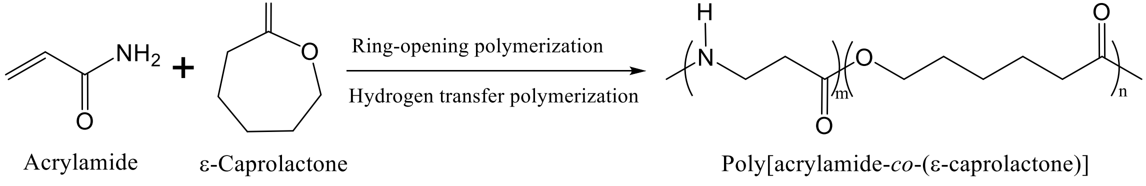
As for the copolyesteramide in this thesis, the present study is concerned with biodegradation, hydrolysis in Table 1. The constitutional unit of polyester: poly(ε-caprolactone) or poly(L-lactic acid) and the constitutional unit of polyamide: polyamide 6 or polyamide 3 are present in polymer backbone. The greater part of the biodegradable plastics put to practical use are aliphatic polyesters. Both poly(L-lactic acid) and poly(ε-caprolactone) are familiar polyesters as practical biodegradable plastics, while their thermal, mechanical properties and biodegradability are insufficient. For example, poly(ε-caprolactone) has the tensile strength of about 20 MPa and the melting point of about 60°C. In contrast, poly(ε-caprolactam) having similar structure has the tensile strength of about 80 MPa and the melting point of 225°C. The difference in poly(ε-caprolactone) and poly(ε-caprolactam) are due to the presence of hydrogen bond between amide linkages. Therefore, introducing amide linkage into aliphatic polyesters was examined in this study. Thus far ε-caprolactam or 2-pyrrolidone have been used with introducing amide linkage unit into poly(ε-caprolactone) chain. Copolymerization of ε-caprolactone with ε-caprolactam or 2-pyrrolidone correspond to introducing polyamide 6 or polyamide 4 units, respectively. The previous study applied polyamide 6 and polyamide 4 unit in copolyesteramides, and revealed the relation between biodegradation and copolyesteramide’s composition. This thesis describes other copolyesteramides containing polyamide 6 or polyamide 3 units. The polyamide 6 and polyamide 3 have no biodegradability under ordinary conditions, while it is high degradability and high hydrophobicity for poly(ε-caprolactone) and low biodegradability for poly(L-lactic acid). It is worth to investigate the tendency for the copolyesteramide which have each unit of different biodegradation. The purpose of the present study for the copolyesteramide was to investigate polymer synthesis, characterization and biodegradation.

Chapter 1 deals with copolyesteramide consisting of L-lactic acid unit and ε-caprolactam unit (constitutional unit of polyamide 6), whose characterization, synthesis method, polymerization and biodegradation were presented and discussed. The copolyesteramide: poly[(L-lactic acid-*co*-(ε-caprolactam)], was synthesized by combination of ring-opening polymerization and condensation polymerization with metal powder as a catalyst (Scheme 1). The biodegradation of amide linkage was demonstrated, and the relationship between biodegradation and polymer composition, namely amide linkage content, was revealed.



Scheme 1

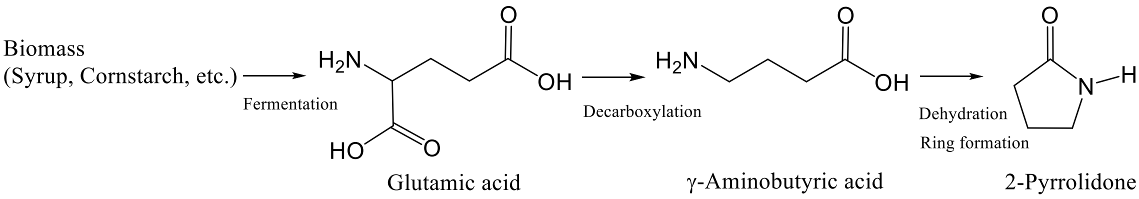
Chapter 2 deals with copolyesteramide consisting of acryl amide unit (β-alanine unit: constitutional unit of polyamide 3) and ε-caprolactone, whose polymerization, characterization, hydrolysis and biodegradation were presented and discussed. The copolyesteramide: poly[acrylamide-*co*-(ε-caprolactone)], was synthesized by combination of ring-opening polymerization and hydrogen transfer polymerization with metal base catalyst (Scheme 2). The influence on simple and enzymatic hydrolysis and biodegradation by the incorporation of amide linkage into polyester were shown for various polymer compositions.



Scheme 2

As for the polyamide in this thesis, the present study is concerned with biodegradation, physical properties in Table 1 and also functionality with polyamide 4 (PA4) as a target polymer backbone. The synthesis of PA4 was first reported by Ney et al.34) in 1953. They succeeded in synthesizing PA4 by the ring-opening polymerization of 2-pyrrolidone (PRN). Since then, the syntheses and properties of PA4 have been investigated intermittently;35-39) however, this topic has received very little attention, and so far, no processes have been developed to realize a practical use of PA4. Nevertheless, some researchers have shown interest in PA4 because of its unique properties, and a few articles on this compound have been published in recent years.40-44)

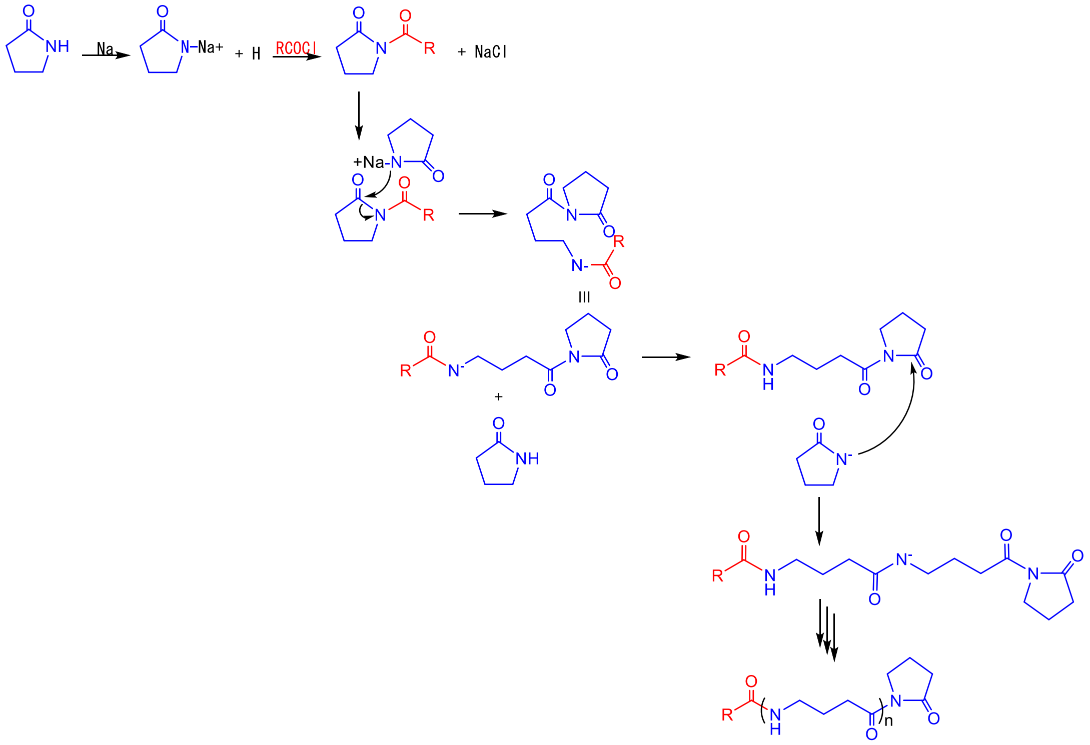
Under these circumstances, the environmental sustainability has received remark for PA4. Thus far PA4 has been found to be biodegradable in various environments such as in soil, sea water, and activated sludge, in spite of its outstanding properties such as its high melting point and tensile strength.40-47) Further, PRN, which is the monomer of PA4, can be derived from glucose through use of glutamic acid and γ-aminobutyric acid by a combination of biochemical and chemical processes (Scheme 3).48,49) The use of biomass provides one promising solution to the depletion of fossil resources (petroleum, etc.) from the viewpoint of green sustainable chemistry. These significant features have gradually reawakened the interest in the study of syntheses, properties, structure,50) biodegradation, and biosynthesis of PA4 monomers.



Scheme 3

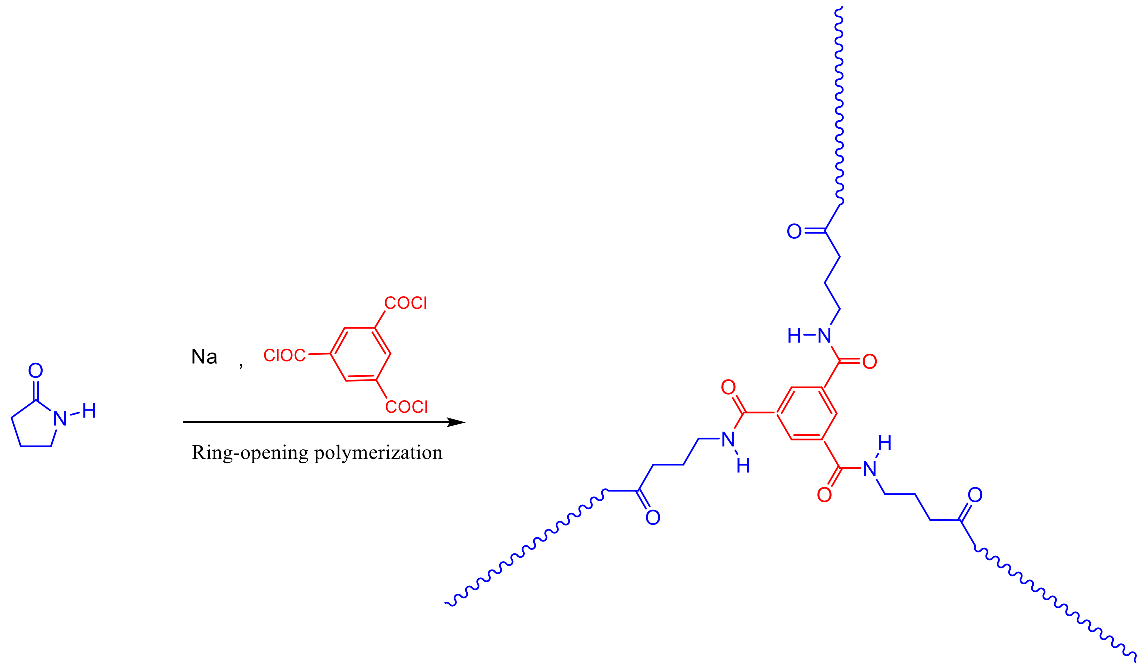
Furthermore, various structures of PA4 can easily be designed because of a polymerization mechanism in which the initiators are attached to the polymer chains. This polymerization mechanism plays a key role in the development of novel PA4 containing unique structures that differ from conventional linear PA4. Specifically, when a base is used as a catalyst and a carboxylic acid derivative is used as an initiator, an amide anion of PRN forms and reacts with the carboxylic acid derivative to produce acylated 2-pyrrolidone. Since the acylated 2-pyrrolidone has a high reactivity, the ring-opening polymerization of

PRN proceeds through an activated monomer mechanism.[35)] In this mechanism, the PA4 chains propagate from the active carboxyl groups on the initiator, thereby facilitating the design of polymeric structures. When initiators having various structures or functional groups are used, the characteristic structure or functionality on the origin of the initiators is incorporated into the PA4 chains. Consequently, the utilization of the activated monomer mechanism enables the modification of the physical properties or the introduction of functionality into the polymer (Scheme 4). Thus the PA4 has the unique features different from the conventional biodegradable plastics, and the possibility was being examined with the aim of practical use.



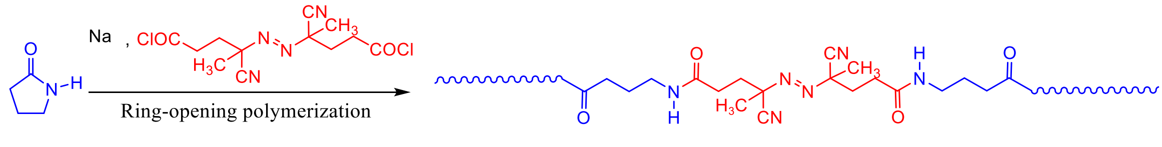
Scheme 4

Chapter 3 deals with polyamide 4 containing branched structure in polymer backbone, whose synthesis, characterization, properties and biodegradation were presented and discussed. The polyamide 4: 3-branched, 4-branched and linear type was synthesized by ring-opening polymerization with metal sodium and several carboxylic acid chlorides as initiators (Scheme 5). The effect on mechanical property by introducing branched structure into polymer backbone was shown. The evidence for biodegradation of branched polyamide 4 was also proved by measuring formed carbon dioxide and nitrate ion.



Scheme 5

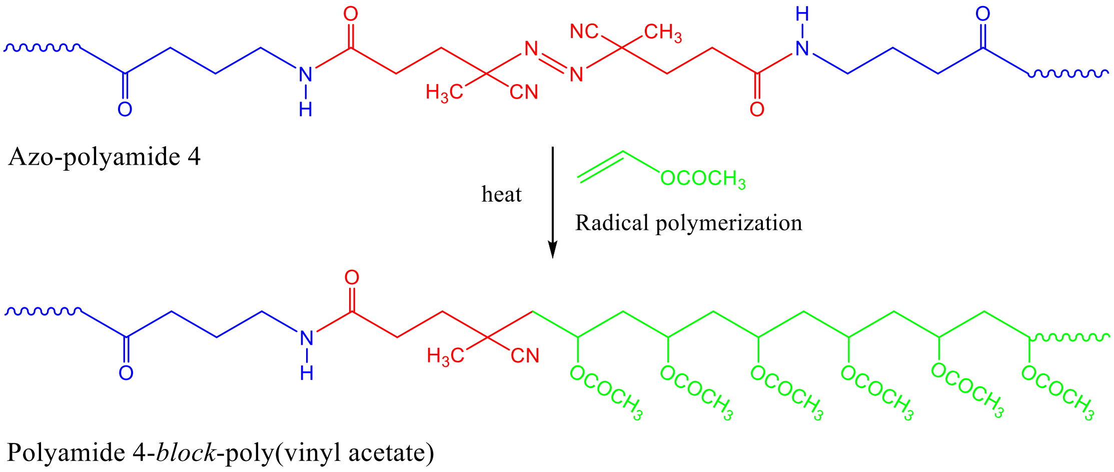
Chapter 4 deals with polyamide 4 containing an azo group (azo-polyamide 4) in polymer backbone, whose synthesis, characterization, initiation activity for the radical polymerization of several vinyl monomers were presented and discussed. The polyamide 4 containing an azo group: polyamide 4 azo macromolecular initiator was synthesized by ring-opening polymerization with metal sodium and an azo compound acid chloride as an initiator (Scheme 6). For several vinyl monomers, the functionality as the polyamide 4 azo macromolecular initiator was confirmed. In particular, the polymerization product for using styrene was examined.



Polyamide4 containing azo group (Azo-polyamide 4)

Scheme 6

Chapter 5 deals with polyamide 4-*block*-poly(vinyl acetate), whose polymerization, characterization, properties, biodegradation and morphology were presented and discussed. The polyamide 4-*block*-poly(vinyl acetate) was synthesized by radical polymerization by using azo-polyamide 4 as an initiator (Scheme 7). The polymerization, thermal and mechanical properties was studied in detail. The biodegradation for polyamide 4 backbone was evaluated by the standard activated sludge.


Azo-polyamide 4

Polyamide 4-*block*-poly(vinyl acetate)

Scheme 7

References

1) F. Rodoriguez; *Chem. Tech.* **1971**, 401.

2) A. L. Andrady; *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1994**, *C34*, 25.

3) D. Spence, C. B. Van Niel; *Ind. Eng. Chem.* **1936**, *28*, 847.

4) W. M. Heap, S.H. Morrell; *J. Appl. Chem.* **1968**, *18*, 189.

5) E. Kuster; *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1979**, *35*, 395.

6) G. S. Kumar, V. Kalpagam, U. S. Nandi; *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1983**, *C22*, 225.

7) R. W. Lenz; *Adv. Polym. Sci.* **1993**, *107*, 1.

8) R. Chandra, R. Rustgi; *Prog. Polym. Sci.* **1998**, *23*, 1273.

9) M. Okada; *Prog. Polym. Sci.* **2002**, *27*, 87.

10) R. A. Gross, B. Kalra; *Science* **2002**, *297*, 803.

11) L. S. Nair, C. T. Laurencin; *Prog. Polym. Sci.* **2007**, *32*, 762.

12) A. P. Gupta, V. Kumar; *Eur. Polym. J.* **2007**, *43*, 4053.

13) I. Vroman, L. Tighzert; *Materials* **2009**, *2*, 307.

14) K. Leja, G. Lewandowicz; *Polish J. Environ. Stud.* **2010**, *2*, 255.

15) A. A. Kumar, K. Karthick, K. P. Arumugam; *Internat. J. Biosci. Biochem. Bioinformat.* **2011**, *1*, 173.

16) B. Imre, B. Pukanszky; *Eur. Polym. J.* **2013**, *49*, 1215.

17) A. C. Fonseca, M. H. Gil, P. N. Simoes; *Prog. Polym. Sci.* **2014**, *39*, 1291.

18) J. Philippa, J. M. S. Hocking; *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1992** *C32,* 35.

19) G. Scott, D. Gilead; *Degradable Polymers*. London: Chapman & Hall; **1999**.

20) J. I. Kroshwitz; *Concise Encyclopedia of Polymer Science and Engineering*. New York: John Wiley & Sons; **1990**.

21) P. J. Hocking; *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1992**, *C32,* 35.

22) D. Satyanarayana, P. R. Chatterji; *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1993**, *C33,* 349.

23) M. Vert, S. M. Li, G. Spenlehauer, P. Guerin; *J. Mater. Sci.* **1992**, *3,* 432.

24) A. Nakayama, N. Kawasaki, I. Arvanitoyannis, J. Iyoda, N. Yamamoto; *Polymer* **1995**, *36*, 1295.

25) A. Nakayama, N. Kawasaki, I. Arvanitoyannis, S. Aiba, N. Yamamoto; *J. Environ. Polym. Degrad.* **1996**, *4*, 205.

26) Y. Maeda, A. Nakayama, N. Kawasaki, K. Hayashi, N. Yamamoto; *Kobunshi Ronbunshu* **1995**, *51*, 724.; *Chem. Abstr.* **1995**, *122*, 56741x.

27) Y. Maeda, A. Nakayama, N. Kawasaki, K. Hayashi, S. Aiba, N. Yamamoto; *J. Environ. Polym. Degrad.* **1996**, *4*, 225.

28) H. Komoto; *Makromol. Chem.* **1968**, *115,* 3.

29) I. Goodman, A. Valavanidis; *Eur. Polym. J.* **1980**, *20*, 539.

30) K. Tomita, N. Hayashi, N. Ikeda, Y. Kikuchi; *Polym. Degrad. Stab.* **2003**, *81*, 511.

31) M. Shimao; *Curr. Opin. Biotechnol.* **2001**, *12,* 242.

32) V. Andreoni, G. Baggi, C.Guita, P. Manfrin; *Int. Biodeterior. Biodegrad.* **1993**, *31*, 41.

33) F. B. Oppermann, S. Pickartz, A. Steinbuchel; *Polym. Degrad. Stab.***1998**, *59,* 337.

34) W. O. Ney Jr., W. R. Nummy, C. E. Barnes; *U.S. Pat.* **1953 May 12**, 2, 638, 463.

35) H. K. Hall Jr; *J. Am. Chem. Soc.* **1958**, *80,* 6404.

36) H. Tani, T. Konomi; *J. Polym. Sci. Part A-1 Polym. Chem.* **1966**, *4,* 301.

37) S. Barzakay, M. Levy, D. Vofsi; *J. Polym. Sci. Part A-1 Polym. Chem.* **1966**, *4*, 2211.

38) H. Sekiguchi, B.Coutin; *J. Polym. Sci. Polym. Chem. Ed.* **1973**, *11*, 1601.

39) J. Roda, J. Kralicek, Z. Bouskova; *Eur. Polym. J.* **1977**, *13*, 119.

40) K. Hashimoto, M. Sudo, K. Ohta, T. Sugimura, H. Yamada, T. Aoki; *J. Appl. Polym. Sci.* **2002**, *86*, 2307.

41) N. Kawasaki, A. Nakayama, N. Yamano, S. Takeda, Y. Kawata, N. Yamamoto, S. Aiba; *Polymer* **2005**, *46*, 9987.

42) N. Yamano, A. Nakayama, N. Kawasaki, N. Yamamoto, S. Aiba; *J. Polym. Environ.* **2008**, *16*, 141.

43) K. Tachibana, K. Hashimoto, M. Yoshikawa, H. Okawa; *Polym. Degrad. Stab.* **2010**, *95*, 912.

44) K. Tachibana, K. Hashimoto, N. Tansho, H. Okawa; *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 2495.

45) K. Hashimoto, T. Hamano, M. Okada; *J. Appl. Polym. Sci.* **1994**, *54*, 1579.

46) K. Tachibana, Y. Urano, K. Numata; *Polym. Degrad. Stab.* **2013**, *98*, 1847.

47) A. Nakayama, N. Yamano, N. Kawasaki, Y. Nakayama; *Polym. Degrad. Stab.* **2013**, *98*, 1882.

48) C. Takahashi, J. Shirakawa, T. Tsuchidate, N. Okai, K. Hatada, H. Nakayama, T. Tateno, C. Ogino, A. Kondo; *Enzyme Microbial. Tech.* **2012**, *51*, 171.

49) N. Yamano, N. Kawasaki, S. Takeda, A. Nakayama; *J. Polym. Environ.* **2013**, *21*, 528.

50) K. Yamauchi, S. Kuroki, I. Ando; *Polymer* **2002**, *43*, 3331.

Chapter 1 Synthesis, characterization and biodegradability of copolyesteramide: poly[L-lactic acid-*co*-(ε-caprolactam)] by (ring-opening/condensation) polymerization

1.1 Introduction

Aliphatic polyesters are well known to be potentially biodegradable, but their thermal and mechanical properties are not sufficient. On the other hand, polyamides are not susceptible to biodegradation except for limited conditions, although their physical properties are excellent. Thus there have been various attempts to synthesize biodegradable copolyesteramides by ring-opening copolymerization, condensation polymerization and ester exchange reactions of polyesters with polyamides1-5). However, there is no report on copolyesteramides obtained by the copolymerization of L-lactic acid (LLA) with ε-caprolactam (CLM). Those monomers, LLA and CLM, are constituent unit for a typical biodegradable polymer and engineering plastics, respectively. Therefore, the copolyesteramides which has both LLA and CLM unit are expected to have unique properties on biodegradation. This chapter deals with the synthesis of novel copolyesteramides, poly[L-lactic acid-*co*-(ε-caprolactam)] by direct reaction of LLA with CLM, and their biodegradability in an activated sludge.

1.2 Experimental

1.2.1 Materials

L-Lactic acid (Wako Pure Chemical Ind., Japan) was used without further purification. This contains 8 to 15 wt% water. ε-Caprolactam (Wako) was recrystallized from acetone. Metal powders of Fe (Ishizu Pharmaceutical, Japan), Sn (Kishida Chemicals, Japan), Mg (Wako), Zn (Wako), Al (Wako) and Cu (Wako) were used as received. Decalin was dried over sodium and distilled at reduced pressure.

1.2.2 Synthesis

Method 1

L-Lactic acid, ε-caprolactam and metal powder were placed in a round-bottomed, three-necked flask equipped with a magnetic stirrer. The mole ratios of L-lactic acid to ε-caprolactam were 25/5, 50/50, and 75/25. The quantity of metal powder was 1 mol% (Fe, Sn, Mg, Zn) or 10 mol% (Al, Cu) vs. the monomers. The mixture was heated to 180°C under argon atmosphere for 8 h, and subsequently under reduced pressure for another 8 h.

The polymer produced was dissolved in methanol, filtered through a glass filter, precipitated with ethyl ether, washed with water and finally dried under reduced pressure.

Method 2

The reaction mixture was heated to 180°C under argon atmosphere for 8 h in the same manner as in method 1. Water in the reaction mixture was removed as decalin azeotrope by refluxing for 13 h. The product was purified in the same manner as described in method 1.

Method 3

The mixture was heated to 180°C under argon atmosphere for 8 h, and subsequently under reduced pressure for another 30 h. Water in the reaction mixture was removed as decalin azeotrope by refluxing for 13 h. The product was purified in the same manner as described in method 1.

1.2.3 Measurement

IR spectra were recorded on a Nicolet 710 FT-IR spectra meter using neat samples on sodium chloride plate. A Jeol Alpha-500 NMR spectrometer was used to obtain ^{1}H NMR spectra (500 MHz). A mixture of formic acid/$CDCl_3$ (1/9 v/v) was used as NMR solvent with tetramethylsilane as an internal standard. Compositions of the copolymers were calculated from NMR spectra. Molecular weight and molecular weight distributions were measured with gel permeation chromatography (Tosoh, HLC-8020) using hexafluoroisopropyl alcohol (HFIP) as an eluent and poly(methyl methacrylate) (SHODEX M-75, Showa Denko, Japan) as molecular weight standards. The column was a TSKgel GMHHR-M with a limited exclusion molecular weight of 4×10^6 $g\cdot mol^{-1}$.

Biodegradability of the products was evaluated from determination of the amount of carbon dioxide evolved by an activated sludge metabolism according to the procedure reported in detail previously6). The CO_2 evolved was trapped by a sodium hydroxide solution (0.025 $mol\cdot L^{-1}$) and the amount was determined as inorganic carbon by a TOC analyzer. Biodegradation of the polymers was calculated by the following equation:

$$\text{Biodegradation in \%} = \text{amount of observed } CO_2 \,/\, \text{amount of theoretical } CO_2 \times 100$$

The observed CO_2 amount was corrected by subtraction of the blank level. The theoretical CO_2 amount was calculated from the structural formula of the copolymers by assuming that oligomers or monomers formed by enzymatic hydrolysis are completely mineralized to CO_2.

1.3 Results and discussion

The polymerization proceeded homogeneously at 180°C. After 8 h, the viscosity of the reaction mixture increased. Figure 1-1 shows variation of molecular weight with time for the reaction mixture under reduced pressure in method 1. The molecular weight appeared to reach about 3000 g·mol^{-1} for 8 h.

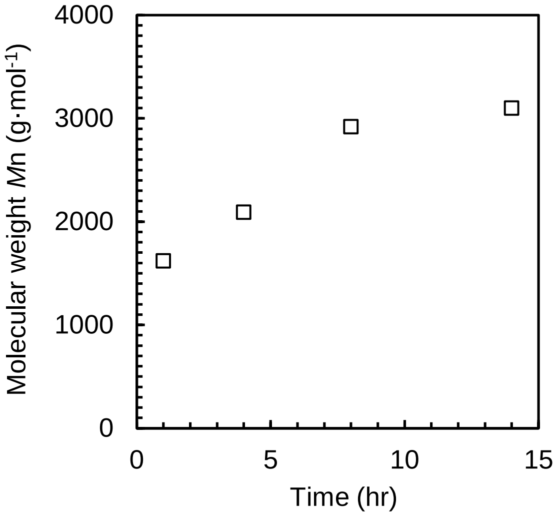


Figure 1-1 Variation of molecular weight with time for reaction mixture under reduced pressure (Sn 1 mol%, 180°C, 0.3 mmHg)

Products were brown, sticky, rubbery or powdery substances. A qualitative survey of the solubility of obtained polymers is given in Table 1-1. Copolymers were soluble in methanol, whereas poly(LLA) and poly(CLM) were insoluble in methanol. This suggests that the products are not a mixture of homopolymers but copolymers. In this series, the solubility depended on the composition of the copolymers rather than the molecular weight. In the case of a high proportion of LLA units, the copolymers were soluble in methanol, tetrahydrofuran, acetone and chloroform. The solubility may reflect the relatively low molecular weight of the produced copolymers, because poly(LLA) is insoluble in tetrahydrofuran and acetone.

Table 1-1 Solubility of poly(LLA-*co*-CLM), poly(LLA), oligo(LLA) and ε-CLM [a)]

Solvent	LLA / CLM 32 / 68 [b)] *M*n: 4790 *M*w: 14200	LLA / CLM 45 / 55 [b)] *M*n: 8370 *M*w: 20400	LLA / CLM 77 / 23 [b)] *M*n: 6230 *M*w: 13900	oligo(LLA)	poly(LLA)	poly(CLM)	ε-CLM
Methanol	++	++	++	++	-	-	++
Tetrahydrofuran	-	-	++	++	-	-	++
Acetone	-	-	++	++	-	-	++
Chloroform	-	-	++	++	++	-	++
Diethyl ether	-	-	-	++	-	-	++
Water	-	-	-	+	-	-	++

a) ++: soluble, +: partially soluble, -: insoluble.
b) mole ratio

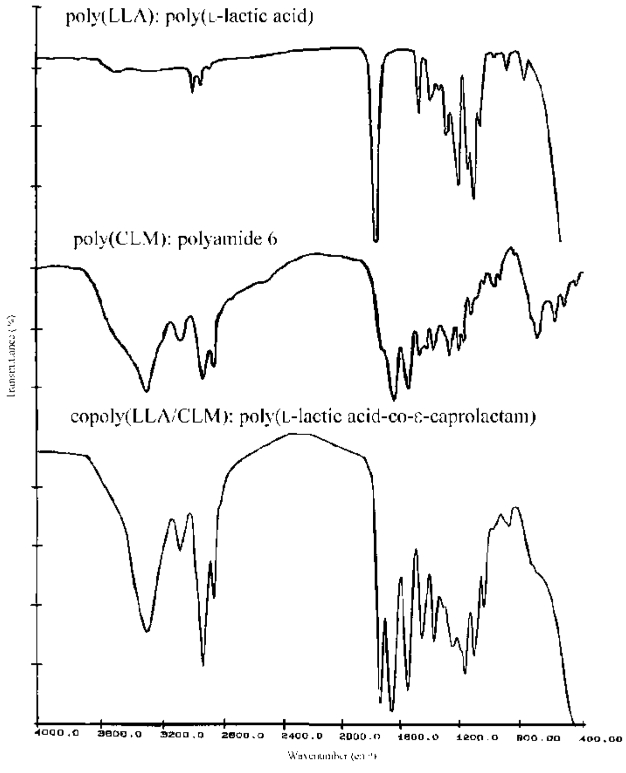


Figure 1-2 IR spectra of poly(LLA), poly(CLM) and poly(LLA-*co*-CLM) (polymer composition LLA/CLM = 45/55)

The representative IR absorption spectra of poly(LLA), poly(CLM) and copolymers (mole ratio LLA/CLM = 45/55) are shown in Figure1-2. An absorption band at 1740 cm^{-1} is due to ester groups. Absorption bands at 1654 and 1545 cm^{-1} were assigned to amide I and amide II, respectively. The spectrum of the copolymer shows characteristic absorptions of the copolyesteramide, i.e., the absorption band of the ester carbonyl group was shifted to a lower wave number compared with that of poly(LLA) (1754 cm^{-1}), while the absorption band of the amide groups was shifted to a higher wave number compared with poly(CLM) (1640, 1541 cm^{-1}).

^{1}H NMR spectra of poly(LLA), poly(CLM) and poly(LLA-*co*-CLM) (mole ratio LLA/CLM = 45/55) are shown in Figure1-3. The ^{1}H NMR spectra exhibited the characteristic signals corresponding to both LLA and CLM units. For the CLM unit, two signals of α-methylene protons were observed at 2.29 and 2.42 ppm, and two further signals of ε-methylene protons were observed at 3.21 and 3.36 ppm, respectively. Furthermore, methylene protons of the LLA unit appeared at 5.14 and 5.30 ppm separately. From the results of solubility, IR absorption spectra and ^{1}H NMR spectra, it can be concluded that the products are poly(LLA-*co*-CLM), not a blend of homopolymers.

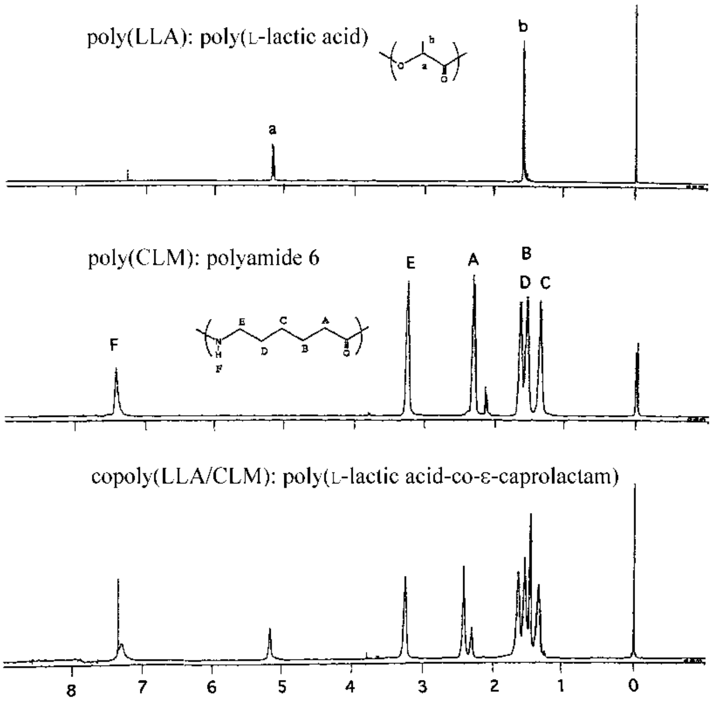


Figure 1-3 ^{1}H NMR spectra of poly(LLA), poly(CLM) and poly(LLA-*co*-CLM) (polymer composition LLA/CLM = 45/55, 500 MHz, solvent: formic acid/CDCl$_3$ 1/9 v/v)

Table 1-2 Results of copolymerization of L-lactic acid with ε-caprolactam (Method 1) a)

Catalyst	Yield (%)	Polymer Composition d) LLA / CLM (mol%)	Mn × 10^{-3} e) (g·mol^{-1})	Mw × 10^{-3} e) (g·mol^{-1})	Mw / Mn e)
none	62	42 / 58	1.6	3.9	2.4
Fe b)	82	46 / 54	2.4	5.9	2.4
Sn b)	62	50 / 50	3.7	9.7	2.6
Mg b)	58	42 / 58	2.8	9.5	3.4
Zn b)	63	43 / 58	3.1	9.6	3.2
Al c)	63	36 / 64	1.6	3.5	2.3
Cu c)	73	48 / 52	2.1	5.2	2.4

a) Feed mole ratio: LLA/CLM = 50/50; L-lactic acid contains 8 to 15 wt% water.
b) 1 mol%.
c) 10 mol%.
d) Mole ratio.
e) GPC solvent: Hexafluoroisopropyl alcohol, standard: Polymethyl methacrylate.

Table 1-3 Results of the copolymerization for varying mole ratios of monomers (Method 1)

Catalyst a)	Feed ratio b) LLA / CLM (mol%)	Yield (%)	Polymer Composition b) LLA / CLM (mol%)	Mn × 10^{-3} c) (g·mol^{-1})	Mw × 10^{-3} c) (g·mol^{-1})	Mw / Mn c)
Fe	75 / 25	45	70 / 30	1.6	3.1	2.0
Fe	50 / 50	82	46 / 54	2.4	5.9	2.4
Fe	25 / 75	55	10 / 90	3.2	10.0	3.1
Sn	75 / 25	49	69 / 31	2.3	4.8	2.1
Sn	50 / 50	62	50 / 50	3.7	9.7	2.6
Sn	25 / 75	25	24 / 76	1.3	2.1	1.7
Zn	75 / 25	39	65 / 35	2.5	5.9	2.4
Zn	50 / 50	63	43 / 57	3.1	9.6	3.2
Zn	25 / 75	23	12 / 88	1.2	1.5	1.3
Al	75 / 25	51	70 / 30	5.2	12.1	2.3
Al	50 / 50	66	44 / 56	13.3	105.0	7.9
Al	25 / 75	50	26 / 74	4.4	3.4	7.8

a) 1 mol%.
b) Mole ratio.
c) GPC solvent: Hexafluoroisopropyl alcohol, standard: Polymethyl methacrylate.

The results of the copolymerization of L-lactic acid with ε-caprolactam by method 1 are given in Table1-2. The yields were over ca. 60% for all copolymerization. The copolymer composition approximately agreed with the feed mole ratio of the monomers. The molecular weight of the copolymers became higher by using metals as a catalyst. Metal powder seemed to be slightly accelerated the polymerization in the steps of ring-opening or condensation.

The influence of the feed ratio of the monomers on the copolymerization is summarized in Table 1-3 (method 1). The yield and the molecular weight of the copolymers were the highest in the case of a feed mole ratio of the monomers of 50/50. The compositions of the copolymers approximately corresponded to the feed ratio of the monomers (Figure 1-4).

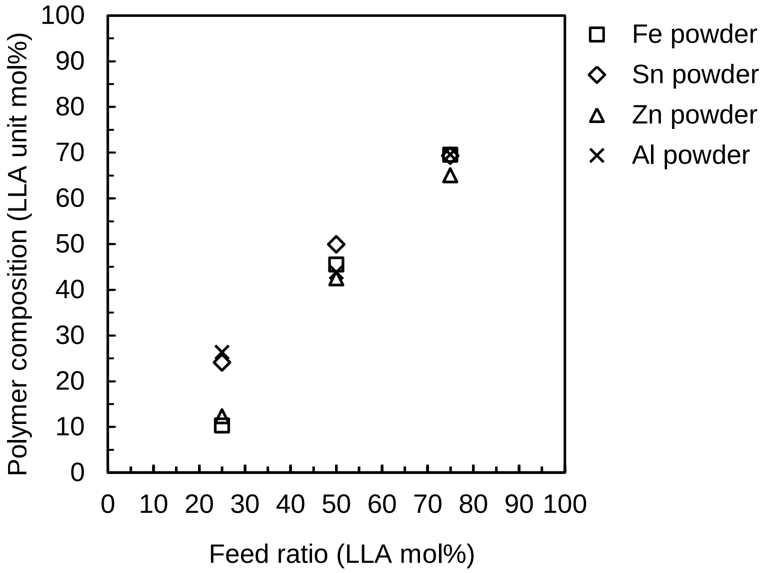
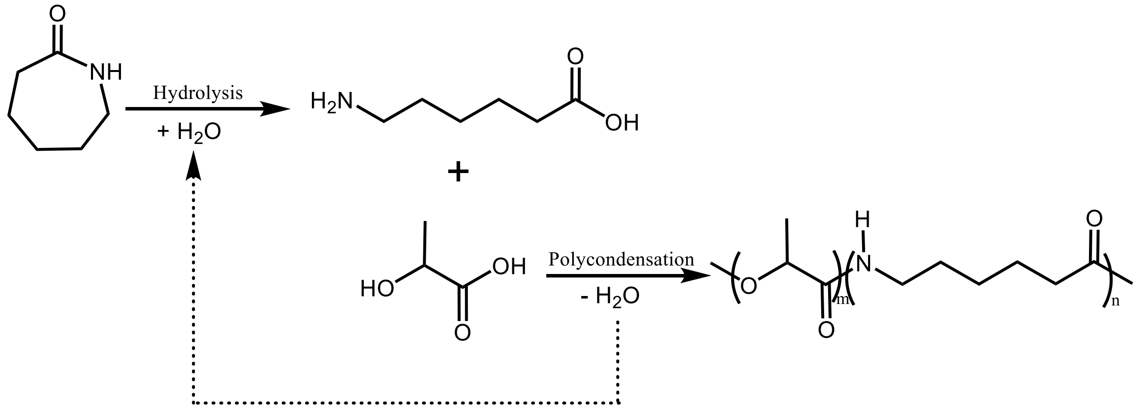


Figure 1-4 Relationship between polymer composition and feed ratio of monomers.

One of the possible reaction pathways is supposed as follows. First, ε-caprolactam reacts with water and becomes ε-aminocaproic acid. Polymerization proceeds by condensation of ε-aminocaproic acid and L-lactic acid. In the case of CLM homopolymerization, a small amount of water acts as a catalyst, and the amount of water is unchanged. On the contrary, in the presence of L-lactic acid, the amount of water is increasing and results in an equilibrium shift from products to reactants. Therefore, in the case of copolymerization, the removal of water is rather important (Scheme 1-1).



Scheme 1-1 Hypothetical reaction mechanism.

Based on these speculations, removal of water from the reaction mixture by azeotropic distillation was tried to increase the molecular weight of the copolymers (method 2). The results are given in Table 1-4. The yields of the copolymers were approximately the same as those obtained via method 1, while the composition of the copolymers roughly agreed with the feed ratio of monomers. The molecular weight became higher by using method 2 and method 3. Therefore, the azeotropic removal of water was effective for these polymerizations.

Table 1-4 Effect of azeotropic distillation on the results of the copolymerization of L-lactic acid with ε-caprolactam (Method 2, Method 3)

Catalyst [a]	Feed ratio [b] LLA / CLM (mol%)	Yield (%)	Polymer Composition [b] LLA / CLM (mol%)	*M*n × 10^{-3} [c] ($g{\cdot}mol^{-1}$)	*M*w × 10^{-3} [c] ($g{\cdot}mol^{-1}$)	*M*w / *M*n [c]
Method 2						
Fe	75 / 25	49	70 / 30	2.8	6.9	2.5
Fe	50 / 50	70	45 / 55	8.4	20.4	2.4
Fe	25 / 75	54	32 / 68	4.8	14.2	3.0
Method 3						
Fe	75 / 25	28	67 / 33	12.0	26.8	2.2
Fe	50 / 50	62	34 / 66	5.6	67.2	12.1
Fe	25 / 75	47	29 / 71	6.2	63.1	10.2

a) 1 mol%.
b) Mole ratio.
c) GPC solvent: Hexafluoroisopropyl alcohol, standard: Polymethyl methacrylate.

Figure 1-5 shows the biodegradation profiles of low molecular weight poly(LLA-*co*-CLM) of different compositions by a standard activated sludge. At the initial step of the biodegradation, in spite of approximately same molecular weights, the rate of biodegradation of poly(LLA-*co*-CLM) with a high content of CLM units was slow, but the difference of biodegradability was small at longer times. The biodegradability was about 60% after 26 days.

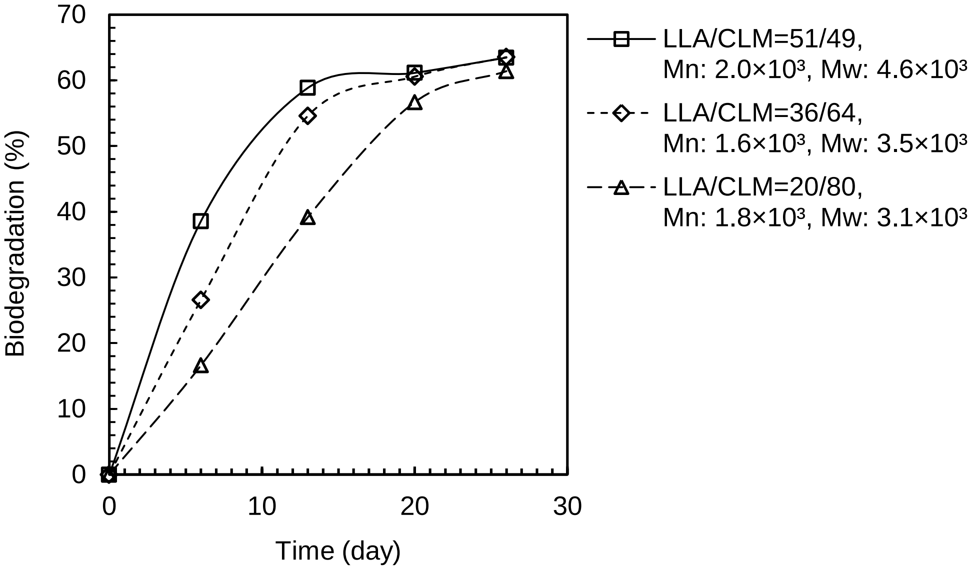


Figure 1-5 Biodegradation profiles of poly(LLA-*co*-CLM) of low molecular weight by a standard activated sludge.

Figure 1-6 shows biodegradation profiles of poly(LLA-*co*-CLM) of relatively high molecular weight by a standard activated sludge. The induction period was a few days, and after around 5 days, the evolution of CO_2 was observed. The copolymers had a higher biodegradability than both homopolymers. The copolymer LLA/CLM = 45/55 showed a higher degradability in spite of a higher molecular weight compared to that of the copolymer LLA/CLM = 32/68.

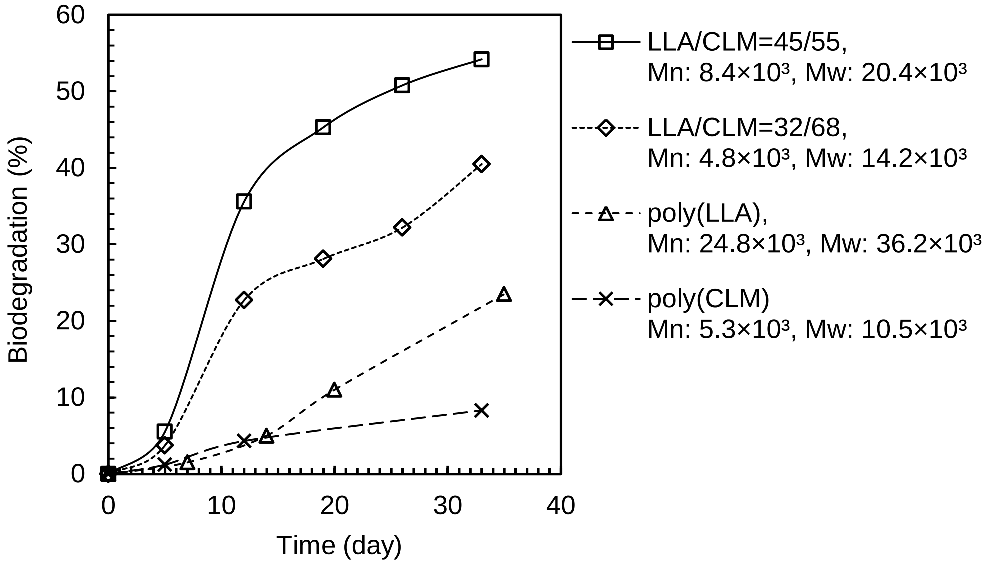


Figure 1-6 Biodegradation profiles of poly(LLA-*co*-CLM) of relatively high molecular weight by a standard activated sludge.

Degraded products, except for CO_2, are expected to be water soluble, and the accumulation of them in a medium can be measured as the total organic carbon concentration (TOC). Figure 1-7 shows the change of TOC values as a function of time. After 5 days, the TOC values were 138 ppm for the copolymer LLA/CLM = 45/55 and 126 ppm for the copolymer LLA/CLM = 32/68, respectively. The high TOC values are due to dissolution of the copolymers in the medium (phosphate buffer solution), because the copolymers were partly soluble in phosphate buffer solution at 30°C. On the other hand, the TOC values rapidly decreased for 2 weeks. This result suggests that the water-soluble organic parts in the medium were metabolized into CO_2 by the activated sludge with the elapse of time. Therefore, the water soluble part is expected not to accumulate in the environment.

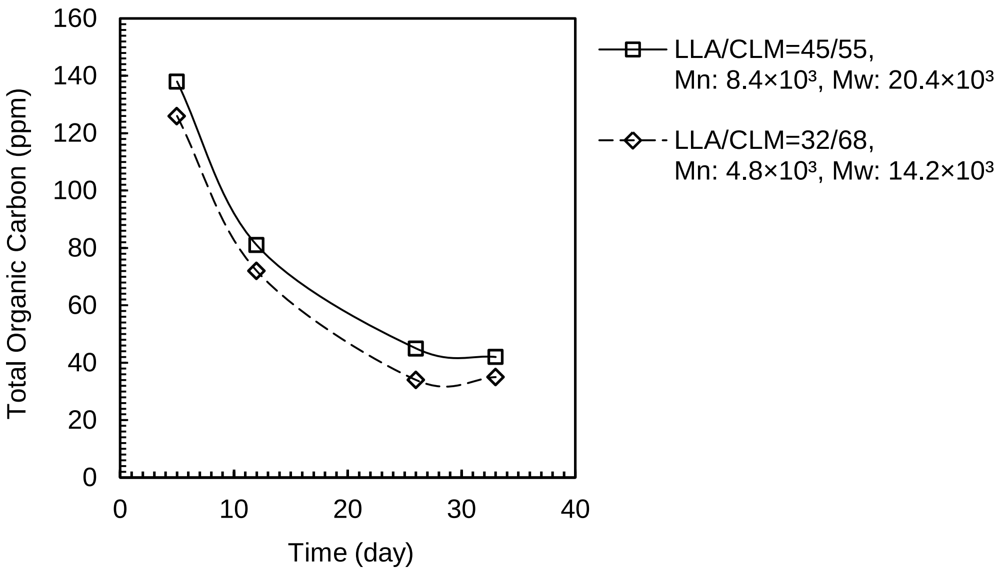


Figure 1-7 TOC profiles based on the soluble polymer and oligomer in a phosphate buffer solution.

From other aspect of the biodegradation by activated sludge, the other poly(LLA-*co*-CLM)s were investigated. Figure 1-8 shows biodegradation profiles of the other poly(LLA-*co*-CLM). Figure 1-9 shows time course of total concentration of NO_2^- and NO_3^- ions in culture medium in the same experiment. The calculated values of concentration of nitrite and nitrate ions were not in agreement with the experimental value, while the order of the concentration were the same as the experiment.

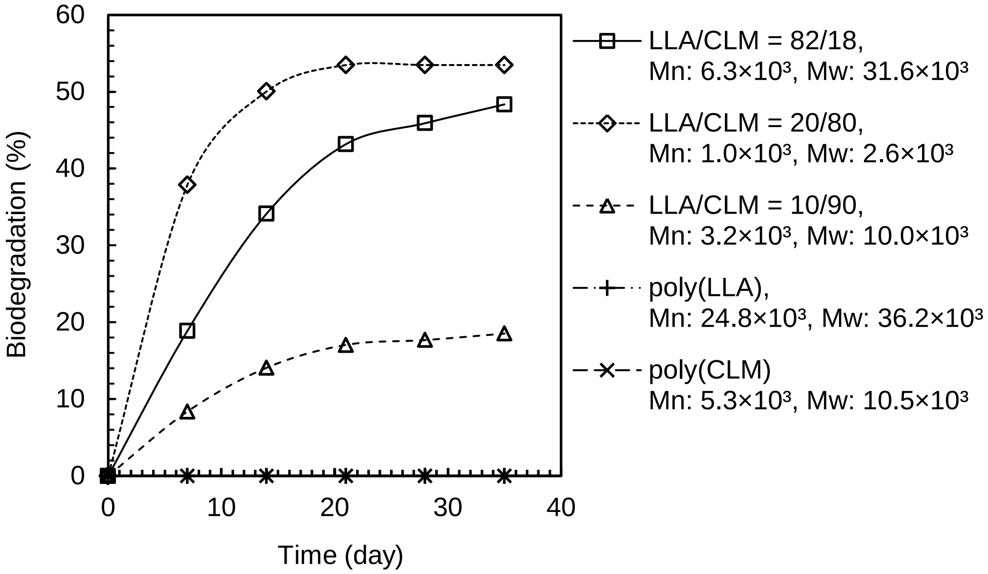


Figure 1-8 Biodegradation profiles of poly(LLA-*co*-CLM) weight by a standard activated sludge.

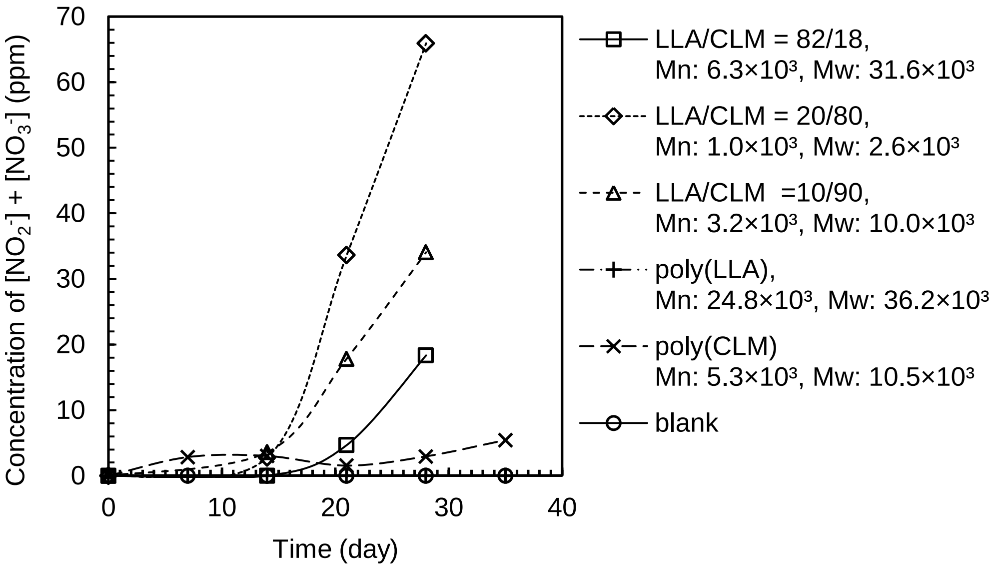


Figure 1-9 Time course of total concentration of NO_2^- and NO_3^- ions in culture medium for biodegradation of poly(LLA-*co*-CLM).

Various poly(LLA-*co*-CLM)s were examined in order to clarify the dependence of biodegradation on polymer composition. Figure 1-10 shows relationship between biodegradation and polymer composition. Both poly(LLA) and poly(CLM) had low biodegradability. As LLA content of poly(LLA-*co*-CLM) increased so did their biodegradability, reaching a peak of about 70% at about 30 mol% to 70 mol% LLA unit. The reason seems to be that the crystallinity decreased and the solubility increased for poly(LLA-*co*-CLM).

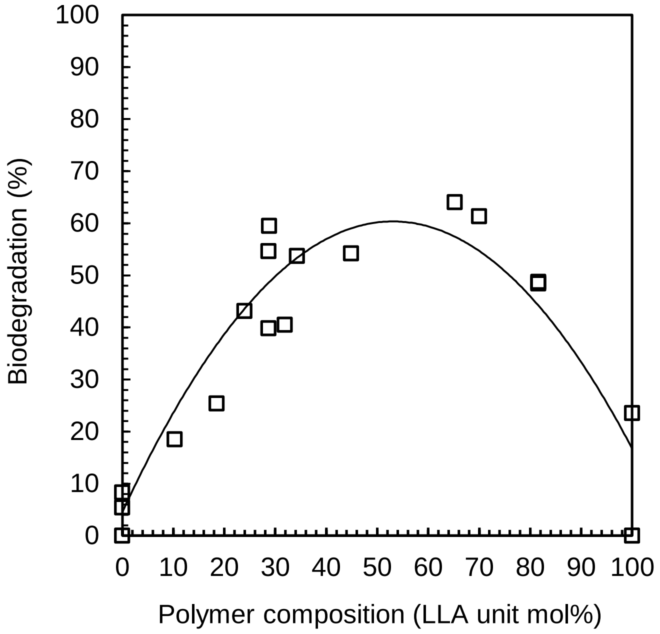


Figure 1-10 Relationship between biodegradation and polymer composition for poly(LLA-*co*-CLM).

1.4 Conclusions

Copolyesteramides: poly(LLA-*co*-CLM) with various compositions were synthesized from L-lactic acid and ε-caprolactam using several metal powders. The presence of metal powder appeared to have a slight effect on promoting polymerization. Azeotropic removal of water from the polymerization system increased the molecular weight of poly(LLA-*co*-CLM). Biodegradation of poly(LLA) or poly(CLM) by an activated sludge was remarkably enhanced by introduction of the other unit, CLM unit or LLA unit. Biodegradation of poly(LLA-*co*-CLM) was affected by polymer composition and exhibited broad peak of about 60 to 65% at about 30 to 70 mol%. With the biodegradation process, poly(LLA-*co*-CLM) was metabolized by an activated sludge to form carbon dioxide, nitrite and nitrate ions.

1.5 References

1) A. Nakayama, T. Higashi, J. Iyoda, M. Ukita, K. Hayashi, N. Yamamoto; *Chem. Express* **1993**, *8*, 181.; *Chem. Abstr.* **1993**, *118*, 170227b.

2) I. Arvanitoyannis, A. Nakayama, N. Kawasaki, N. Yamamoto; *Polymer* **1995**, *36*, 2947.

3) K. E. Gonsalves, X. Chen, J. A. Cameron; *Macromolecules* **1992**, *25*, 3309.

4) I. Goodman, M. T. Rodriguez; *Macromol. Chem. Phys.* **1996**, *197*, 881.

5) Ger. **1993**, 4327024, Bayer AG, invs.: R. Timmerman, R. Dujardin, R. Koch; *Chem. Abstr.* **1995**, *123*, 84346m.

6) Y. Maeda, A. Nakayama, N. Kawasaki, K. Hayashi, S. Aiba, N. Yamamoto; *J. Environ. Polym. Degrad.* **1996**, *4*, 225.

Chapter 2 Synthesis, characterization and biodegradability of copolyesteramide: poly[acrylamide-*co*-(ε-caprolactone)] by (ring-opening/hydrogen transfer) polymerization

2.1 Introduction

Since Breslow et al. have reported that the hydrogen transfer polymerization of acrylamide in the presence of basic initiators produced poly(β-alanine) (Nylon 3),1) the polymerization mechanisms,2-7) physical properties8,9) and structures10,11) have been studied in detail by several researchers. However, there have been done only few researches on the hydrogen transfer copolymerization of acrylamide with other monomers. To the author's knowledge, only Ito et al. have published the hydrogen transfer copolymerization of acrylamide (AA) with ε-caprolactone (CLN).12) In their study, AA was polymerized with CLN using butyllithium, butylmagnesium bromide and metal alkoxides as initiators to synthesize block copolyesteramides. The polymer chain of this copolyesteramide consists of a CLN repeating unit (ester unit) and an AA repeating unit (β-alanine unit). Poly(CLN) which consists of a CLN repeating unit is commercially available as biodegradable plastic13) and several studies on its biodegradability have been carried out.14) Since poly(CLN) is biodegradable, it is expected that the poly[acrylamide-*co*-(ε-caprolactone)] is biodegradable too but there are no researches published yet. It is therefore worthwhile to investigate their biodegradability. This chapter deals with the polymerization of AA with CLN by mainly using calcium hydride as initiator, characterization of the poly(AA-*co*-CLN). Furthermore, non-enzymatic hydrolyses of the poly(AA-*co*-CLN) in water under different conditions, enzymatic hydrolyses and biodegradation by a standard activated sludge were described.

2.2 Experimental

2.2.1 Materials

Acrylamide (Nakarai chemicals, Japan) was recrystallized from ethyl acetate and dried in vacuo. ε-Caprolactone (Wako Pure Chemical Ind., Japan) was distilled under reduced pressure. *n*-Butyllithium (Kishida Chemicals Co., Japan), calcium hydride (Kishida, Japan) and sodium (Wako, Japan) were used as received. Lipase (*Rhizopus arrhizus*, enzyme activity 50000 U·mL^{-1}; Boehringer Mannheim, Germany) for enzymatic hydrolysis tests was used as received. A standard activated sludge was provided from the Chemicals

Evaluation and Research Institute, Japan.

2.2.2 Synthesis

Method 1

A typical procedure was as follows. The Polymerization was performed in an ampoule which was filled with AA (2.84 g, 40 mmol), CLN (4.57 g, 40 mmol) and the initiator. The ampoule was evacuated, sealed and then heated in an oil bath at 120°C for 2 days. The initiators used were *n*-butyllithium, *n*-butyllithium + *tert*-butyl alcohol (1/0.7 mol/mol) and *n*-butyllithium + triphenylmethanol (1/1 mol/mol). The mole ratios of the monomers, AA to CLN, were 25/75, 33/67, 50/50, 67/33, and 75/25. The concentration of the initiators was 1 mol% for the total monomer quantities. The copolymerization products were precipitated in a large amount of methanol which contained a small amount of hydrochloric acid. Then the precipitates were washed with methanol and water to remove the water soluble poly(acrylamide) and dried in vacuo.

Method 2

AA (4.26 g, 60 mmol), CLN (6.85 g, 60 mmol) and calcium hydride (0.051 g, 1.2 mmol) were placed in a round-bottomed, three-necked flask equipped with a mechanical stirrer. The reaction was carried out at 150°C under argon atmosphere for 24 h. The reaction mixture was dissolved in chloroform or formic acid, filtered through a glass filter, poured into a large amount of diethyl ether to precipitate the polymer, and the polymers were dried in vacuo then. The copolymerizations were carried out under various mole ratios of the monomers.

Method 3

The procedure was essentially the same as method 2, except as initiator a mixture of calcium hydride and sodium was used. Each concentration was 1 mol% for the total monomer quantities.

2.2.3 Measurement

FT-IR spectra were recorded on the Nicolet 710 FT-IR spectrophotometer using neat samples on a sodium chloride plate or a KBr pellet. The Jeol Alpha-500 NMR spectrometer was used to obtain ^{1}H NMR spectra (500 MHz) and ^{13}C NMR spectra (125 MHz). A mixture of formic acid/$CDCl_3$ (1/9 v/v) was used as a solvent with tetramethylsilane as an internal standard. Compositions of the copolymers were calculated from ^{1}H NMR spectra.

The molecular weight was measured with a gel permeation chromatography system (Tosoh, HLC-8020) at 40°C. Conditions for the copolyesteramides soluble in chloroform were as follows. column: TSKgel G3000HXL (limited exclusion molecular weight 4×10^5 $g\cdot mol^{-1}$), molecular weight standard: polystyrene (TSK standard polystyrene; Tosoh Corp., Japan), eluent: chloroform 0.6 $mL\cdot min^{-1}$. For the copolyesteramide soluble in hexafluoroisopropyl alcohol (HFIP), column: TSKgel GMHHR-M (limited exclusion molecular weight 4×10^6 $g\cdot mol^{-1}$), molecular weight standard: poly(methyl methacrylate) (SHODEX M-75; Showa Denko, Japan), eluent: HFIP 0.5 $mL\cdot min^{-1}$.

Hydrolysis in distilled water

Samples (25 mg) were immersed in distilled water (2 mL) and allowed to stand at 37°C with occasionally shaking for 48 h. Supernatants of the hydrolysis solutions were filtered through a membrane filter (DISMIC-25P PTFE 0.20 μm; Advantec, Japan), and the concentration of the water-soluble organic substances in the filtrate was measured by a total organic carbon analyzer (TOC-5000; Shimadzu Corp., Japan). The amount of carbon in polymer was calculated from ^1H NMR spectra. From the concentration of the total organic carbon (TOC) and the amount of carbon in polymer, the degradation of the samples were determined.

Degradation in % = amount of carbon in solution / amount of carbon in polymer × 100

Hydrolysis in an autoclave

Samples (25 mg) were immersed in distilled water (10 mL) or 0.1 N hydrochloric acid (10 mL) and heated in an autoclave for sterilization (Tomy, SD-30ND, 125°C, 1.3 $kgf\cdot cm^{-2}$) for 1 or 2 h. The TOC concentration in the hydrolysate was measured as described above.

Enzymatic hydrolysis

The copolymer sample (25 mg) was placed into a test tube filled with 2 mL of phosphate buffer (KH_2PO_4/Na_2HPO_4, pH7.0) and a lipase solution (25 μL, enzyme activity 1250 U) was added. The test tube was incubated at 37°C with occasional shaking for 24 h. The TOC concentration was measured as described above. The TOC concentration of the test solution without lipase was measured as control experiment. The degradation was estimated as described in previous papers.[15-17)]

Biodegradation by an activated sludge

Biodegradability of the copolyesteramides was evaluated from determination of the amount of carbon dioxide (CO_2) evolved by a standard activated sludge metabolism according to the procedure reported in a previous paper.[18)] The CO_2 evolved was trapped by sodium hydroxide solution (0.025 $mol \cdot L^{-1}$) and determined as inorganic carbon by the TOC analyzer. The duration of the biodegradation test was about 1 month and the amount of CO_2 was measured every a week. Biodegradation of the polymer was calculated by the following equation:

$$\text{Biodegradation in \%} = \text{amount of observed } CO_2 \,/\, \text{amount of theoretical } CO_2 \times 100$$

The observed CO_2 amount was corrected by subtraction of the CO_2 amount of the blank experiment. The theoretical CO_2 amount was calculated from the structural formula of the copolymers assuming that degraded products are completely mineralized to CO_2.

2.3 Results and discussion

Polymerization

The results of the copolymerization of AA with CLN by method 1 and method 2 are given respectively in Table 2-1 and Table 2-2. The copolymers containing a richer CLN unit than the feed ratios of monomers were obtained in all cases using *n*-butyllithium as initiator. This fact is probably due to higher reactivity of *n*-butyllithium to ε-caprolactone. In order to produce AA rich copolymer or random copolymer, the copolymerizations by modified initiators, lithium alkoxides, formed by *n*-butyllithium with *tert*-butyl alcohol or triphenylmethanol were attempted. However, the results were not successful.

Table 2-1 Results of the copolymerization of acrylamide with ε-caprolactone (method 1)

Initiator a)	Feed ratio b) AA / CLN (mol%)	Yield (%)	Polymer composition b) AA / CLN (mol%)	*M*n × 10^{-3} (g·mol^{-1}) $CHCl_3$ c) | HFIP d)	*M*w × 10^{-3} (g·mol^{-1}) $CHCl_3$ c) | HFIP d)	*M*w / *M*n $CHCl_3$ c) | HFIP d)
n-BuLi						
	25 / 75	46	6 / 94	7.1 | ----	9.5 | ----	1.4 | ----
	33 / 67	52	25 / 75	2.0 | ----	4.3 | ----	2.1 | ----
	50 / 50	23	25 / 75	4.5 | ----	6.2 | ----	1.4 | ----
	67 / 33	10	15 / 85	1.8 | ----	2.6 | ----	1.4 | ----
	75 / 25	9	21 / 79	2.0 | ----	2.9 | ----	1.5 | ----
n-BuLi + *tert*-BuOH						
	25 / 75	56	15 / 85	6.9 | ----	9.7 | ----	1.4 | ----
n-BuLi + Ph_3COH						
	25 / 75	39	17 / 83	12.8 | ----	18.6 | ----	1.5 | ----

a) 1 mol%.
b) Mole ratio.
c) GPC solvent: Chloroform, standard:Polystyrene
d) GPC solvent: Hexafluoroisopropyl alcohol, standard: Polymethyl methacrylate.

To improve the production of copolymer, calcium hydride that is used for drying CLN19) was adapted as mild initiator in method 2. In this case, no polymerization initiated at room temperature. On the other hand, when the reaction vessel was immersed in an oil bath at 150°C, the reaction started rapidly. After 15 min, the internal temperature of the reaction vessel rose to around 200°C and the viscosity of the reaction mixture increased. The influence of the initiator concentration on the polymer yield was examined. It was observed that the yield became lower as the initiator concentration decreased (initiator concentration; yield: 1.0 mol%; 89%, 0.5 mol%; 47%, 0.25 mol%; 21%). Lower initiator concentrations were tried because the hydrogen transfer copolymerization of AA hardly occurred, whereas the radical homopolymerization was predominant to form poly(acrylamide). Poly(acrylamide) was produced through radical vinyl polymerization as a by-product. The results were quite different to those using *n*-butyllithium as the initiator and the copolymers containing rich AA repeating units (β-alanine unit) were also obtained in yield over 80%.

Table 2-2 Results of the copolymerization of acrylamide with ε-caprolactone (method 2)

Initiator [a]	Feed ratio [b] AA / CLN (mol%)	Yield (%)	Polymer composition [b] AA / CLN (mol%)	*M*n × 10^{-3} (g·mol^{-1}) CHCl$_3$ [c] | HFIP [d]	*M*w × 10^{-3} (g·mol^{-1}) CHCl$_3$ [c] | HFIP [d]	*M*w / *M*n CHCl$_3$ [c] | HFIP [d]
CaH$_2$	10 / 90	89	7 / 93	8.3 | ----	13.8 | ----	1.7 | ----
	17 / 83	88	11 / 89	6.2 | ----	10.2 | ----	1.6 | ----
	20 / 80	86	13 / 87	4.8 | ----	9.6 | ----	2.0 | ----
	25 / 75	95	17 / 83	1.7 | ----	3.6 | ----	2.1 | ----
	33 / 67	89	21 / 79	1.3 | ----	4.2 | ----	3.4 | ----
	40 / 60	88	36 / 64	1.0 | ----	2.7 | ----	2.6 | ----
	50 / 50	87	38 / 62	0.7 | 37.3, 1.3	1.2 | 11.7, 2.3	1.8 | 3.1, 1.8
	67 / 33	93	52 / 48	---- | 20.1, 1.3	---- | 78.7, 2.0	---- | 3.9, 1.6
	72 / 28	94	62 / 38	---- | 1.6	---- | 2.9	---- | 1.8
	75 / 25	94	73 / 27	---- | 20.2, 1.3	---- | 73.6, 2.1	---- | 3.7, 1.6
	80 / 20	90	79 / 21	---- | 3.0	---- | 11.0	---- | 3.7
	91 / 9	93	92 / 8	---- | 3.0	---- |6.2	---- | 2.1

a) 1 mol%.
b) Mole ratio.
c) GPC solvent: Chloroform, standard:Polystyrene
d) GPC solvent: Hexafluoroisopropyl alcohol, standard: Polymethyl methacrylate.

The polymerization was traced by measuring ^{1}H NMR spectra and molecular weight of the reactant. The time-course of the polymerization using calcium hydride is shown in Figure 2-1. CLN was consumed 88% in 30 min, nearly 100% in 1 h, while AA was consumed 52% in 30 min, 75% in 1 h analyzing signals due to monomer and polymer. The polymerization seemed to proceed rapidly since the molecular weight after 30 min was almost the same as after 20 h.

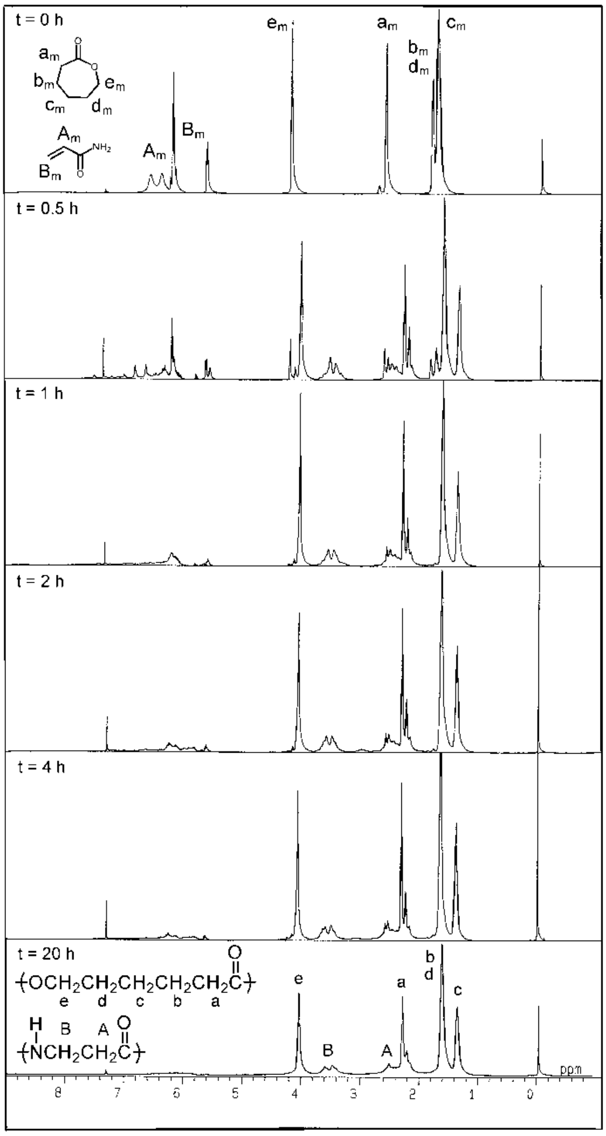
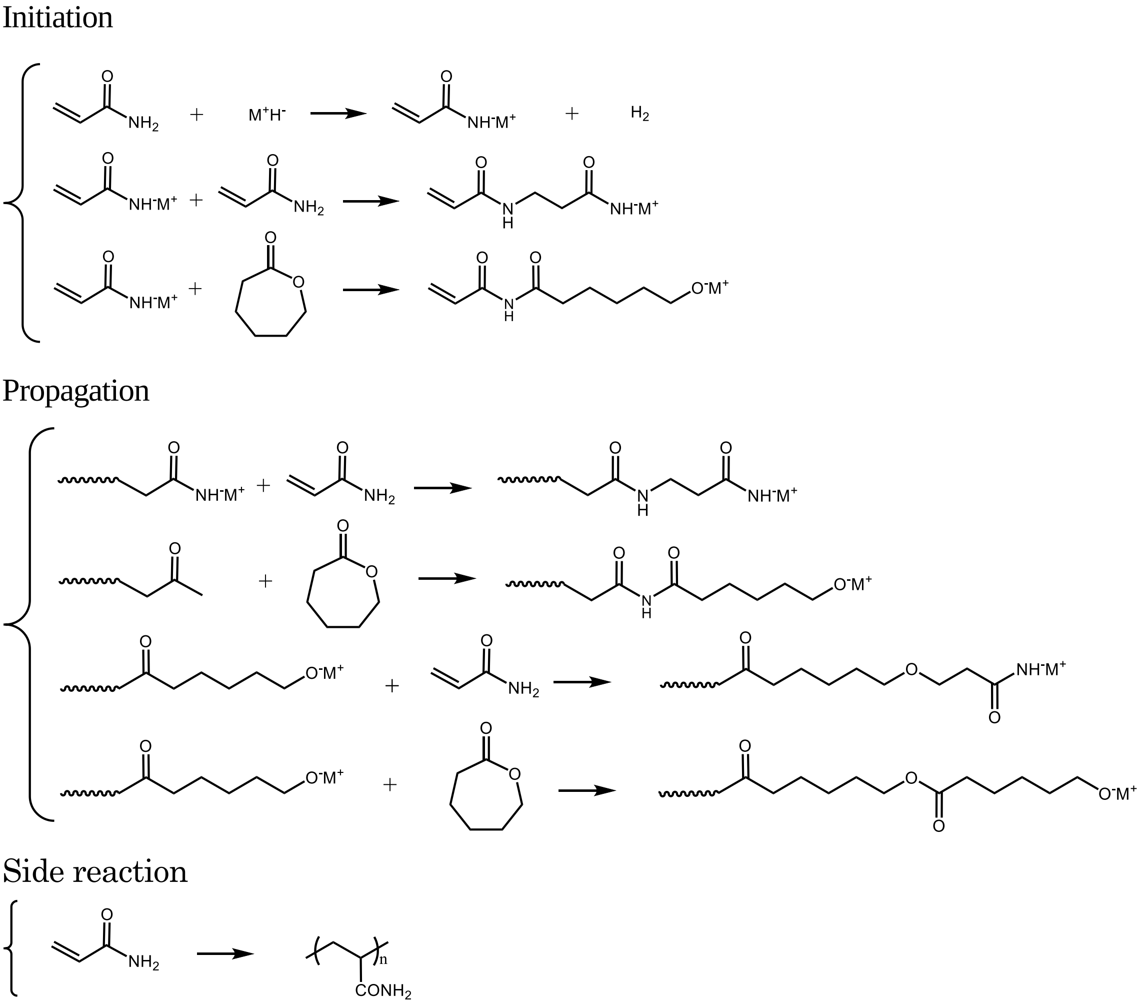


Figure 2-1 ^{1}H NMR spectrum of the time-course of polymerization (500 MHz, solvent chloroform-d, feed mole ratio AA/CLN = 50/50, initiator CaH$_2$, reaction temperature 150°C).

CLN did not homopolymerize under the same conditions, however, AA homopolymerized. These facts indicate that calcium hydride reacts initially with AA to generate activated species and then CLN polymerizes rapidly to produce the copolyesteramide. It is considered that the reaction mechanism consists of following elementary reaction (Scheme 2-1).



Scheme 2-1

With the aim obtaining higher molecular weight for the copolyesteramide, the mixture of calcium hydride and sodium as initiator was used in method 3 (Table 2-3). The remarkable increase in molecular weight and differences in composition and structure of the product polymer were not observed compared to method 2.

Table 2-3 Results of the copolymerization of acrylamide with ε-caprolactone (method 3)

<table>
<tr><th>Initiator [a]</th><th>Feed ratio [b]
AA / CLN
(mol%)</th><th>Yield
(%)</th><th>Polymer composition [b]
AA / CLN
(mol%)</th><th>Mn × 10^{-3}
(g·mol^{-1})
CHCl$_3$ [c] | HFIP [d]</th><th>Mw × 10^{-3}
(g·mol^{-1})
CHCl$_3$ [c] | HFIP [d]</th><th>Mw / Mn
CHCl$_3$ [c] | HFIP [d]</th></tr>
<tr><td>CaH$_2$ + Na</td><td>5 / 95</td><td>91</td><td>3 / 97</td><td>13.4 | ----</td><td>26.1 | ----</td><td>2.0 | ----</td></tr>
<tr><td></td><td>10 / 90</td><td>84</td><td>4 / 96</td><td>7.6 | ----</td><td>1.3 | ----</td><td>1.7 | ----</td></tr>
<tr><td></td><td>17 / 83</td><td>86</td><td>8 / 92</td><td>6.1 | ----</td><td>10.3 | ----</td><td>1.7 | ----</td></tr>
<tr><td></td><td>20 / 80</td><td>88</td><td>10 / 90</td><td>5.5 | ----</td><td>9.6 | ----</td><td>1.7 | ----</td></tr>
<tr><td></td><td>25 / 75</td><td>86</td><td>16 / 84</td><td>1.5 | ----</td><td>4.1 | ----</td><td>2.8 | ----</td></tr>
<tr><td></td><td>33 / 67</td><td>90</td><td>27 / 73</td><td>0.9 | ----</td><td>3.1 | ----</td><td>3.4 | ----</td></tr>
<tr><td></td><td>40 / 60</td><td>87</td><td>31 / 69</td><td>1.2 | 2.1</td><td>2.3 | 5.0</td><td>1.9 | 2.4</td></tr>
<tr><td></td><td>44 / 56</td><td>94</td><td>27 / 73</td><td>---- | 22.0, 1.4</td><td>---- | 34.6, 2.6</td><td>---- | 1.6, 1.9</td></tr>
<tr><td></td><td>50 / 50</td><td>90</td><td>39 / 61</td><td>---- | 2.3</td><td>---- | 7.7</td><td>---- | 3.4</td></tr>
<tr><td></td><td>60 / 40</td><td>100</td><td>44 / 56</td><td>---- | 2.4</td><td>---- | 5.4</td><td>---- | 2.2</td></tr>
<tr><td></td><td>67 / 33</td><td>100</td><td>53 / 47</td><td>---- | 2.3</td><td>---- | 6.3</td><td>---- | 2.8</td></tr>
<tr><td></td><td>72 / 28</td><td>96</td><td>56 / 44</td><td>---- | 1.5</td><td>---- | 2.7</td><td>---- | 1.8</td></tr>
</table>

a) 1 mol%.
b) Mole ratio.
c) GPC solvent: Chloroform, standard:Polystyrene
d) GPC solvent: Hexafluoroisopropyl alcohol, standard: Polymethyl methacrylate.

The polymer composition and the molecular weight in method 2 and method 3 are plotted as a function of the feed ratio of monomers in Figure 2-2 and Figure 2-3, respectively. The polymer compositions were proportional to the feed ratios of monomers and the copolyesteramides with higher content of AA repeating unit (β-alanine unit) were obtained differently for the *n*-butyllithium experiments. The AA repeating unit (β-alanine unit) content in the copolyesteramides was lower than in the monomers. This difference could be attributed to the partly sublimation of AA during the polymerization. The solubility of the copolyesteramide was dependent on the composition and therefore chloroform or hexafluoroisopropyl alcohol was used as eluents for GPC measurements. The molecular weights of the copolyesteramides in the case of hexafluoroisopropyl alcohol are higher than for the same copolyesteramides in chloroform. The molecular weights of the chloroform soluble copolyesteramides were lower with increasing AA content.

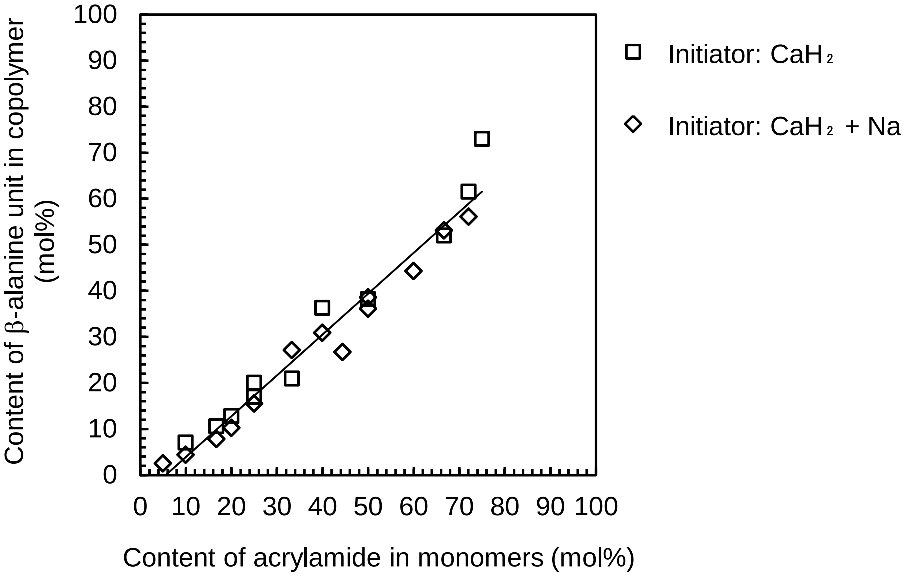


Figure 2-2 Relationship between polymer composition and monomer feed ratio.

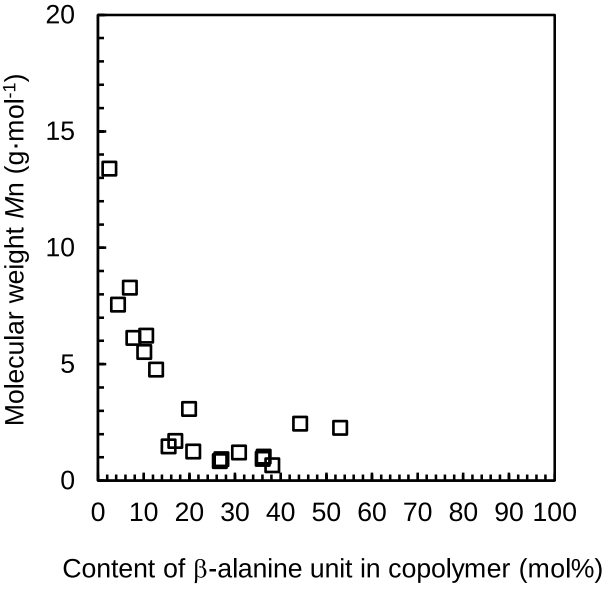


Figure 2-3 Relationship between molecular weight and polymer composition.

Characterization

Copolymerization products were white or pale yellow and sticky paste or powdery substances. Solubility of the copolymers in chloroform depends on the composition. The solubility decreased with increasing AA repeating unit (β-alanine unit) content in the copolymers. The copolymers with AA repeating unit content higher than 45% were insoluble in chloroform. The IR spectrum of the copolymer with polymer composition of AA/CLN = 55/45 is shown in Figure 2-4. Several characteristic absorption bands were observed in the spectrum: carbonyl group of ester at 1731 cm^{-1}, carbonyl and amine group of amide (amide I and II) at 1655 cm^{-1}, 1549 cm^{-1}, respectively. These observations suggest that acrylamide polymerized by Michael reaction, namely hydrogen transfer polymerization, formed a poly(β-alanine) (Nylon 3) structure.

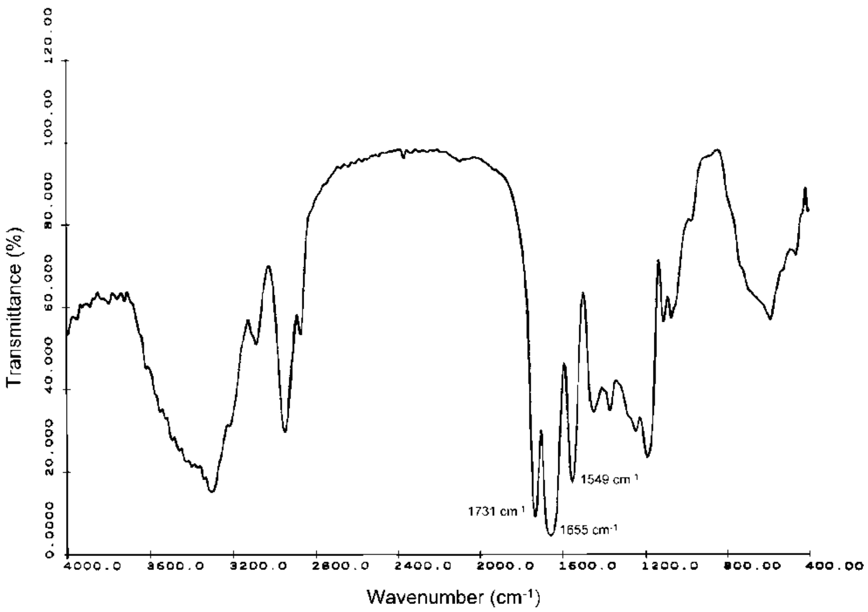


Figure 2-4 IR spectrum of copolyesteramide (polymer composition AA/CLN = 55/45).

Figure 2-5 shows the ^{1}H NMR spectrum of the same sample and the peaks could be assigned as shown in the spectrum. Peaks a, b, c, d and e were assigned to the CLN repeating unit. The two peaks attributable to the methylene protons adjacent to the carbonyl group and those adjacent to the oxygen atom were observed at $\delta = 2.36, 4.11$ ppm (a, e), respectively. The two peaks attributable to the central methylene protons (c) and the peripheral methylene protons (b+d) were observed at $\delta = 1.39$ and $\delta = 1.66$ ppm, respectively. The peaks, A and B, were assigned to the AA repeating unit. The two peaks attributable to the methylene protons adjacent to the carbonyl group and those adjacent to the nitrogen atom were observed at δ = 2.58 and δ = 3.52 ppm (A and B), respectively. Those signals are due to homo sequences. Furthermore, signals due to hetero sequences were observed at δ = 2.26 and δ = 2.49 ppm (a (-CLN-AA-) and A (-AA-CLN-)). The total number of the signals was less than expected. This disagreement can be explained by overlapping of homo and hetero sequence signals. Based on the analysis of homo and hetero sequences in the 2.2 ppm to 2.8 ppm region, the copolymer had a block structure even at the polymer composition (AA/CLN) in the vicinity of 50/50. By studying the ^{13}C NMR spectra, carbonyl signals of the CLN repeating unit (173 ppm) and AA repeating unit (β-alanine unit, 174 ppm) were observed, however, the signal for polyacrylamide (182 ppm) was not observed. These observations from the IR, ^{1}H NMR and ^{13}C NMR spectra clearly supported the idea that the copolymerization of AA with CLN proceeds via a hydrogen transfer process.

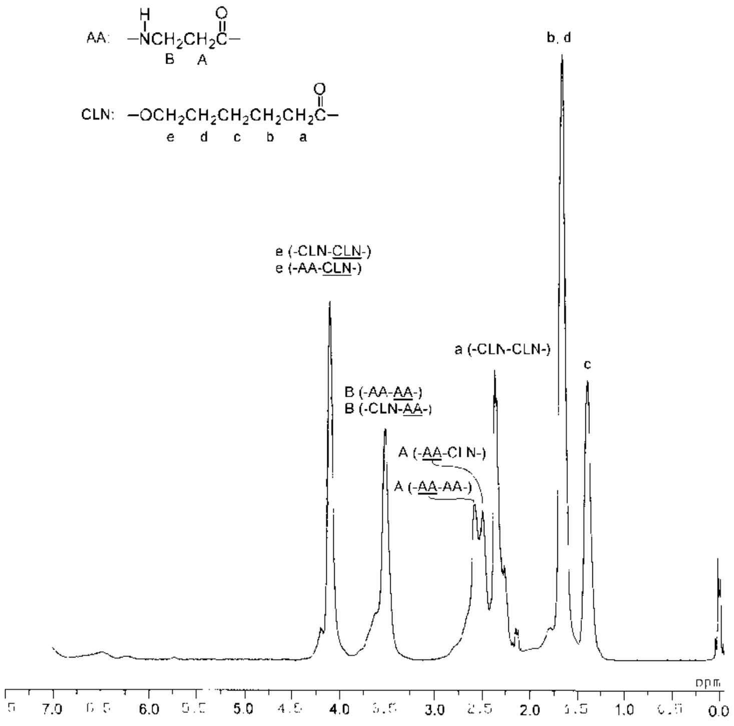


Figure 2-5 ^{1}H NMR spectrum of coplyesteramide (polymer composition AA/CLN = 55/45, 500 MHz, solvent: formic acid/chloroform-d v/v = 1/9).

Hydrolysis in distilled water

In order to examine the hydrolysis of the copolyesteramides, several samples were immersed in distilled water at 37°C for 48 h. Under these conditions, the copolyesteramides slightly hydrolyzed as shown in Figure 2-6.

Hydrolysis in an autoclave

An autoclave was used for hydrolysis experiments in order to raise the degradation rate of the copolyesteramides. Figure 2-6 shows the relationship between degradation rate% and polymer composition under various experimental conditions. Poly(CLN) and the copolyesteramide containing a small amount of AA repeating unit (β-alanine unit) show low degradability, whereas the degradability roses with increasing β-alanine content of the copolyesteramide. The high degradability seems to be due to increased hydrophilicity with an increase in the AA repeating unit (β-alanine unit) in the copolyesteramide. The hydrolyzability rose by using the autoclave compared to simple hydrolysis experiments. In this case, no difference of degradation degree was observed between 1 h and 2 h hydrolysis. Since the acid catalyst has been used for hydrolyzing poly(β-alanine) (Nylon 3) to β-alanine,1) 0.1 N hydrochloric acid was used for this degradation test. The degradation rate of the copolyesteramide increased dramatically for 2 h. It was proved to be effective to use the acid catalyst for the hydrolysis of the copolyesteramides under these comparatively mild conditions such as the autoclave for sterilization. These two points, insertion of AA repeating unit (β-alanine unit) into the poly(CLN) chain and the acid-catalyzed hydrolysis of the copolymer were useful to reproduce oligomers and monomers because poly(CLN) was hardly hydrolyzed under these conditions. This means that commercially available poly(CLN) can be degraded easily to oligomers or monomers by modifying the hydrophilicity. The modification by the copolymerization with AA becomes suitable for chemical recycling.

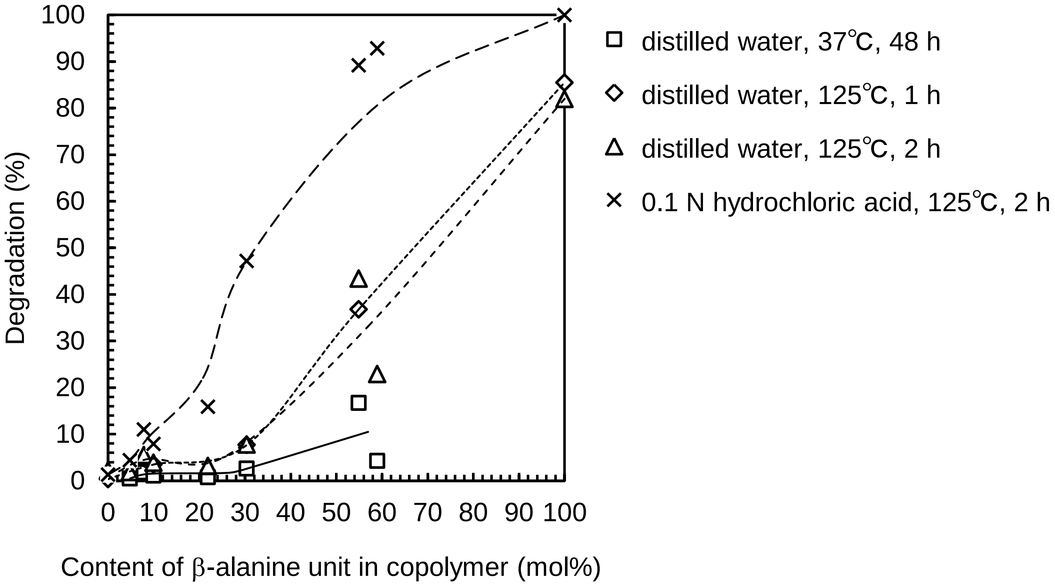


Figure 2-6 Relationship between percent degree of non-enzymatic hydrolysis and polymer composition for copolyesteramide.

Enzymatic hydrolysis

The copolyesteramides were enzymatically hydrolyzed by lipase from *Rhizopus arrhizus*. Figure 2-7 shows the relationship between enzymatic hydrolysis rate% by lipase and the polymer composition. The enzymatic hydrolysis rate of the copolyesteramides ranging in AA repeating unit (β-alanine unit) content from 10% to 30% was higher than that of poly(CLN), whereas the rate decreased over 40% AA repeating unit content. The whole tendency was loose peak pattern. This pattern is explained by weighing hydrophilicity of AA repeating unit (β-alanine unit) against activity of lipase for amide bond. In other words, increasing hydrophilicity by introducing AA repeating unit (β-alanine unit) enhances interaction between the copolyesteramide and water, whereas increasing AA repeating unit (β-alanine unit) content depresses enzymatic reaction of lipase on the copolyesteramide.

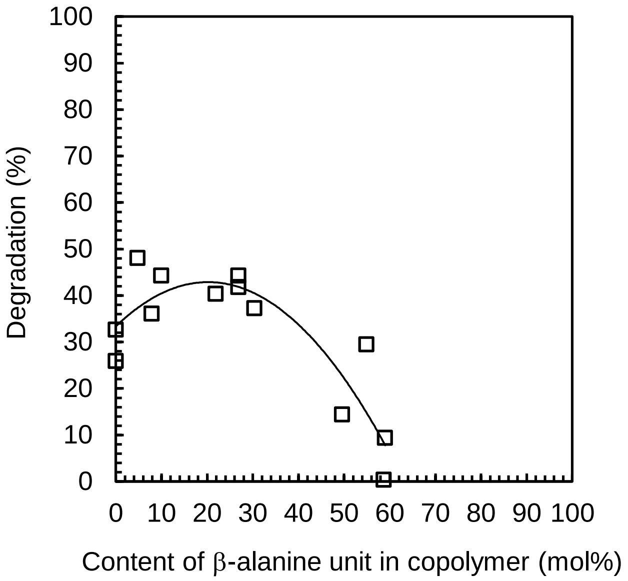


Figure 2-7 Relationship between percent degree of enzymatic hydrolysis and polymer composition for copolyesteramide by lipase (*Rhizopus arrhizus*).

Figure 2-8 shows the ^{1}H NMR spectra of the water-soluble product and residue after enzymatic hydrolysis. In the chart of the water soluble part, the signal intensity of hydroxymethylene proton (-CH_2OH, $\delta = 3.7$ ppm) of a hydroxycaproic acid unit at a terminal and hydroxyl group proton (-OH, $\delta = 5.3$ ppm) increased. This observation suggests that the polymer chains are hydrolyzed at the site of ester bond. The molecular weight of the recovered water soluble product was about 130 (mixture of monomer and dimer) from these signals intensities. The composition of the residues scarcely changed compared with original polymer samples.

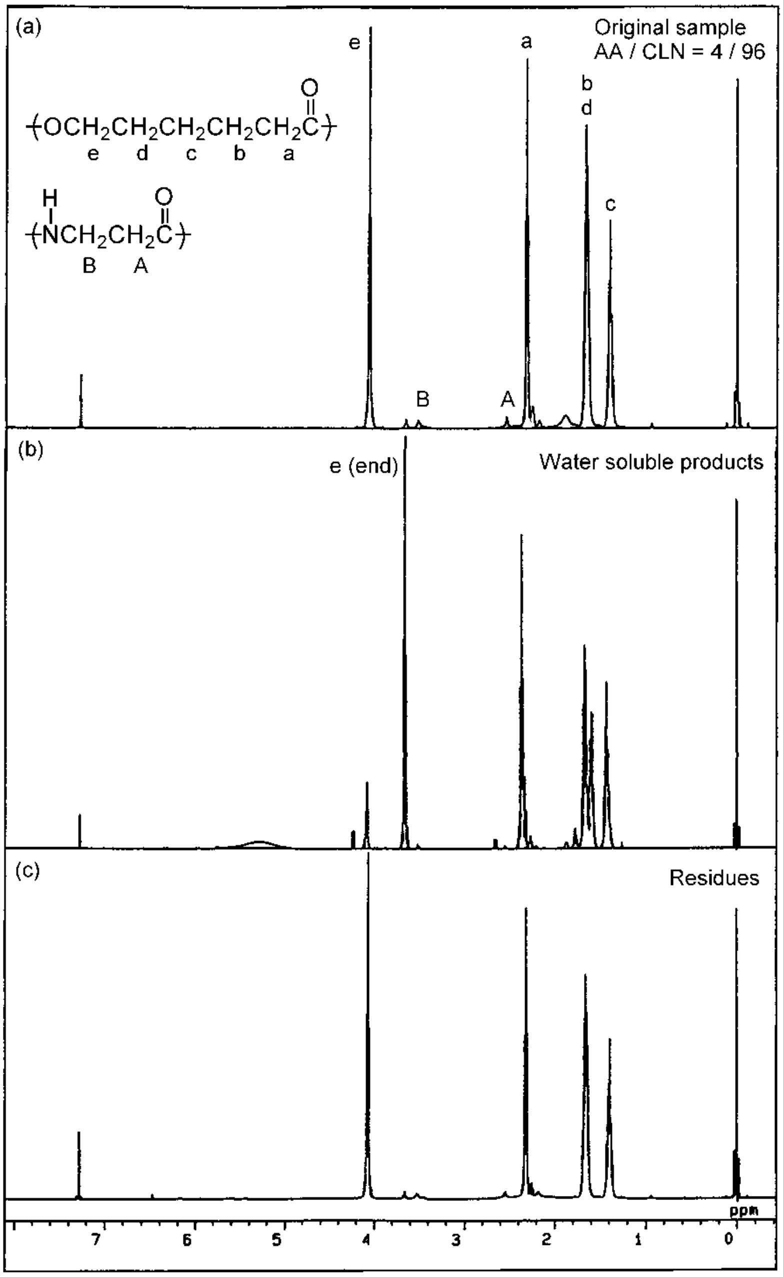


Figure 2-8 ^{1}H NMR spectra of (a) original sample (polymer composition AA/CLN = 96/4), (b) water soluble products and (c) residues after enzymatic hydrolysis.

Biodegradation by a standard activated sludge

Figure 2-9 shows the biodegradation profiles of the copolyesteramide by a standard activated sludge. The biodegradation of the copolyesteramides (polymer composition: AA/CLN = 62/38, 27/73, 16/84, 13/87) reached 22, 45, 19, 18%, respectively after 28 days. The samples with different molecular weight and almost same polymer composition (AA/CLN = 16/84, $M\text{n} = 1.5\times10^3$; AA/CLN = 13/87, $M\text{n} = 4.8\times10^3$) were degraded to the same extent. The samples with different polymer composition but almost same molecular weight (AA/CLN = 62/38, $M\text{n} = 1.6\times10^3$; AA/CLN = 27/73, $M\text{n} =0.9\times10^3$; AA/CLN = 16/84, $M\text{n} = 1.5\times10^3$) exhibited different degradation rates.

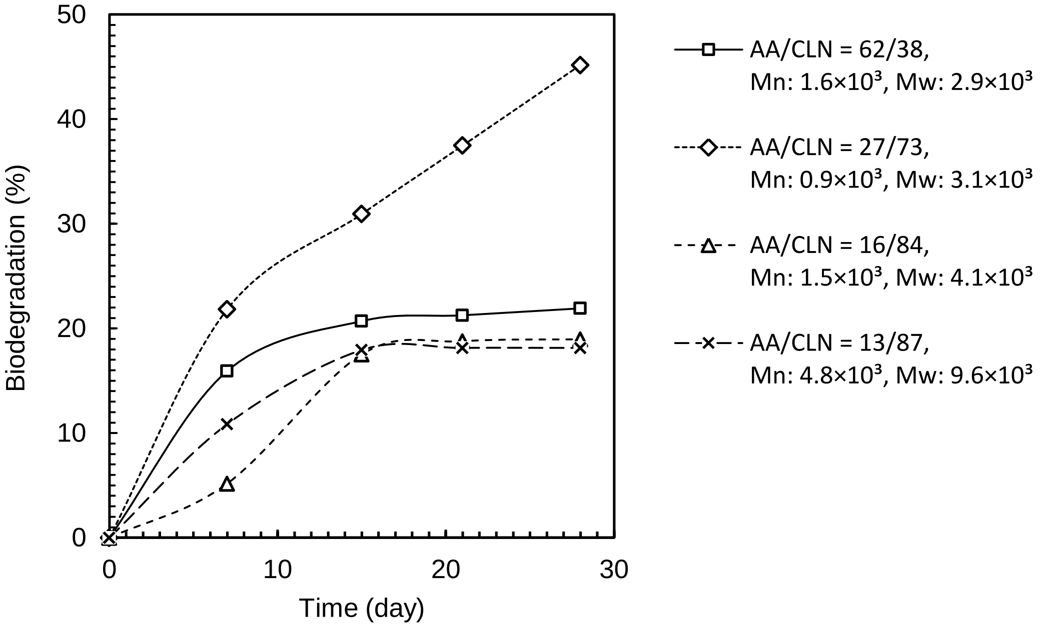


Figure 2-9 Biodegradation profiles of copolyesteramide by a standard activated sludge.

Figure 2-10 shows the biodegradation of various compositions of the copolyesteramide after 4 weeks. The dependence of the polymer composition on the biodegradation was similar to the tendency in the enzymatic hydrolysis. This suggests that the first step of the biodegradation proceeds by, not simple hydrolysis, but enzymatic hydrolysis.

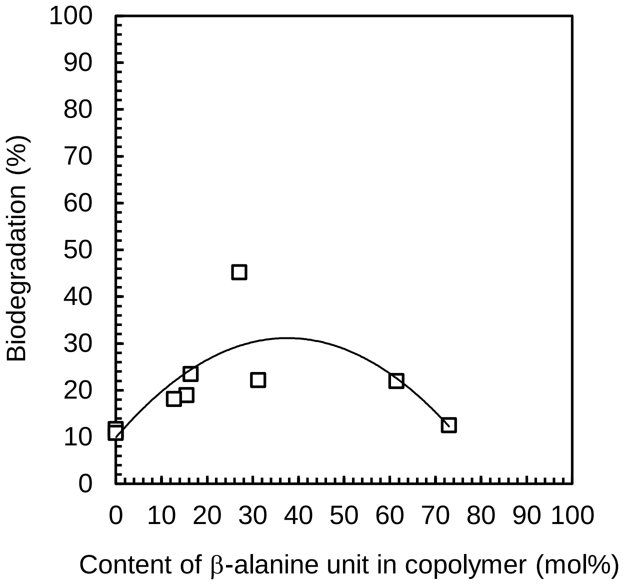


Figure 2-10 Relationship between percent degree of biodegradation and polymer composition for copolyesteramide by a standard activated sludge.

2.4 Conclusions

Copolyesteramides, poly[acrylamide-*co*-(ε-caprolactone)] with various compositions were synthesized by hydrogen transfer/ring-opening copolymerization of acrylamide (AA) with ε-caprolactone (CLN) in the presence of calcium hydride or calcium hydride+sodium metal as initiators. These series of calcium hydride were effective for the synthesis of the copolyesteramide in a wide range of polymer composition (AA/CLN = 10/90 to 90/10). The copolyesteramide was readily hydrolyzed in the presence of hydrochloric acid (0.1 N) at 125°C in an autoclave (e.g. AA/CLN = 59/41, degradation 93%). The copolyesteramide was also hydrolyzed enzymatically by lipase from *Rhizopus arrhizus*. The behavior of the enzymatic hydrolysis differed to the non-enzymatic hydrolysis. The enzymatic hydrolyzability was remarkable in the range of the AA repeating unit (β-alanine unit) from 10 to 40 mol% (e.g. AA/CLN = 27/73, degradation 44%), while, the degradability for the non-enzymatic hydrolysis rose with increasing AA repeating unit content. The biodegradation of the copolyesteramide was evaluated using a standard activated sludge (e.g. AA/CLN = 27/73 biodegradation 45%). The relationship between the biodegradation and the polymer composition was similar for the standard activated sludge and the enzymatic hydrolysis.

2.5 References

1) D. S. Breslow, G. E. Hulse, A. S. Matlack; *J. Am. Chem. Soc.* **1957**, *79*, 3760.

2) N. Ogata; *Makromol. Chem.* **1960**, *40*, 55.

3) L. Trossarelli, M. Guaita, G. Camino; *Makromol. Chem.***1967**, *105*, 285.

4) L. Trossarelli, M. Guaita, G. Camino; *J. Polym. Sci., Part C: Polym. Lett.* **1969**, *22*, 721.

5) G. Camino, M. Guaita, L. Trossarelli; *Makromol. Chem.* **1970**, *136*, 155.

6) H. Tani, N. Oguni, T. Araki; *Makromol. Chem.* **1964**, *76*, 82.

7) A. Leoni, S. Franco, G. Polla; *J. Polym. Sci.* **1968**, *6*, 3187.

8) J. Masamoto, K. Sasaguri, C. Ohizumi, K. Yamaguchi, H. Kobayashi; *J. Appl. Polym. Sci.* **1970**, *14*, 667.

9) U. Morgenstern, W. Berger; *Makromol. Chem.* **1992**, *193*, 2561.

10) S. Munoz-Guerra, J. M. Fernandez-Santin, A. Rodriguez-Galan, J. A. Subirana; *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 733.

11) J. D. Glickson, W. Berger; *Makromol. Chem.* **1992**, *193*, 2561.

12) K. Ito, K. Baba, Y. Yamashita; *Kogyo Kagaku* **1965**, *68*, 703; *Chem. Abstr.* **1965**, *63*, 5750h.

13) M. Ito; *Plastics* **1998**, *49*, 49.

14) D. E. Perrin, J. P. English; “Polycaprolactone”, in *Handbook of Biodegradable Polymers*, A. J. Domb, J. Kost, D. M. Wiseman, Editos; Harwood Academic Publishers, Amsterdam **1997**.

15) A. Nakayama, N. Kawasaki, I. Arvanitoyannis, S. Aiba, N. Yamamoto; *J. Environ. Polym. Degrad.* **1996**, *4*, 205.

16) A. Nakayama, N. Kawasaki, Y. Maeda, I. Arvanitoyannis, S. Aiba, N. Yamamoto; *J. Appl. Polym. Sci.* **1997**, *66*, 741.

17) A. Nakayama, N. Kawasaki, Y. Maeda, I. Arvanitoyannis, S. Aiba, N. Yamamoto; *Polymer* **1998**, *39*, 1213.

18) Y. Maeda, A. Nakayama, N. Kawasaki, K. Hayashi, S. Aiba, N. Yamamoto; *J. Environ. Polym. Degrad.* **1996**, *4*, 225.

19) T. Ouhadi, C. Stevens, P. Teyssie; *Makromol. Chem.: Suppl.* **1975**, *1*, 191.

Chapter 3 Synthesis, characterization, properties and biodegradability of polyamide 4: branched polyamide 4 by ring-opening polymerization

3.1 Introduction

In the research field of biodegradation of polymers, various studies on syntheses and estimation of polymers have been conducted on polymers containing hydrolysable linkage in the main chain such as polyester, copolyester, copolyesterether and copolyesteramide.[1,2] Most studies, however, have not focused on biodegradation of polymers containing only amide linkage in the main chain, namely, polyamide and copolyamide. To our knowledge, a little work is available in the published literature on the subject.[3-9]

The object polymer of this study, polyamide 4 (PA4) was initially synthesized by combining 2-pyrrolidone (PRN), basic catalysts, and acyl compounds by Ney et al.[10] Since then, extensive efforts have been made to investigate PA4[11-20] and its properties. Nevertheless, PA4, which is difficult to mold, and has unspecified suitability for applications, has not been put to practical use, which hampered the subsequent research. Under inactive research circumstances, it has been found that PA4 is biodegradable in various environments such as in soil, sea water, and activated sludge.[21-28] According to these findings, there is a possibility that the PA4 becomes attractive biodegradable materials due to their excellent thermal and mechanical properties based on their high melting point (260°C).[29] Further, the environmental sustainability of PA4 have been focused. That is, PA4 was synthesized by PRN, which can be easily prepared from biomass. Specifically, PRN can be obtained via the decarboxylation of glutamic acid derived from glucose into γ-aminobutyric acid by a biological process and via the cyclization of γ-aminobutyric acid into PRN by a chemical process.[30,31] The use of biomass provides one promising solution to the depletion of fossil resources (petroleum, etc.) from the viewpoint of green sustainable chemistry. Of late, these significant features have gradually reawakened the interest in the study of syntheses, properties, structure,[32] biodegradation, and biosynthesis of PA4 monomers. Furthermore, improvement in properties of the PA4 makes it possible to apply in wide practical use. For this purpose, modifying the properties of PA4 by copolymerization was attempted, because it would be expected to facilitate the synthesis of copolyesteramide by ring-opening copolymerization of PRN and lactones. On the other hand, the modification of the properties includes the changing of the polymer chain's structure such as introducing the branched structure. For instance, there have been several investigations of introducing the branched structure into biodegradable polyesters,[33-37) however, there seems to be little work for the PA4. It should additionally be noted that PA4 is synthesized by the anionic ring-opening polymerization of PRN, which progresses via an activated monomer mechanism. In this mechanism, the PA4 chains propagate from the active carboxyl groups on the initiator, thereby facilitating the design of polymer structures such as branched structure. It is, therefore, important to investigate correlation between structure and the properties of the PA4. This chapter deals with the synthesis of PA4 containing branched structure in main chain, their properties and biodegradation.

3.2 Experimental

3.2.1. Materials

2-Pyrrolidone (Tokyo Kasei Kogyo Co., Japan) was distilled under reduced pressure. Sodium (Wako Pure Chemical Industries, Japan) was used after removing impurities on the surface. Tetrahydrofuran (Wako, Japan) was distilled from calcium hydride. Benzoyl chloride (Wako, Japan), terephthaloyl dichloride (Wako, Japan), isophthaloyl dichloride (Kanto Chemical Co., Japan), benzene-1,3,5-tricarbonyl trichloride (Wako, Japan) were used without further purification. Biphenyl-3,3’,5,5’-tetracarbonyl tetrachloride was prepared by the method as described in synthesis part. A standard activated sludge was provided from the Chemicals Evaluation and Research Institute, Japan.

3.2.2. Synthesis

5-Iodo-*m*-xylene (10.0 g, 43.1 mmol), copper powder (10.0 g, 157 mmol) was heated to 280°C for about 1 h, and then copper powder (5.0 g, 79 mmol) was added. The mixture was allowed to stand for 20 h at 270–280°C, the stirring being continued throughout. Finally, copper powder (5.0 g, 79 mmol) was added again and the mixture was maintained at the same temperature for 3 h. After cooling to room temperature, acetone (80 mL) was poured into the reaction vessel and the solid residue was removed by using glass filter and filter paper. The filtrate was purified by the use of silica gel column chromatography. The solvent was removed from the purified filtrate to yield a colorless crystals, 3,3’,5,5’-tetramethylbiphenyl, 2.56 g, in 57% yield.

The mixture of 3,3’,5,5’-tetramethylbiphenyl (0.30 g, 1.43 mmol), water (100 mL), potassium permanganate (2.26 g, 14.3 mmol) was slowly heated to boiling with continual stirring until the permanganate color disappeared or paled. This required 3 days. The mixture was filtered through glass filter and the filter cake washed with hot water. The combined filtrate was filtered through a filter paper. When the filtrate was slightly acidified by cautiously adding concentrated hydrochloric acid, white fluffy precipitate was formed. The precipitate was filtered off, washed with water, and dried in vacuo. Biphenyl-3,3’,5,5’-tetracarboxylic acid obtained was 0.12 g (yield 25%).

To a small round-bottom flask was charged Biphenyl-3,3’,5,5’-tetracarboxylic acid (0.66 g, 2.0 mmol), thionyl chloride (20 mL, 274 mmol) and toluene (20 mL). The suspension was refluxed till it became almost homogeneous (it took about 1 day). The mixture was filtered through a filter paper to remove a small amount of insoluble solid. After the filtration, the excess of thionyl chloride and toluene were removed by evaporation under reduced pressure. The ivory powder, Biphenyl-3,3’,5,5’-tetracarbonyl tetrachloride (0.67 g) was obtained in a 83% yield.

3.2.3 Polymerization

A typical procedure was as follows. 2-Pyrrolidone (4.26 g, 50 mmol) and sodium (0.0345 g, 1.5 mmol) were placed in round-bottom flask equipped with a magnetic stirrer. The reaction mixture was heated to 50°C under reduced pressure. After the sodium was reacted completely with 2-pyrrolidone, a carboxylic acid derivative (benzoyl chloride 0.105 g, 0.75 mmol) dissolved in tetrahydrofuran (0.2 mL) was added into the flask. The mixture was maintained at 50°C under reduced pressure for approximately 24 h. The polymerization mixture was dissolved in formic acid and precipitated in acetone followed by washing with water and with methanol.

3.2.4 Processing

All the films of the polyamide 4 were prepared by dissolving in 2,2,2-trifluoroethanol (8–14%, w/v), subsequently drying at room temperature for 2 days. The films were cut into rectangles (5×30 mm^2) and both edges of the specimens were fixed by square card board (25×25 mm^2) taking gauge distance 10 mm.

3.2.5 Measurement

The Jeol alpha-500 NMR spectrometer was used to obtain ^{1}H NMR spectra (500 MHz). A saturated methanol-d_4 with calcium chloride was used as a solvent with tetramethylsilane as internal standard. Weight-average molecular weights and molecular weight distributions were determined by gel permeation chromatography using the Tosoh HLC-8220 GPC system. Two columns (TSK gel Super HM-N, TSK gel Super H-RC; Tosoh Co., Japan) were used with hexafluoroisopropyl alcohol (HFIP; Central Glass Co., Japan) as an eluent (0.2 $mL\cdot min^{-1}$) at 40°C. The thermal property of the synthesized polymers was investigated by DSC, using a DSC3100S (Bruker AXS K.K., Japan). All the scans were carried out from 30 to 275°C at a heating rate of 10 $°C\cdot min^{-1}$ in a nitrogen atmosphere. Data for melting temperature (Tm) were taken from the peak top of the first heating scan. The mechanical property of the polymers was measured by a tensile testing. The tensile testing of the test piece was carried out using a TENSILON/UTM-4-100 testing machine (Toyo Baldwin Co., Ltd, Japan) with a 5 kg load cell and the cross speed was maintained 10 $mm\cdot min^{-1}$ at room temperature. The gauge length was maintained at 10 mm. The thickness of each test piece was measured at three points before testing and a minimum value was adopted.

Biodegradation by an activated sludge

Biodegradability of the polyamide 4 was evaluated from determination of the amount of carbon dioxide (CO_2) evolved by a standard activated sludge metabolism in conformity to the procedure reported in ISO14852 and a previous paper.38) The evolving CO_2 was trapped by sodium hydroxide solution (0.025 $mol\cdot L^{-1}$) and determined as inorganic carbon with a total organic carbon analyzer, TOC-5000 (Shimadzu Co., Japan). The duration of the biodegradation test was about 1 month and the amount of CO_2 was measured every week. Biodegradation of the polyamide 4 was calculated by the following equation:

Biodegradation in % = (amount of observed CO_2 / amount of theoretical CO_2) × 100

The observed CO_2 amount was corrected by subtraction of the CO_2 amount of the blank experiment. The theoretical CO_2 amount was calculated from the structural formula of the polyamide 4 assuming that degraded products are completely mineralized to CO_2. Furthermore, the polyamide 4 also contains nitrogen, and hence nitrite ion and nitrate ion seem to form in culture media when the polyamide 4 was degraded and metabolized by the activated sludge. In order to confirm and determine the formation of nitrite ion and nitrate ion, ion chromatography was performed. An ion chromatography system (conductivity monitor CM-8020, dual plunger pump DP-8020, column oven CO-8020; Tosoh Co., Japan) was operated as follows. Columns (TSK gel IC-Anion-PWXL; Tosoh Co., Japan) were used with TSK eluent IC-Anion-A (Tosoh Co., Japan) as an eluent (1.2 mL·min^{-1}) at 40°C.

3.3 Results and discussion

Linear and branched polyamide 4's were prepared by the ring-opening polymerization of 2-pyrrolidone. In order to examine an influence on yields and molecular weights, the polymerizations were carried out using benzoyl chloride (BzC), terephthaloyl dichloride (Bz14DCC), isophthaloyl dichloride (Bz13DCC), benzene-1,3,5-tricarbonyl trichloride (Bz135TCC) and Biphenyl-3,3',5,5'-tetracarbonyl tetrachloride (Bp3355TCC) as the initiators at various concentrations.

Table 3-1 shows the effects of concentration of individual initiators on yield and molecular weights of polymers. BzC, Bz14DCC and Bz13DCC were used for synthesizing the linear polyamide 4 (end type, straight type, bent type) as the initiators. In each case, there was a faint tendency for the yields to decrease when the initiator concentration was low. The yields did not decrease abruptly up to the concentration 0.75 mol%. The weight-average molecular weights remained about 40000 for using BzC, even if the initiator concentration was 0.75 mol%.

Next, Bz135TCC was used for synthesizing a three-branched polyamide 4 as the initiator. In the case of using Bz135TCC, the yields of the polymers showed concentration dependence of the initiator and of the catalyst. The polymer yields hardly changed from 3.0 to 0.75 mol% of the initiator concentration, below which it decreased abruptly. In such a case of low initiator concentration (under 0.45 mol%), the yields remained a few percentages even the polymerization was continued for a long time. This low yield is probably due to deactivation of active site for propagation by very small amounts of impurities in the reaction system. On the other hand, in the case of the initiator at concentrations higher than 4.5 mol%, a gelation occurred. Consequently, the yields of soluble parts of the polymerization products decreased. The total yields of the products were almost the same as the initiator concentration at 3.0–0.75 mol%.

Furthermore, Bp3355TCC was used for synthesizing a four-branched polyamide 4 as the initiator. In this case, the yield also decreased when the initiator concentration was low. On the other hand, raising the initiator concentration (3.0 mol%) resulted in gelation similar to Bz135TCC initiated polymerization.

It should be emphasized that the gelation occurred only by using the initiators having branched structure. The gelation for each of the initiators with branched structure, shown in

Table 3-1, occurred above a certain concentration. When the initiator without branched structure (Bz14DCC, Bz13DCC) was used, no gelation occurred even if the initiator concentration was raised to 12 mol%.

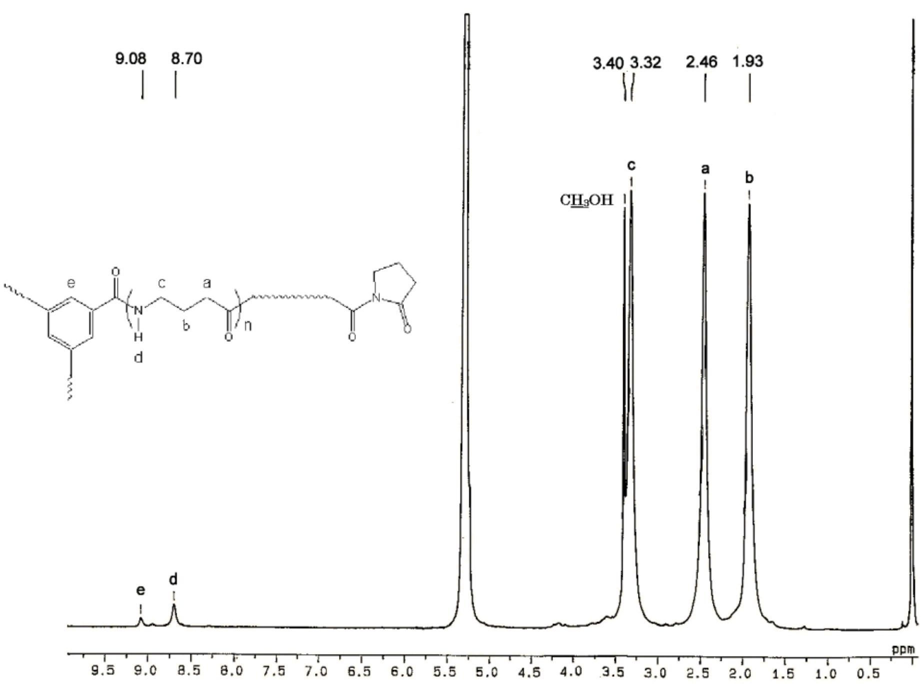
Figure 3-1 shows a ^{1}H NMR spectra of the polyamide 4 synthesized by using Bz135TCC and Bp3355TCC as the initiators. ^{1}H NMR spectrum in Figure3-1(a) displays characteristic signals for the methylene protons (b, a, c) at chemical shifts of 1.9, 2.5, 3.3 ppm and amide protons (d) at 8.7 ppm in the polyamide 4 chains. The peak denoted (e) at 9.1 ppm is the aromatic protons of the initiator. The mean degree of polymerization of each arm for the three-branched polyamide 4 was determined by ^{1}H NMR. In the case of initiator concentration 1.0 mol% (3.0 mol% for carbonyl chloride), the mean degree of polymerization was evaluated to be 53 from the integration ratio of signal (e) (intensity 0.188 for 3H) to signal (b) (intensity 20 for 2H). This estimation was in rough agreement with the corresponding calculated value (the calculation value = 33). In Figure 3-1(b), the peaks denoted (B, A, C, D) were assigned to the protons on the polyamide 4 chain part that is the same as the three-branched polyamide 4. The peaks denoted (E) at 8.9 ppm and (F) at 8.3 ppm come from the aromatic protons of the initiator, Bz3355TCC. The intensity of these peaks (E) and (F) weakened and the peak width broadened compared to other aromatic proton peaks of the linear polyamide 4. The reason seems to be that the aromatic molecule part was centered in the four-branched polyamide 4 chains, thereby depressed, so that uniforming of a local magnetic field did not occur.39) Although the peak intensity of aromatic part seemed lack accuracy, the mean degree of polymerization of each arm for the four-branched polyamide 4 was also determined by ^{1}H NMR. In the case of initiator concentration 0.375 mol% (1.5 mol% for carbonyl chloride), the mean degree of polymerization was evaluated to be 78 from the integration ratio of signal (E) and (F) (intensity 0.192 for 6H) to signal (B) (intensity 20 for 2H). This estimation was in rough agreement with the corresponding calculated value (the calculation value = 67). These rough agreements for the degree of polymerization, namely the discrepancy of the degree of the polymerization can be explained as follows. Since the bulk polymerization of 2-pyrrolidone proceeds with rapid solidification, propagation of polymer chains becomes heterogeneous and the polymers of different chain length form. When these mixtures of the polymers were purified, the polymers of short length were removed.

Table 3-1 Ring-opening polymerization of 2-pyrrolidone with several acyl chlorides as initiators

Initiator (mol%) [a]	Catalyst (mol%) [b]	Yield (%)	$Mn \times 10^{-3}$ [c] ($g \cdot mol^{-1}$)	$Mw \times 10^{-3}$ [c] ($g \cdot mol^{-1}$)	Mw / Mn [c]	Tm (^{o}C) [d]
BzC: linear(end) type						
0.75	1.5	34	16.4	46.8	2.56	263.0
1.5	3.0	55	19.9	46.7	2.35	261.9
3.0	6.0	58	17.3	52.1	3.01	262.3
Bz14DCC: linear(straight) type						
0.75	1.5	70	65.0	109.3	1.68	265.6
3.0	6.0	72	17.2	57.2	3.32	260.8
6.0	9.0	76	20.9	39.9	1.91	255.9
12.0	18.0	66	10.1	17.9	1.77	239.1
Bz13DCC: linear(bent) type						
0.75	1.5	53	47.9	87.0	1.82	263.2
3.0	6.0	81	22.9	48.5	2.12	259.7
12.0	18.0	69	14.0	25.1	1.79	247.1
Bz135TCC: 3-branched type						
0.15	0.3	0	---	---	---	---
0.3	0.6	0	---	---	---	---
0.3	0.6	5.9 (4 days)[e]	10.2	18.3	1.80	256.2
0.45	0.9	3.5 (6 days)[e]	5.2	8.7	1.67	233.0
0.75	1.5	62	58.7	102.8	1.75	264.5
1.5	3.0	59	42.9	85.1	1.98	263.6
3.0	6.0	63	20.4	75.2	3.69	264.4
4.5	9.0	12, (58 gel)[f]	---	---	---	---
6.0	9.0	37, (36 gel)[f]	---	---	---	---
9.0	18.0	11, (49 gel)[f]	---	---	---	---
Bp3355TCC: 4-branched type						
1.5	3.0	32	39.4	82.5	2.09	260.8
2.0	4.0	46	29.7	92.8	3.12	262.6
3.0	6.0	(73 gel)[f]	---	---	---	---

a) mol% means conversion from quantities of carboxyl chloride groups in the initiator.
b) Calculated from quantities of sodium.
c) Determined by GPC; eluent: Hexafluoroisopropyl alcohol, standard: Polymethyl methacrylate.
d) Determined by DSC.
e) Polymerization time.
f) Yield of gel part.

(a) Bz135TCC



(b) Bp3355TCC

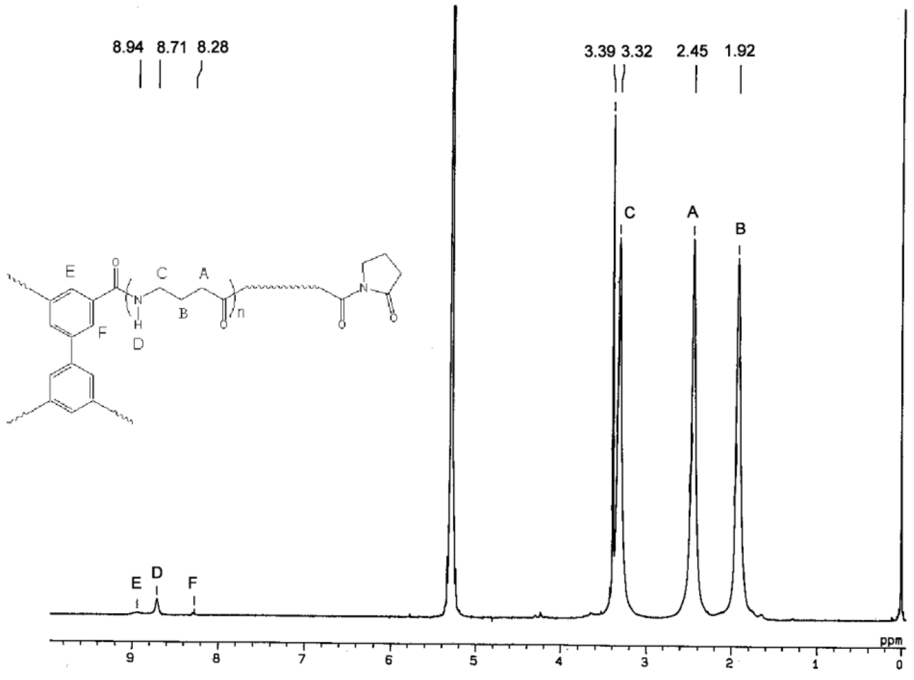


Figure 3-1 ^{1}H NMR spectra of branched polyamide 4. (a) Three-branched type synthesized by using benzene-1,3,5-tricarbonyl trichloride as an initiator, (b) Four-branched type synthesized by using biphenyl-3,3',5,5'-tetracarbonyl tetrachloride as an initiator.

Turning now to the effect of introducing branched architecture into the polyamide 4 chain on properties, melting point and tensile strength of the linear and branched polyamide 4's were measured. Figure3-2 summarizes the melting points at the peak top (*T*m) of the polyamide 4's in Table3-1 and in additional measurements. It depicts the relationship between the weight-average molecular weight (*M*w) and *T*m of the linear and branched polyamide 4's. The difference in melting points between the linear and branched polyamide 4 was not found over the whole molecular weight range measured (*M*w > 10^4). When the *M*w range is in several ten thousands, difference of the polymer structure scarcely affects bulk property such as melting point. The reason seems to be that the branched polyamide 4, with high molecular weight, includes low proportion of amorphous domain, owing to chain branching. In other words, the effect of amorphous domain based on long chain branching is negligible in comparison to the effect based on short branching. In contrast the dependence of the melting points on the molecular weight was observed clearly in low molecular weight region. The melting points showed a positive dependence for molecular weights up to 40×10^3 above which it showed nearly constant (265°C), even so, the plotting points slightly scattered.

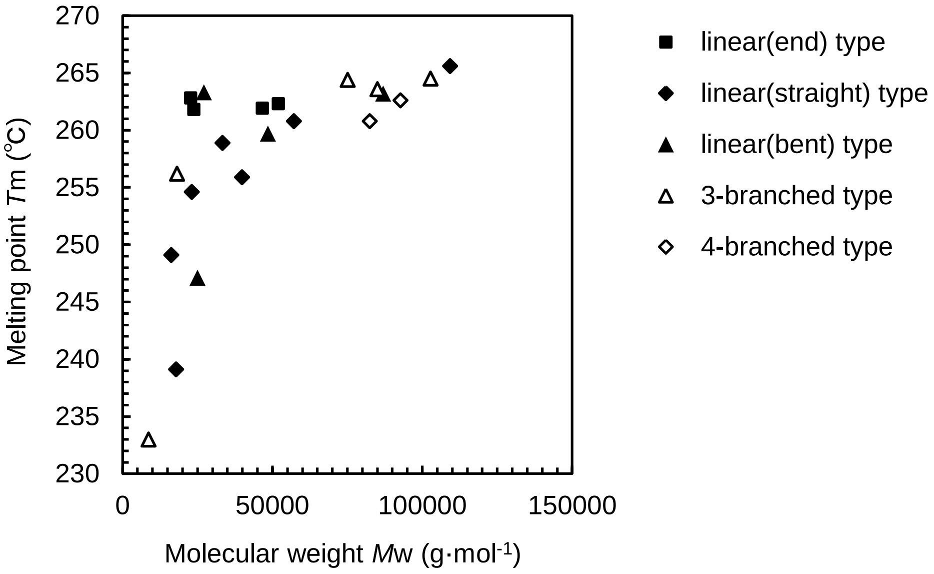


Figure 3-2 Melting points of linear and branched polyamide 4 plotted against weight-average molecular weight.

Figure 3-3 provides a plot of tensile strength against log *M*w for the polyamide 4. The error bars indicate the probable error in measured values. The tensile strength of the polyamide 4 showed positive molecular weight dependence. As shown in Figure 3-3, the tensile strength of the branched polyamide 4 was higher than that of linear polyamide 4 over the molecular weight range measured. With high molecular weight of the branched polyamide 4, the polymer chains become longer and hence the intermolecular chain entanglement of the polymer occurs. This intermolecular chain entanglement leads to a decrease of polymer chain mobility. It has been known that polymer chain mobility is a crucial factor in determining the mechanical properties of polymers. One typical example of this is that branched polymers have greater melt viscosities than those of linear chains of same molecular weight.[40)] By analogy with this, the high tensile strength of the branched polyamide 4 is interpreted as the effect of the entanglement of the polymer chain.

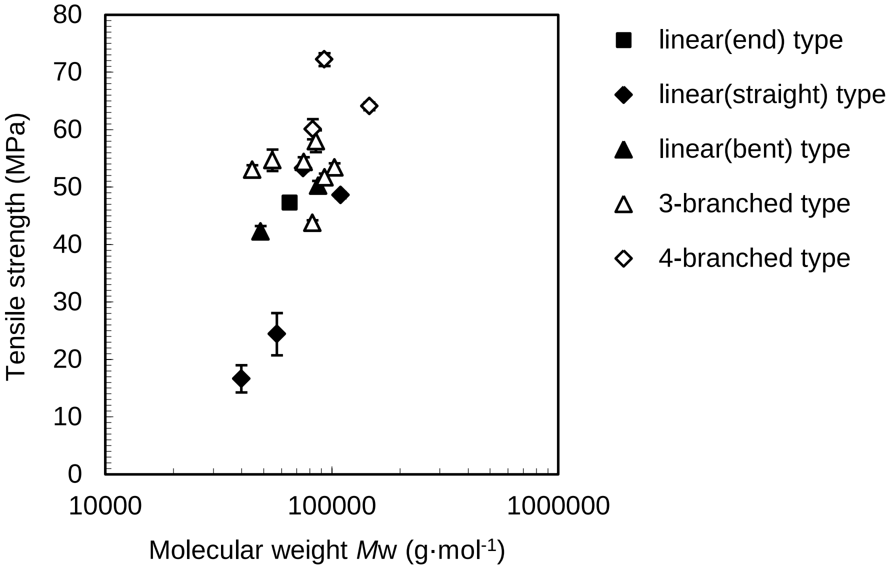


Figure 3-3 Tensile strength of linear and branched polyamide 4 films plotted against weight-average molecular weight.

Figure 3-4 shows a plot of elongation at break against log *M*w for the polyamide 4, measured at room temperature. The elongation at break of the polyamide 4 shows positive molecular weight dependence, however, the relationship between polymer chain structure and elongation at break were not clear.

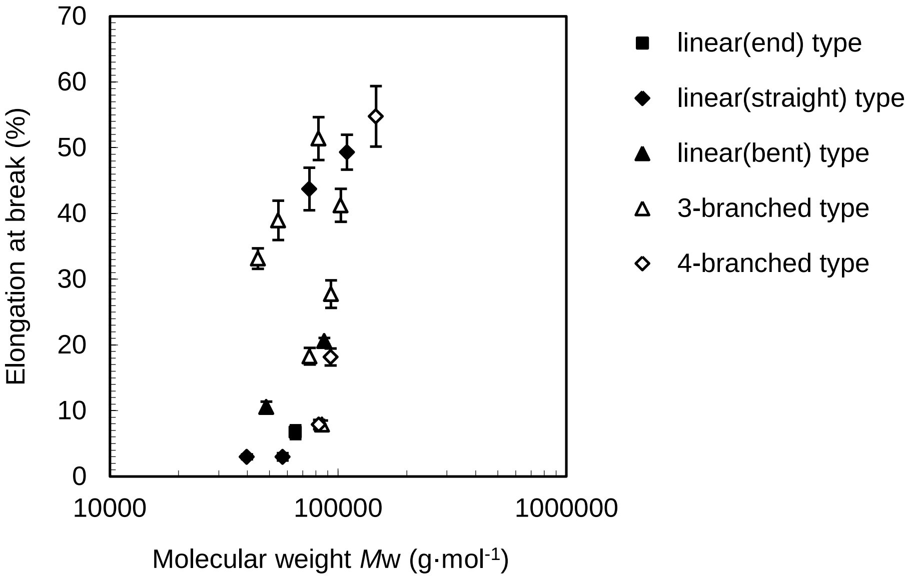


Figure 3-4 Elongation at break of linear and branched polyamide 4 films plotted against weight-average molecular weight.

Figure 3-5 shows the biodegradation profiles of the branched polyamide 4 (three-branched type: Mw = 85.1×10^3, four-branched type: Mw = 82.5×10^3) by the standard activated sludge. The biodegradation of the polyamide 4's reached to 39, 41%, respectively, after 21 days and thereafter kept constant. It appeared that the activity of the activated sludge fell. When the activated sludge was newly added to the culture media, the biodegradation of the three-branched and the four-branched polyamide 4 reached to 81, 49%, respectively, after 77 days. In the same way, the biodegradation of the linear polyamide 4 was evaluated. With linear polyamide 4's (straight type: Mw = 109.3×10^3, bent type: Mw = 87.0×10^3), the biodegradation were 48% (28 days), 46% (27 days), respectively.

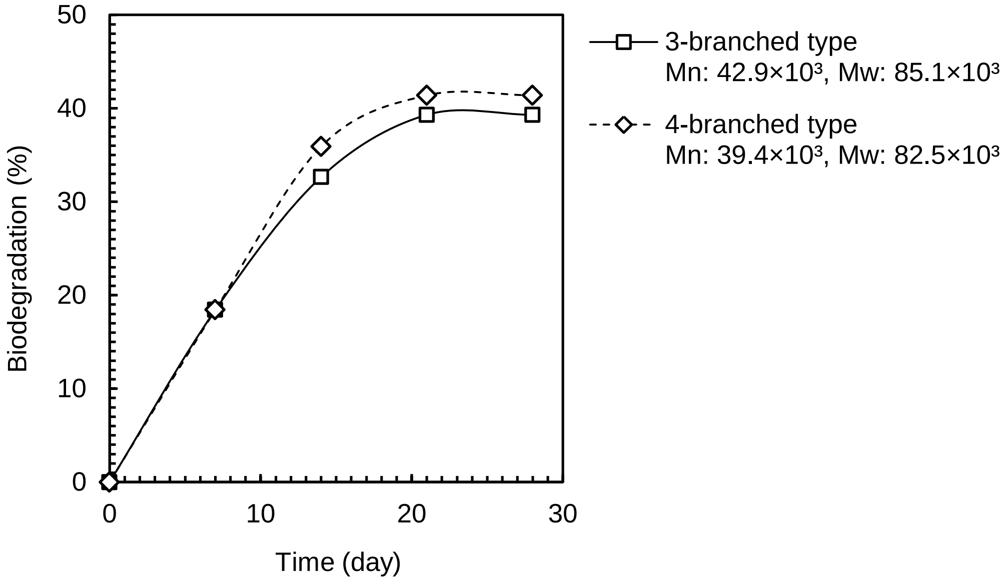


Figure 3-5 Biodegradation profiles of branched polyamide 4 by a standard activated sludge.

It is thought that the nitrogen of the polyamide 4 was metabolized by microbes in the activated sludge and was converted into inorganic compounds in the culture media. For clarifying metabolism, ion chromatography was used for measuring the concentration of inorganic nitrogen component, nitrite ion (NO_2^-) and nitrate ion (NO_3^-), in the culture media. Figure 3-6 shows the time course of the concentration of the inorganic nitrogen components evolved by the biodegradation of the polyamide 4 (four-branched type: $M\mathrm{w} = 82.5\times10^3$) in the culture media. The polyamide 4 was biodegraded by the activated sludge and then NO_2^- and NO_3^- were formed. From the total concentration of NO_2^- and NO_3^-, the biodegradation was estimated as follows.

Constitutional repeating unit of the polyamide 4

$-(-NHCH_2CH_2CH_2CO-)_n-$

formula weight of the unit 85.10, atomic weight of N 14.01

weight of N in polyamide 4 (0.2 g)

$0.2\times(14.01/85.10) = 0.0329$ g.

Assuming that the polyamide 4 was mineralized completely in culture media (500 mL), concentration of N (theoretical) is $0.0329/0.5 = 0.0658\ \mathrm{g\cdot L^{-1}} = 65.8$ ppm.

concentration of NO_2^- and NO_3^- in culture media.

(observed) NO_2^- 0 ppm, NO_3^- 117.1 ppm content ratio of N in NO_2^- and NO_3^-

formula weight of NO_2^- 46.01

content ratio of N for NO_2^- 14.01/46.01 = 0.304

formula weight of NO_3^- 62.00

content ratio of N for NO_3^- 14.01/62.00 = 0.226

concentration of N (observed) is 0×0.304+117.1×0.226 = 26.5 ppm

hence, the biodegradation is (26.5/65.8)×100 = 40.3%.

In this case, the degree of biodegradation estimated from inorganic nitrogen component was identical with that estimated from CO_2 evolved (41%).

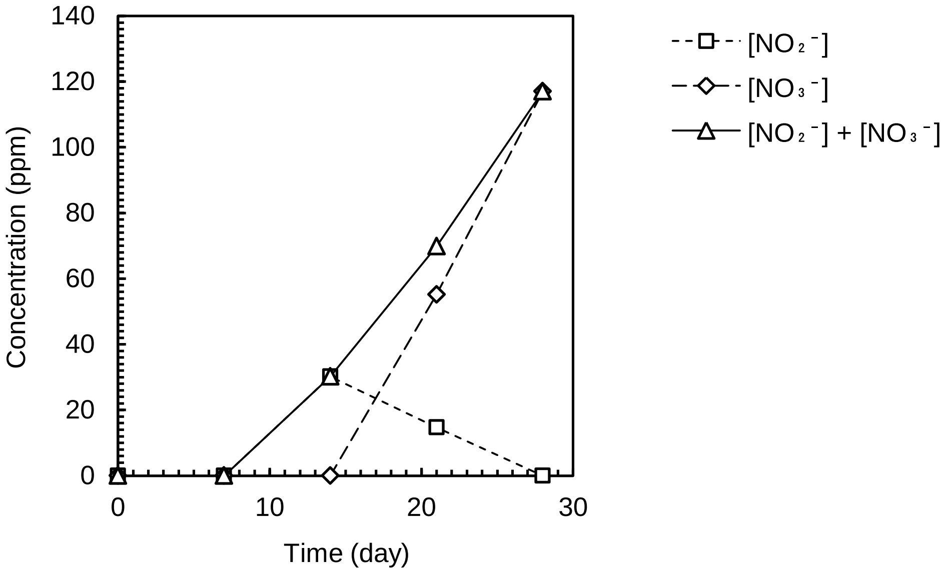


Figure 3-6 Time course of concentration of NO_2^-, NO_3^- and NO_2^-+NO_3^- in culture media for biodegradation by a standard activated sludge.

3.4 Conclusions

The novel branched polyamide 4 was synthesized by using polybasic acid chloride (tribasic acid chloride and tetrabasic acid chloride) as initiators having branched structure. When the concentration of the initiators with branched structure exceeded a certain value (4.5 mol% for three-branched type, 3.0 mol% for four-branched type), gelation partly occurred. The melting points of the polyamide 4 approached 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 polyamide 4 chains. Turning 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.

3.5 References

1) R. Chandra, R. Rustgi; *Prog. Polym. Sci.* **1998**, *23*, 1273.

2) J. P. Eubeler, M. Bernhard, T. P. Knepper; *Trends Anal. Chem.* **2010**, *29*, 84.

3) D. M. Ennis, A. Kramer; *J. Food. Sci.* **1975**, *40*, 181.

4) M. Nagata, T. Kiyotsukuri; *Eur. Polym. J.* **1992**, *28*, 1069.

5) I. Arvanitoyannis, E. Nikolaou, N. Yamamoto; *Angew. Makromol. Chem.* **1994**, *221*, 67.

6) I. Arvanitoyannis, E. Nikolaou, N. Yamamoto; *Polymer* **1994**, *35*, 4678.

7) I. Arvanitoyannis, E. Nikolaou, N. Yamamoto; *Macromol. Chem. Phys.* **1995**, *196*, 1129.

8) I. Arvanitoyannis, E. Psomiadou, N. Yamamoto; *Polymer* **1995**, *36*, 2957.

9) A. Demicheli, S. Russo, A. Mariani; *Polymer* **2000**, *41*, 1481.

10) W. O. Ney Jr., W. R. Nummy, C. E. Barnes; *U.S. Patent* **1953 May 12**, 2, 638, 463.

11) H. K. Hall Jr.; *J. Am. Chem. Soc.* **1958**, *80*, 6404.

12) G. Champetier, H. Sekiguchi; *J. Polym. Sci.* **1960**, *48*, 309.

13) S. Barzakay, M. Levy, D. Vofsi; *Polym. Lett.* **1965**, *3*, 601.

14) H. Tani, T. Konomi; *J. Polym. Sci. Part A-1* **1966**, *4*, 301.

15) S. Barzakay, M. Levy, D. Vofsi; *J. Polym. Sci. Part A-1* **1966**, *4*, 2211.

16) P. A. Howell; *J. Phys. Chem.* **1969**, *73*, 2294.

17) H. Sekiguchi, B. Coutin; *J. Polym. Sci. Polym. Chem. Ed.* **1973**, *11*, 1601.

18) M. Kuskova, J. Kralicek, J. Roda; *Eur. Polym. J.* **1977**, *13*, 665.

19) N. Takahashi, F. Suzuki, A. Maeda, K. Onozato; *Sen-i Gakkaishi* **1980**, *36*, 189.

20) T. Konomi, C. Toyoki, W. Mizukami, C. Shimizu; *Sen-i Gakkaishi* **1982**, *38*, 200.

21) K. Hashimoto, T. Hamano, M. Okada; *J. Appl. Polym. Sci.* **1994**, *54*, 1579.

22) K. Hashimoto, M. Sudo, K. Ohta, T. Sugimura, H. Yamada; *J. Appl. Polym. Sci.* **2002**,

86, 2307.

23) N. Kawasaki, A. Nakayama, N. Yamano, S. Takeda, Y. Kawata, N. Yamamoto, S. Aiba; *Polymer* **2005**, *46*, 9987.

24) N. Yamano, A. Nakayama, N. Kawasaki, N. Yamamoto, S. Aiba; *J. Polym. Environ.* **2008**, *16*, 141.

25) K. Tachibana, K. Hashimoto, M. Yoshikawa, H. Okawa; *Polym. Degrad. Stab.* **2010**, *95*, 912.

26) K. Tachibana, K. Hashimoto, N. Tansho, H. Okawa; *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 2495.

27) K. Tachibana, Y. Urano, K. Numata; *Polym. Degrad. Stab.* **2013**, *98*, 1847.

28) A. Nakayama, N. Yamano, N. Kawasaki, Y. Nakayama; *Polym. Degrad. Stab.* **2013**, *98*, 1882.

29) R. L. Miller; in *Polymer Handbook, 4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grulke, Editors; Wiley: New York, **1999**, Section VI, p. 33.

30) C. Takahashi, J. Shirakawa, T. Tsuchidate, N. Okai, K. Hatada, H. Nakayama, T. Tateno, C. Ogino, A. Kondo; *Enzyme Microbial. Tech.* **2012**, *51*, 171.

31) N. Yamano, N. Kawasaki, S. Takeda, A. Nakayama; *J. Polym. Environ.* **2013**, *21*, 528.

32) K. Yamauchi, S. Kuroki, I. Ando; *Polymer* **2002**, *43*, 3331.

33) S. H. Kim, Y. K. Han, Y. H. Kim, S. I. Hong; *Makromol. Chem.* **1992**, *193*, 1623.

34) K. R. Gorda, D. G. Peiffer; *J. App.l Polym. Sci.* **1993**, *50*, 1977.

35) I. Arvanitoyannis, A. Nakayama, N. Kawasaki, N. Yamamoto; *Polymer* **1995**, *36*, 2947.

36) I. Arvanitoyannis, A. Nakayama, E. Psomiadou, N. Kawasaki, N. Yamamoto; *Polymer* **1996**, *37*, 651.

37) F. Sanda, H. Sanada, Y. Shibasaki, T. Endo; *Macromolecules* **2002**, *35*, 680.

38) Y. Maeda, A. Nakayama, N. Kawasaki, K. Hayashi, S. Aiba, N. Yamamoto; *J. Environ. Polym. Degrad.* **1996**, *4*, 225.

39) F. A. Bovey, G. V. D. Tiers, G. Filipovich; *J. Polym. Sci.* **1959**, *38*, 73.

40) V. C. Long, G. C. Berry, L. M. Hobbs; *Polymer* **1964**, *5*, 517.

Chapter 4 Synthesis, characterization and functionality of polyamide 4 containing azo group: polyamide 4 azo macromolecular initiator

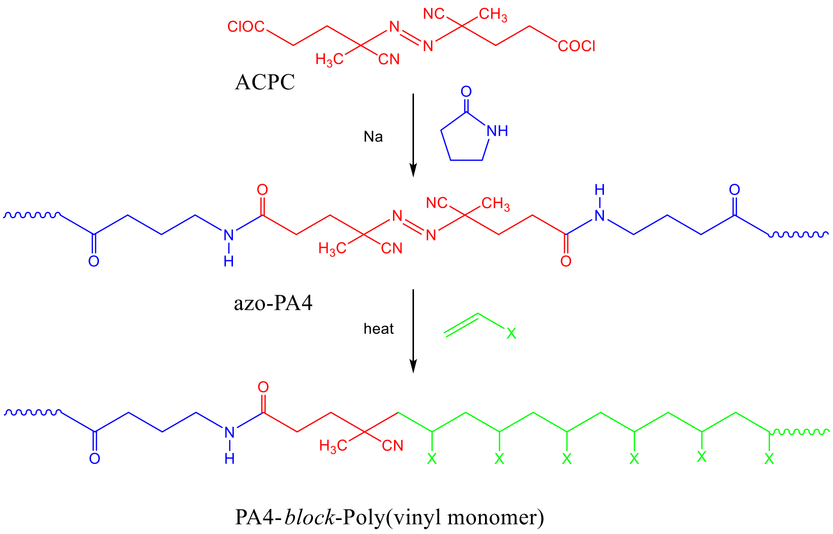
4.1 Introduction

Polyamide 4 (PA4) has excellent thermal and mechanical properties because of the strong hydrogen bonds among its polymer chains. Further, various structures of PA4 can easily be designed because of a polymerization mechanism in which the initiators are attached to the polymer chains. This polymerization mechanism plays a key role in the development of novel PA4 containing unique structures that differ from conventional linear PA4. Specifically, when a base is used as a catalyst and a carboxylic acid derivative is used as an initiator, an amide anion of 2-pyrrolidone forms and reacts with the carboxylic acid derivative to produce acylated 2-pyrrolidone. Because the acylated 2-pyrrolidone has high reactivity, the ring-opening polymerization of 2-pyrrolidone proceeds through an activated monomer mechanism.1) When initiators having various structures or functional groups are used, the characteristic structure or functionality arising from initiators is incorporated into the PA4 chains. Consequently, the utilization of the activated monomer mechanism mentioned previously enables the modification of the physical properties or the introduction of functionality into the polymer. An example for introducing of characteristic structure was shown in the preceding chapter. Namely, a branched structure was formed in PA4 when a polybasic acid chloride was used as an initiator. The branched PA4 showed superior tensile strength to that of linear PA4 (e.g., four-branched type, 72 MPa).2)

On the other hand, it was selected an azo group which exhibited polymerization activity toward vinyl monomers to provide functionality to PA4. When 2-pyrrolidone was polymerized with an initiator containing an azo group, the resulting polyamide 4 containing an azo group (azo-PA4) was a radical generator and an initiator for the PA4-*block*-poly(vinyl monomer) (Scheme 4-1). Over the last few decades, numerous investigations have been carried out on azo macromolecular initiators synthesized by polycondensation or polyaddition.3-13) Two types of synthetic pathways can be used to synthesize block copolymers: vinyl polymerization followed by ring-opening polymerization and vice versa. However, to the best of our knowledge, very few azo macromolecular initiators have been synthesized with the ring-opening polymerization in the first step.14,15) The advantages of the latter synthetic path (the synthesis of an azo-PA4 macromolecular initiator with the ring-opening polymerization in the first step) are as follows:

1. The molecular weight (MW) of the azo-PA4 macromolecular initiator can be controlled.
2. The method can be applied to vinyl monomers that have polar groups (polar groups suppress the polymerization of 2-pyrrolidone; therefore, the polymerization of the vinyl monomers should be conducted after the synthesis of PA4.)16-18)
3. The macromolecular initiator can be synthesized directly from the azo reagent with 2-pyrrolidone (the synthesis of the initiator by ring-opening polymerization requires only one step, whereas the synthesis by polycondensation requires the formation of a PA4 chain first and the subsequent introduction of azo groups.).

This chapter deals with synthesis of azo-PA4 and investigation of application for the radical polymerization of vinyl monomers as azo macromolecular initiators.



Scheme 4-1 Synthesis of azo-PA4 macromolecular initiator and PA4-*block*-poly(vinyl monomer).

4.2 Experimental

4.2.1 Materials

2-Pyrrolidone (Kishida Chemical, Osaka, Japan) was distilled under reduced pressure. Sodium (Wako Pure Chemical Industries, Osaka, Japan) was used after removing impurities on surface. 4,4’-Azobiscyanopentanoic acid (Wako Pure Chemical), thionyl chloride (Kishida Chemical), *n*-hexane (Wako Pure Chemical), tetrahydrofuran (Wako Pure Chemical), 2,2,2-trifluoroethanol (Kishida Chemical), and formic acid (Wako Pure Chemical) were used as received. Styrene (St), methyl acrylate (MA), methyl methacrylate

(MMA), vinyl acetate (VA), acrylic acid (AA), and *N*-vinyl-2-pyrrolidone (NVP) (Wako Pure Chemical) were purified by distillation.

4.2.2 Synthesis of 4,4’-azobiscyanopentanoyl chloride (ACPC)

4,4’-Azobiscyanopentanoic acid (5.00 g; 17.8 mmol) was dispersed in thionyl chloride (60 mL; 823 mmol) in an ice–water bath under an argon atmosphere, after which it was incubated at room temperature overnight. The reaction product was then passed through a glass filter to remove the insoluble fraction. The filtrate was subsequently concentrated by the evaporation of thionyl chloride in vacuo to give a white solid.5) The yield was 62%.

4.2.3 Synthesis of azo-PA4

A typical procedure was as follows. 2-Pyrrolidone (4.26 g, 50 mmol) and sodium (0.069 g, 3 mmol) were placed in a round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was then heated to 50°C under reduced pressure. After the sodium reacted completely with 2-pyrrolidone, *n*-hexane (5 mL) was added to the flask. The hydrocarbon with low boiling temperature plays a role in inhibiting temperature rise in polymerization. The reaction mixture was then cooled in an ice–water bath carefully in a manner that prevented the 2-pyrrolidone from solidifying, after which ACPC (0.238 g, 0.75 mmol) dissolved in tetrahydrofuran (1 mL) was added to the flask. The reaction mixture was kept in the ice–water bath until the viscosity increased greatly, at which point it was brought to room temperature. After the *n*-hexane was evaporated under reduced pressure, the mixture was maintained at room temperature for approximately 20 h to complete polymerization. The polymerization mixture was subsequently dissolved in 2,2,2-trifluoroethanol (50 mL) containing formic acid (0.14 g, 3 mmol) and passed through a filter paper. The filtrate was concentrated by evaporation under reduced pressure and precipitated in acetone, after which it was washed with water followed by methanol and then dried. The yield was 55%.

4.2.4 Polymerization of vinyl monomers by azo-PA4

The following procedure was generally used. In a 50 mL recovery flask equipped with a vacuum adapter and a magnetic stirrer, azo-PA4 (*M*n 6900, 0.5 g, 0.072 mmol) was dissolved in 5 mL of 2,2,2-trifluoroethanol, after which St (1.20 g, 11.5 mmol) was added. The reaction mixture was subsequently frozen by the immersion of the reaction vessel in a dry ice/ethanol bath and then degassed in vacuo. Argon was passed through the vessel to displace the air by three freeze–thaw cycles. After the vessel was filled with argon, the mixture was maintained at 60°C for approximately 24 h. The polymerization mixture was then poured into acetone to form a precipitate, which was subsequently dried. To remove the homopolymer polystyrene (PSt), the polymerization product was washed with 150 mL of chloroform for 24 h with a Soxhlet extractor. The yield was 83%.

4.2.5 Characterization

Fourier transform infrared spectra were recorded on a Nicolet AVATAR360 FT-IR spectrophotometer (Thermo Fisher Scientific K.K., Yokohama, Japan) with KBr pellet containing samples. ^{1}H NMR spectra were measured with a JEOL (Tokyo, Japan) JNMECA-500 NMR spectrometer (500 MHz). A mixture of formic acid-d$_2$ and chloroform-d (1/9 v/v) was used as the solvent. The molecular weights (MW) were determined by gel permeation chromatography (GPC) with a Tosoh (Tokyo, Japan) HLC-8220 GPC system. Two columns (TSK gel Super HM-N, TSK gel Super H-RC, Tosoh) were used with hexafluoroisopropyl alcohol (HFIP; Central Glass Co., Tokyo, Japan) as an eluent (0.2 mL·min^{-1}) at 40°C. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC3100S calorimeter (Bruker AXS K. K., Yokohama, Japan). All scans were carried out from 30 to 300°C at a heating rate of 10°C·min^{-1} in a nitrogen atmosphere.

4.3 Results and discussion

Synthesis of azo-PA4

Azo-PA4 was synthesized from 2-pyrrolidone with ACPC as the initiator. The optimum temperature for the polymerization of 2-pyrrolidone was 40–60°C. When ACPC which is thermolabile was used, polymerization was carried out at a lower temperature [in the vicinity of the melting temperature (*T*m) of 25°C] with a longer polymerization time. After purification, azo-PA4 was obtained as a white powder or granule.

The products were mainly characterized by IR and ^{1}H NMR spectroscopy to confirm the production of azo-PA4. The IR spectra revealed amide I (1636 cm^{-1}) and amide II (1541 cm^{-1}) absorptions related to PA4. Nevertheless, no absorption band derived from the nitryl group in the ACPC portion of the azo-PA4 was observed (2240–2260 cm^{-1}).[19] The absence of the band may have occurred because the relative concentration of the ACPC portion of azo-PA4 was present at exceedingly low levels, and the nitryl absorption of the azobiscyanopentanoate was very weak.

^{1}H NMR signals corresponding to the methylene protons from the PA4 portion were observed at 1.83, 2.26, and 3.25 ppm, which were assigned to the b, a, and c positions, respectively. Furthermore, a weak signal reflecting the methyl proton of the azobiscyanopentanoate portion was clearly observed at 1.68 ppm. On the basis of the intensity ratio of the methyl proton (1.68 ppm) to the methylene proton (1.83 ppm), the content of azobiscyanopentanoate portion was estimated to be 2 mol % when 2 mol % of the initiator ACPC was used for polymerization.

The results of synthesis of azo-PA4 are given in Table 4-1. Sodium metal was used to generate 2-pyrrolidone anion. During this reaction, a lower concentration of the initiator (ACPC) was used to keep 2-pyrrolidone anion to some extent. When a high concentration of initiator was used, a polymer with a low weight-average molecular weight (*M*w) was obtained in high yield (run 6 and 7). Run 3 (initiator: 1.5 mol% and catalyst: 4.5 mol%) showed the highest number-average molecular weight (*M*n) and *M*w.

Table 4-1 Results of polymerization of 2-pyrrolidone by 4,4’-azobiscyanopentanoyl chloride as an initiator

Run No.	Initiator (mol%) [a]	Catalyst (mol%) [b]	Yield (%)	$M\text{n}\times10^{-3}$ [c] ($\text{g}\cdot\text{mol}^{-1}$)	$M\text{w}\times10^{-3}$ [c] ($\text{g}\cdot\text{mol}^{-1}$)	*M*w/*M*n
1	0.5	3.5	4	8.3	13.4	1.62
2	1.0	4.0	7	8.1	12.0	1.48
3	1.5	4.5	37	22.1	35.3	1.59
4	2.0	5.0	48	15.3	29.0	1.89
5	3.0	6.0	55	14.0	22.4	1.61
6	4.0	7.0	78	12.6	21.4	1.69
7	6.0	9.0	70	11.1	16.9	1.52

a) converted concentration from quantities of chlorocarboxyl groups in the initiator.
b) calculated from quantities of sodium.
c) determined by GPC; eluent: hexafluoroisopropyl alcohol, standard: polymethyl methacrylate).

Figure 4-1 provides a plot of molecular weight (MW) against the concentration of the initiator (runs 3–7, Table 4-1). The MWs of azo-PA4 tended to increase with decreasing concentration of the initiator. Taken together, these findings indicate that control of the PA4 chain length in the block polymer was possible. To maintain a high MW and yield, it was important to use a balanced concentration of the initiator.

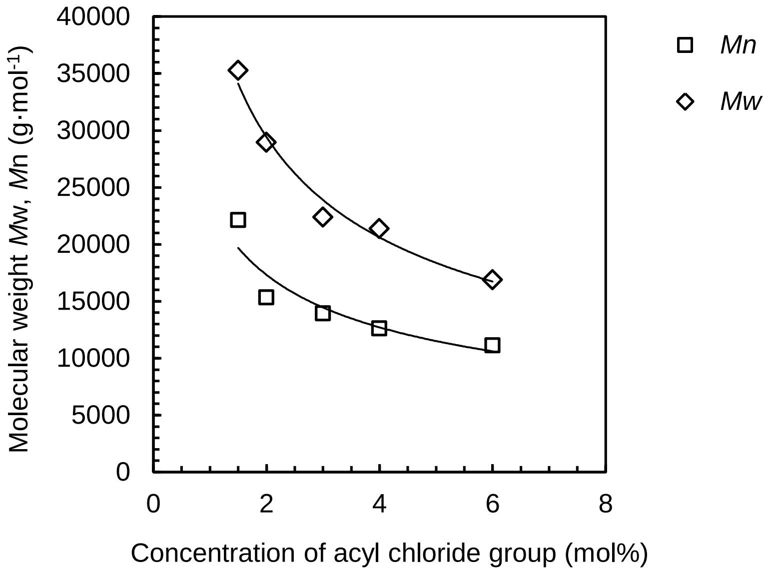


Figure 4-1 Relationship between MW of azo-PA4 and concentration of acyl chloride groups in ACPC.

Radical polymerization of vinyl monomers with azo-PA4

The results of the polymerization of St by azo-PA4s are summarized in Table 4-2. Three kinds of azo-PA4s with different MWs were used. To clarify the relationship between the polymerization increment of St (P-I) and the quantity of St monomer (M), (P-I) and M were normalized against quantity of initiator (I). This normalization was carried out for easy comparison. When the feed ratio (M/I) was small, St was not polymerized (run 1, Table 4-2). In situations in which M/I ranged from approximately 50 to 1800; (P-I)/I was proportional to M/I (Figure 4-2). The conversion of St did not reach 100% because a solvent was used for polymerization. Suitable amounts of 2,2,2-trifluoroethanol were used for dissolving azo-PA4 completely in runs 1–5. Among these runs, the initial concentration of St for run 5 was the highest and resulted in a high conversion of the monomer. The MWs of these polymerization products could not be measured by GPC because the products were not dissolved in common GPC eluents, even in HFIP. Instead, it was possible to estimate the calculated MW of the products with increments of St units per azo-PA4 initiator molecule.

Table 4-2 Results of polymerization of styrene by azo-PA4 as an initiator

Run No.	I azo-PA4 [a] (g) ; (mmol)	M Styrene (g) ; (mmol)	M/I Feed ratio (mol/mol)	P Yield [e] (g) , (%)	P-I (= ΔM) Increments of St unit (g) ; (mmol)	(P-I)/I ΔM/I (mol/mol)	Calcd. MW [f] (g·mol^{-1})
1	0.50 ; 0.051 [b]	0.25 ; 2.4	47	0.50 , 66.7	0 ; 0	0	4.9×10^3
2	1.00 ; 0.079 [c]	1.00 ; 9.6	122	1.18 , 59.0	0.18 ; 1.72	21.8	8.6×10^3
3	0.50 ; 0.072 [d]	1.20 ; 11.5	160	1.41 , 82.9	0.91 ; 8.74	121.4	16.1×10^3
4	0.50 ; 0.051 [b]	2.00 ; 19.2	376	1.99 , 79.6	1.49 ; 14.31	280.6	34.1×10^3
5	0.25 ; 0.026 [b]	5.00 ; 48.0	1846	4.87 , 92.8	4.62 ; 44.36	1706.2	182.6×10^3

a) Mole of azo-PA4 calculated from measured value (Mn) by GPC. e.g. for run 2, 1.00/(12.7run 2, 1.00 / (12.7×10^3) = 0.079 mmol.
b) Mn: 9.8×10^3 , Mw: 19.0×10^3.
c) Mn: 12.7×10^3, Mw: 24.6×10^3.
d) Mn: 6.9×10^3, Mw: 10.9×10^3.
e) Soxhlet extraction with only chloroform.
f) e.g. MW of run 2 = 21.8 × 104.15 (formula weight of St) + 12700 (Mn of azo-PA4) / 2 = 8.6×10^3.

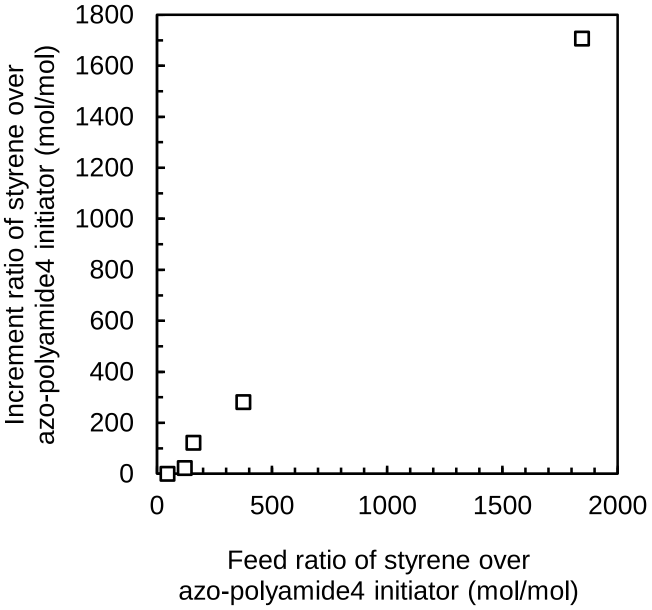


Figure 4-2 Relationship between the increment ratio and feed ratio.

To confirm initiation activity of azo-PA4, the polymerization of St was attempted according to the procedure described in the Experimental section. To remove the homopolymers (PSt and PA4) from the crude polymer, Soxhlet extraction was carried out separately with chloroform (PSt was soluble, and PA4 was insoluble) and 2,2,2-trifluoroethanol (PSt was insoluble, and PA4 was soluble) as extracting solvents for each 24 h. The products obtained from the extraction were purified to give a white powder. As a control, the polymerization of St was attempted with a PA4 free of azo groups. In this control experiment, the polymerization of St did not occur.

Figure 4-3 shows the IR absorption spectrum of the purified polymerization product (run 3 in Table 4-2). In addition to the NH stretching vibrations (3298 cm^{-1}) and carbonyl stretching vibrations (1641 and 1542 cm^{-1}) caused by the PA4 portion, the vibrational bands of an aromatic ring in the PSt portion were observed at 1942, 1869, 1802, and 1741 cm^{-1}. These characteristic absorption peaks suggested copolymer formation; therefore, it can be stated that azo-PA4 had polymerization activity for St.

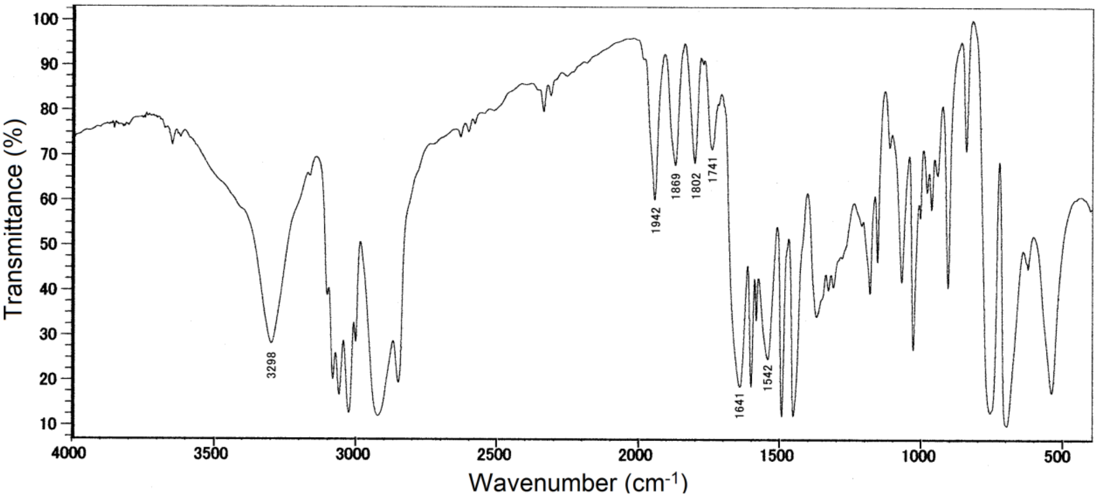


Figure 4-3 IR absorption spectrum of PA4-*block*-PSt (run 3 in Table 4-2).

Figure 4-4 shows an example of the ^{1}H NMR spectrum of the purified polymerization product that did not contain homopolymers (run 3, Table 4-2). Nevertheless, signals based on both the PA4 portion and the PSt portion were observed. These results indicate that the product was a block polymer of PA4 and PSt. The assignments are described in Figure 4-4. ^{1}H NMR was also used to determine the polymer composition in molar percentage by calculation of the peak areas of the PA4 and the PSt portions. The ratio of this polymer ([PA4]/[PSt]) was 4/96. The symbols [PA4] and [PSt] represent constitutional repeating units of PA4 and PSt, respectively.

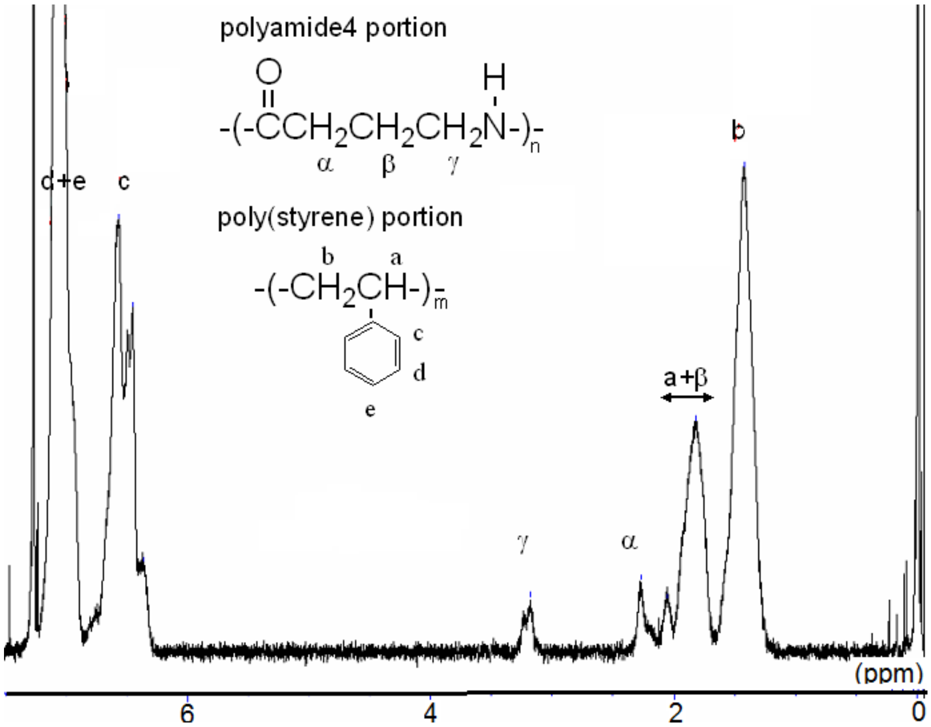


Figure 4-4 ^{1}H NMR spectrum of PA4-*block*-PSt (run 3 in Table 4-2).

Table 4-3 summarizes the polymer compositions of PA4-*block*-PSt for various feed ratios of azo-PA4 to St after purification by Soxhlet extraction. Despite variations in the feed ratio, the polymer compositions were approximately constant ([PA4]/[PSt] = 4/96–6/94). These results show that these copolymers had rich St in the polymer chains compared to the feed ratio. For the purpose of analyzing the components of the polymerized products, the products were separated into the chloroform-soluble, 2,2,2-trifluoroethanol-soluble, and insoluble fractions by stepwise Soxhlet extraction. The mass fractions of each component were found to be dependent on the polymerization conditions. For example, in the case of run 2 (Table 4-2), the (P-I)/I values were low; that is, the value for the insoluble fraction (block copolymer) was only 33%, and those for the chloroform-soluble and 2,2,2-trifluoroethanol-soluble fractions were 6 and 61%, respectively. On the other hand, run 4 had a high (P-I)/I, and the insoluble fraction (block copolymer) comprised 67%, whereas chloroform accounted for 13%, and 2,2,2-trifluoroethanol accounted for 20%. The samples that had a large (P-I)/I contained more insoluble than soluble portions. These findings indicate that the PA4-rich copolymer fraction might have been removed from the products by the Soxhlet extraction step, whereas these show bonding between the PSt chain and PA4 chain to form block copolymers.

Table 4-3 Polymer composition of polyamide 4-*block*-polystyrene for feed ratio of azo-polyamide 4 to styrene after purification by Soxhlet extraction

Run No.	[PA4] a) (Unit of azo-PA4) (g) ; (mmol)	[PSt] (Styrene) (g) ; (mmol)	[PA4]/[PSt] (Feed ratio) (mol/mol)	[PA4]/[PSt] e) (Polymer composition) (mol/mol)
2	1.00 ; 11.8 c)	1.00 ; 9.6	55/45	5/95
3	0.50 ; 5.9 d)	1.20 ; 11.5	34/66	4/96
4	0.50 ; 5.9 b)	2.00 ; 19.2	24/76	4/96
5	0.25 ; 2.9 b)	5.00 ; 48.0	6/94	6/94

a) molar of feed amount are calculated from formula weight of constitutional repeating unit of azo-polyamide 4
b) *M*n: 9.8×10^3 , *M*w: 19.0×10^3
c) *M*n: 12.7×10^3, *M*w: 24.6×10^3
d) *M*n: 6.9×10^3, *M*w: 10.9×10^3
e) Soxhlet extraction with chloroform and 2,2,2-trifluoroethanol separately

Thermal analysis of the copolymer was carried out with DSC. Figure 4-5 shows the DSC thermogram obtained upon the heating of the product. The temperature of the small peak (254°C) was close to the *T*m of PA4 (260–265°C).2,20) As a result, this transition was attributed to the melting of the PA4 segments. The steplike transition, which occurred in the range 111–114°C, likely corresponded to the glass transition temperature (*T*g) of PSt (91–128°C); therefore, this transition was attributed to the *T*g of the PSt segments. The DSC thermogram revealed the expected block nature of the copolymer. Similar thermograms were obtained for other copolymers, such as the values of 112–116°C (*T*g) and 253°C (*T*m) in run 2 and 107–116°C (*T*g) and 260°C (*T*m) in run 4.

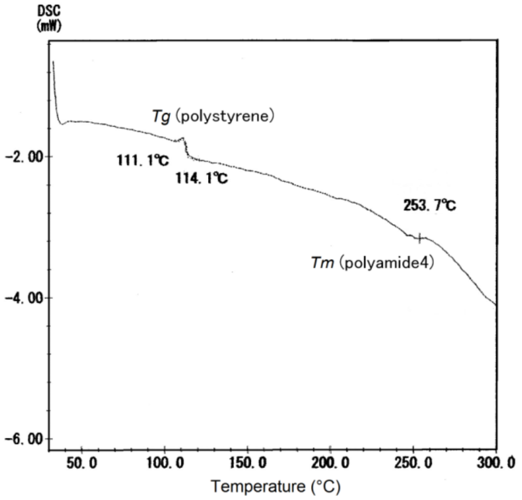


Figure 4-5 DSC thermogram of PA4-*block*-PSt (run 3 in Table 4-2).

In light of the IR, ^{1}H NMR, and DSC data, azo-PA4 was found to be an effective initiator for polymerization of St.

Several vinyl monomers were also used to confirm the initiation activity of azo-PA4 (Mn = 6.9 × 10^3). The polymerization products were purified as described previously. To remove the vinyl homopolymer, chloroform or methanol was used. The removal of PA4 was difficult because 2,2,2-trifluoroethanol is a good solvent for all copolymers and PA4. Therefore, Soxhlet extraction for purification was only carried out with chloroform or methanol.

Figure 4-6 shows the GPC curves of azo-PA4 and the polymerization products of several vinyl monomers. With the exception of the St copolymers, the products were soluble in HFIP; therefore, HFIP was used as the eluent for GPC measurement. Obvious increases in the MWs were observed after the polymerization of each vinyl monomer by azo-PA4, and the MW distributions were fairly large (2–8). On the basis of the GPC analysis, the initiation activity of azo-PA4 for radical polymerization was evident.

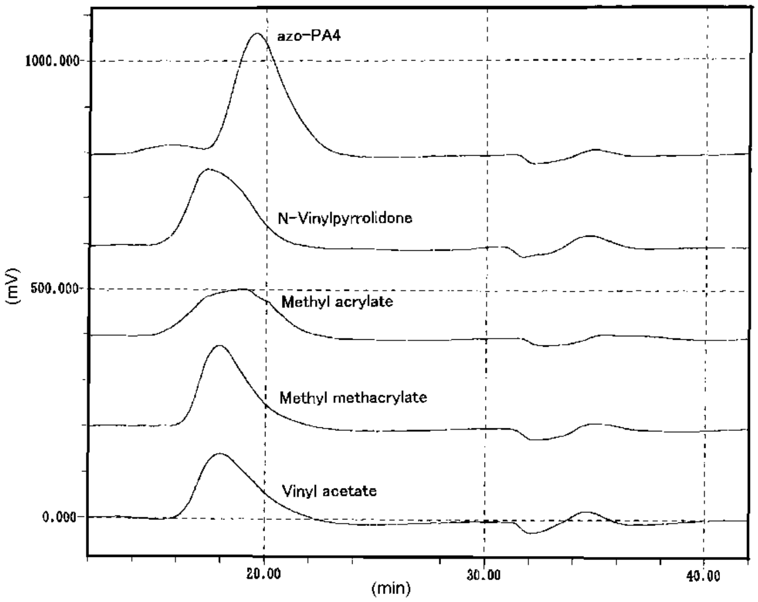


Figure 4-6 GPC curves of azo-PA4 and the polymerization products of several vinyl monomers.

Table 4-4 summarizes the results of the radical polymerization. The feed amount of vinyl monomers was set to 11.5 mmol, which was approximately 160 times greater than that of azo-PA4. The conversions of vinyl monomer (ΔM/M) were 6–76%, depending on the type of monomer used. St and MA were polymerized especially well. NVP seemed to be a poor monomer for the azo-PA4 initiator. Moles of increments (ΔM) were calculated from the formula weight of each monomer and normalized against the quantity of initiator (ΔM/I). From the ΔM/I, the MWs for runs 1–6 were calculated. With the exception of *N*-vinylpyrrolidone (run 6), there were not extreme differences between the calculated MWs and the *M*n values measured by GPC.

Table 4-4 Results of polymerization of several vinyl monomers by azo-PA4 [a] as an initiator

Run No.	Vinyl monomer	M Monomer feed (g) ; (mmol)	M/I [b] Feed ratio (mol/mol)	P Yield (g) ; (%)	P-I = ΔM Increments (g) ; (mmol)	(P-I)/I ΔM/I (mol/mol)	ΔM/M (%)	*M*n×10^3 [c], *M*w×10^3 [c] ($\mathrm{g\cdot mol^{-1}}$)	MW×10^{-3} Calcd. ($\mathrm{g\cdot mol^{-1}}$) [e]
1	St	1.20 ; 11.5	160	1.41 ; 82.9	0.91 ; 8.74	121.4	75.8	--- [d], --- [d]	16.1
2	MA	0.99 ; 11.5	160	1.19 ; 79.9	0.69 ; 8.15	113.2	69.7	12.5 , 103.5	13.2
3	MMA	1.15 ; 11.5	160	0.89 ; 53.9	0.39 ; 3.90	54.2	33.9	17.2 , 48.7	8.9
4	VA	0.99 ; 11.5	160	0.76 ; 51.0	0.26 ; 3.02	41.9	26.3	14.1 , 49.5	7.1
5	AA	0.83 ; 11.5	160	0.73 ; 54.9	0.23 ; 3.19	44.3	27.7	8.9 , 13.4	6.6
6	NVP	1.28 ; 11.5	160	0.58 ; 32.6	0.08 ; 0.72	10.0	6.3	23.4 , 116.0	4.6

a) Azo-PA4 0.50 g (0.072 mmol) *M*n; 6922 *M*w; 10940 *M*w/*M*n; 1.580.
b) $11.5 \times 10^{-3} / (0.50 / 6922) = 160$.
c) Determined by GPC; eluent: hexafluoroisopropyl alcohol, standard: poly(methyl methacrylate).
d) Not measurable for insolubility in hexafluoroisopropyl alcohol (GPC eluent).
e) For example, MW of run 2 = 113.2 × 86.09 (formula weight of MA) + 6900 (*M*n of azo-PA4) / 2 = 13.2×10^3.

The polymerizations proceeded in every run, but the degree of polymerization varied, depending on the vinyl monomers. One of the reasons for this appeared to be differences in the chain-transfer constants to monomers [$C_M \times (10^4)$] and to solvents [C_S ($\times 10^4$)] and termination rate constants [k_t ($\times 10^{-6}$)] of individual monomers. The values of C_M, C_S, and k_t reported in the literature were somewhat different from each other.[21,22] Therefore, the data were selected from the vicinity of the median in the case of wide variations, and the averages were calculated (Table 4-5).

Table 4-5 Average chain transfer constants and termination rate constants by calculating data in the literature

	C_M × 10^4	C_S(acetone) × 10^4	C_S(ethanol) × 10^4	C_S(toluene) × 10^4	k_t × 10^{-6}
Styrene (St)	0.84±0.08 a)	0.41±0.9 a)	1.47±0.15 a)	0.14±0.16 a)	21±9 b)
Methyl acrylate (MA)	0.18±0.12 a)	0.23 a)	---	2.7 a)	31±24 b)
Methyl methacrylate (MMA)	0.11±0.02 a)	0.195 a)	0.40 a)	0.27±0.03 a)	26±2 b)
Vinyl acetate (VA)	2.18±0.1 a)	11.9±0.15 a)	25 a)	23.0±2.06 a)	70±33 b)
Acrylic acid (AA)	---	---	---	---	2.6 d)
N-Vinyl-2-pyrrolidone (NVP)	4.0 c)	---	---	---	600±200 b)

a) 60°C. b) 25°C. c) 20°C. d) 23°C.

For example, the data of St (C_M) were 0.6, 0.6, 0.6, 0.75, 0.79, 0.85, 0.92, 1.1, and 1.37 in the literature. Using these data, an average of 0.84 and a probable error of 0.06 were calculated. On the basis of the calculated results, the order of each chain-transfer constant and k_t was as follows:

C_M: MMA < MA < St < VA < NVP,

$C_{S(acetone)}$: MMA ≤ MA ≤ St < VA,

$C_{S(ethanol)}$: MMA < St < VA,

$C_{S(toluene)}$: St ≤ MMA < MA < VA,

k_t: AA < St ≤ MMA ≤ MA < VA < NVP.

As judged from the order of values, VA and NVP showed large values of C_M, C_S, and k_t. These findings indicated that VA and NVP suppressed propagation and, thereby, decreased the constitutional repeating unit of vinyl monomer in the block polymer chain. This speculation was in good agreement with the polymerization results presented in Table 4-4.

4.4 Conclusions

In this study, it was shown that azo group could be easily introduced into PA4 chains through activated monomer mechanism with the ring-opening polymerization of 2-pyrrolidone. Azo-PA4 had an initiation activity for the radical polymerization of a variety of vinyl monomers and could be used as an azo-PA4 macromolecular initiator. Where St was polymerized by azo-PA4, the polymerization products were composed of a PA4 block and PSt block. The resulting block copolymers are expected to be additives that could improve the thermal stability and impact resistance. Furthermore, the block copolymer could also be used as a compatibilizer between PA4 and polyolefins. Because the block copolymer (PA4-*block*-PSt) is composed of PA4 and PSt segments, the block copolymer has miscibility to each homopolymer.

4.5 References

1) H. K. Hall Jr.; *J. Am. Chem. Soc.* **1958**, *80*, 6404.

2) N. Kawasaki, A. Nakayama, N. Yamano, S. Takeda, Y. Kawata, N. Yamamoto, S. Aiba; *Polymer* **2005**, *46*, 9987.

3) J. Furukawa, S. Takamori, S. Yamashita; *Angew. Makromol. Chem.* **1967**, *1*, 92.

4) J. J. Laverty, Z. G. Gardlund; *J. Polym. Sci: Polym. Chem. Ed.* **1977**, *15*, 2001.

5) A. Ueda, S. Nagai; *J. Polym. Sci. Part A: Polym. Chem.* **1984**, *22*, 1611.

6) A. Ueda, S. Nagai; *J. Polym. Sci. Part A: Polym. Chem.* **1987**, *25*, 3495.

7) C. I. Simionescu, E. Comanita, V. Harabagiu, B. C. Simionescu; *Eur. Polym. J.* **1987**, *23*, 921.

8) C. I. Simionescu, V. Harabagiu, E. Emanita, V. Hamciuc, D. Giurgiu, B. C. Simionescu; *Eur. Polym. J.* **1990**, *26*, 565.

9) K. Matsukawa, A. Ueda, H. Inoue, S. Nagai; *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 2107.

10) H. Kinoshita, N. Takata, T. Arai; *Makromol. Chem.* **1993**, *194*, 2335.

11) Y. Haneda, H. Terada, M. Yoshida, A. Ueda, S. Nagai; *J. Polym. Sci. Part A: Polym.*

Chem. **1994**, *32*, 2641.

12) E. E. Hamurcu, B. Hazer, B. M. Baysal; *Polymer* **1997**, *38*, 2981.

13) T. Hirano, R. Amano, T. Fuji, K. Onimura, H. Tsutsumi, T. Oishi; *Polym. J*. **1999**, *31*, 864.

14) Y. Yagci; *Polym. Commun*. **1985**, *26*, 7.

15) Y. Yagci, I. E. Serhatli, P. Kubisa, T. Biedron; *Macromolecules* **1993**, *26*, 2397.

16) Y. Yamashita, Y. Murase, K. Ito; *J. Polym. Sci. Polym. Chem. Ed*. **1973**, *11*, 435.

17) J. Stehlicek, J. Sebenda; *Eur. Polym. J.* **1977**, *13*, 949.

18) J. Stehlicek, J. Sebenda; *Eur. Polym. J.* **1977**, *13*, 955.

19) C. J. Pouchert; *The Aldrich Library of Infrared Spectra*, 3*rd ed.*; Aldrich Chemical: Milwaukee, WI, **1981**; p 516.

20) R. L. Miller; in *Polymer Handbook, 4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grullke, Editors.; Wiley: New York, **1999**, Section VI, p 33.

21) A. Ueda, S. Nagai; in *Polymer Handbook, 4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grullke, Editors.; Wiley: New York, **1999**, Section II, p 97.

22) M. Kamachi, B. Yamada; in *Polymer Handbook, 4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grullke, Editors.; Wiley: New York, **1999**, Section II, p 77.

Chapter 5 Synthesis, properties, biodegradation and morphology of polyamide 4-*block*-poly(vinyl acetate) via a polyamide 4 azo macromolecular initiator

5.1 Introduction

The synthesis of polyamide 4 (PA4) is possible at temperatures near the melting point (25°C) of 2-pyrrolidone (PRN). Because of this mild synthetic reaction condition, the initiator, which contains the thermolabile group, can be used in polymerization without thermal decomposition. In the preceding chapter, when 4,4’-azobiscyanopentanoyl chloride was used to initiate the polymerization, the PA4-containing azo group (azo-PA4) was obtained. This azo group generates radicals with the elimination of nitrogen gas for heating to approximately 60°C, which means that the azo-PA4 functions as a macromolecular initiator. The azo-PA4 made it possible to polymerize various vinyl monomers and the formation of the block copolymer was confirmed by conducting an experiment using styrene as the monomer. Thus far, azo macromolecular initiators with a single azo group in the polymer chain have been employed in two types of procedures to utilize the 4,4’-azobiscyanopentanoyl group to synthesize polyamide-*block*-vinyl polymers. The first type involves a three-step procedure, for example, the synthesis of 4,4’-azobiscyanopentanoyl lactam, followed by the preparation of the vinyl polymer with a lactam end-group by radical polymerization and the anionic ring-opening polymerization of lactam monomers, in this order.1-3) The other type of procedure also includes three steps, for example, the preparation of the polyamide prepolymer by anionic ring-opening polymerization, followed by the synthesis of the azo macromolecular initiator by reacting the polyamide with 4,4’-azobiscyanopentanoyl chloride, and the radical polymerization of vinyl monomers by the azo macromolecular initiator, in this order.4) The former type is difficult to apply to polar vinyl monomers such as vinyl acetate (VAc), and both types have the disadvantage of requiring a three-step procedure for the synthesis of polyamide-*block*-vinyl polymers. Modifying the procedure would make it possible to synthesize azo-PA4 by taking advantage of the low polymerization temperature of PRN and to reduce the number of steps in the synthesis of polyamide 4-*block*-vinyl polymers to two-steps.

For the present study, VAc was selected among the various vinyl monomers, because it offers the following two beneficial features when polymerized: poly(vinyl acetate) (PVAc) are amorphous polymers with a softening point of 35–50°C,5) while PA4 are crystalline polymers with a high melting point of 260°C.6) Moreover, PVAc differs from PA4 in terms of its solubility parameter (δ)7) and the difference may result in immiscibility. Thus, the combination of a crystalline block consisting of PA4 and an amorphous block consisting of PVAc is expected to exhibit specific properties originating from the phase formed by two immiscible blocks.8-11) Therefore, this chapter deals with the synthesis of polyamide 4-*block*-poly(vinyl acetate) by using azo-PA4, their thermal and mechanical properties, biodegradability, and morphology.

5.2 Experimental

5.2.1 Materials

Reagents and starting materials were treated as follows: 2-pyrrolidone (Kishida Chemical, Osaka, Japan) was distilled under reduced pressure, followed by drying over calcium hydride; sodium (Wako Pure Chemical Industries, Osaka, Japan) was used after removing impurities from the surface; 4,4'-azobiscyanopentanoyl chloride was prepared by the halo-de-hydroxylation of 4,4'-azobiscyanopentanoic acid (Wako Pure Chemical Industries) with thionyl chloride (Kishida Chemical), as described in an earlier paper.14) 2,2,2-trifluoroethanol (Kishida Chemical) and chloroform (Wako Pure Chemical Industries) were used as received; vinyl acetate (Wako Pure Chemical Industries) was purified by distillation. The PA4 compounds containing the azo group (azo-PA4) were prepared by anionic ring-opening polymerization of PRN using 4,4'-azobiscyanopentanoyl chloride as an initiator, as described in the chapter 4.

5.2.2 Polymerization of vinyl acetate by azo-PA4

A typical polymerization procedure was performed as follows. To a 50 mL round-bottomed flask, azo-PA4 with *M*n 17800 g·mol^{-1} (0.50 g, 0.028 mmol from 0.50/17800) was added and dissolved in 2,2,2-trifluoroethanol (7 mL). Subsequently, VAc (1.50 g, 17.4 mmol) was added to the flask and the mixture was homogenized at room temperature. The mixture was degassed using five freeze-pump-thaw cycles in a dry ice-ethanol bath to replace the atmosphere with argon. The flask, which was equipped with an argon balloon, was maintained under an argon atmosphere and immersed into a silicone oil bath at 60°C for 24 h. Then, a vacuum pump was connected to the flask while still hot, and the solvent, 2,2,2-trifluoroethanol, and the residual VAc were removed by evaporation. In an attempt to purify the polymerization mixture, PVAc was extracted from the resulting mixture with chloroform for 2 days by using Soxhlet extraction. The resulting polymerization products were dried by storing them in a heated desiccator under reduced pressure. Aside from the polymerization products, the chloroform extract was recovered by evaporation. The desired polymerization product (insoluble in chloroform) and the extract (soluble in chloroform) weighed 1.02 g (51.0%) and 0.45 g (22.5%), respectively.

5.2.3 Characterization

The molecular weight (Mn, Mw) and the distribution (Mw/Mn) of the products were determined by gel permeation chromatography (GPC, HLC-8220 GPC system, Tosoh Corporation, Tokyo, Japan). Poly(methyl methacrylate) standards (Shodex Standard M-75, Shimadzu GLC Ltd., Tokyo, Japan) were used for plotting a calibration curve. All GPC measurements were carried out using two columns (TSK gel Super HM-N, Tosoh) for samples with separate double-tandem reference columns (TSK gel Super H-RC, Tosoh) connected separately and maintained at 40°C, and by using hexafluoroisopropyl alcohol (HFIP, Central Glass Co., Ltd., Tokyo, Japan) as the eluent at a 0.2 mL·min^{-1} flow rate.

The structure and composition of the polymers were determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy (JNM-ECA-500 NMR spectrometer 500 MHz, JEOL Ltd., Tokyo, Japan) using deuterated methanol CD_3OD containing lithium chloride (0.25 g·mL^{-1}) as the solvent. The concentration of the specimen was about 25 mg·mL^{-1}.

The melting temperature (Tm) and heat of fusion (ΔHm) were measured by differential scanning calorimetry (DSC, DSC 3100S Calorimeter, Bruker AXS K.K., Yokohama, Japan). Samples (4–6 mg) were analyzed at a heating rate of 10°C·min^{-1} and 30–350°C under a nitrogen atmosphere.

The tensile strength and elongation at break of the film specimens were measured by using a universal tensile testing machine (Auto Com/AC-50C, T.S.E Co., Ltd., Yokohama, Japan). The specimens were pulled in a vertical direction at a rate of 10 mm·min^{-1} with a 100 N load cell at room temperature and the gauge length between the chucks was 10 mm. The thickness of each specimen was measured at three points before testing and a minimum value was adopted. The mechanical properties reported here correspond to the average values of at least 5–15 measurements.

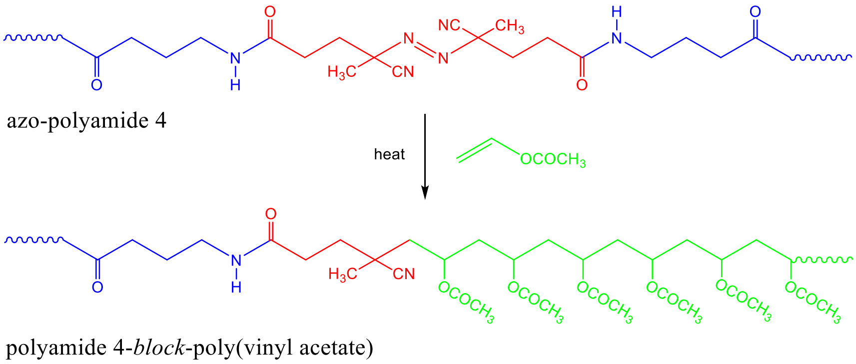
The biodegradation% of the polymers by a standard activated sludge metabolism was evaluated by using a closed manometric respirometer system (BOD TESTER 200F and COOLNIT CL-150R system, Taitec Co., Ltd., Koshigaya, Japan). A polymer sample (30 mg) was dispersed in 200 mL of an inorganic culture medium as described in ISO 14851, and 20 mL (dry weight: 20 mg) of a standard activated sludge (Chemicals Evaluation and Research Institute, Japan) was added to the medium. In a closed-system culture vessel, the generated carbon dioxide was absorbed at 27°C by calcium hydroxide on a pan placed in the vessel, and the amount of consumed oxygen was measured by determining the decrease in the volume by reading the scale on a burette immersed in the thermostat bath. This procedure was conducted for about one month to carry out the biodegradation test. The observed amount of oxygen consumed as a result of the condition of the polymer sample was corrected by subtracting the amount of oxygen consumed depending on the condition of the activated sludge only. The biodegradation% of the polymer sample was calculated by dividing the observed amount of oxygen consumed by the theoretical amount of oxygen required, which is the total amount of oxygen required for converting all of the carbon into carbon dioxide, nitrogen into nitrate ions, and hydrogen into water contained in the PA4 units (but not in the PVAc units) of the polymer samples when all of the PA4 units have been biodegraded.

The laser microscopy measurements presented in this article were all performed on a shape measurement laser microscope (VK-X2101VK-X200 system, Keyence Corporation, Osaka, Japan). Thin films for laser microscopy were prepared by coating a dilute solution of 2,2,2-trifluoroethanol of the polymer sample onto a clean glass slide.

5.3 Results and discussion

Synthesis, Purification, and Analysis

VAc was polymerized with azo-PA4 in 2,2,2-trifluoroethanol at 60°C for about 24 h (Scheme 5-1).



Scheme 5-1 Radical polymerization of VAc by azo-PA4.

Besides the formation of copolymer, the radical polymerization of VAc by azo-PA4 causes a chain transfer reaction and recombination, such that both the homopolymers PVAc and PA4 may be produced. Therefore, to separate the copolymer from the obtained polymerization product mixture, a Soxhlet extraction with chloroform was performed to remove PVAc from the mixtures.

The molecular weights and weight distributions of the separated polymerization products were measured by GPC. Figure 5-1 shows the GPC profiles for azo-PA4 (a) and the obtained copolymers (b, c, and d) with different monomer feed ratios using the same azo-PA4 initiator (I3 series in Table 5-1). The GPC traces of each product showed broadened elution peaks and were eluted faster than the original azo-PA4. The molecular weight distribution between azo-PA4 and the series of separated products was clearly different. Although a few examples of the obtained GPC curves showed a very faint shoulder, the shape of the curves was nearly unimodal. This suggested that the separated products almost consisted of the block copolymers.

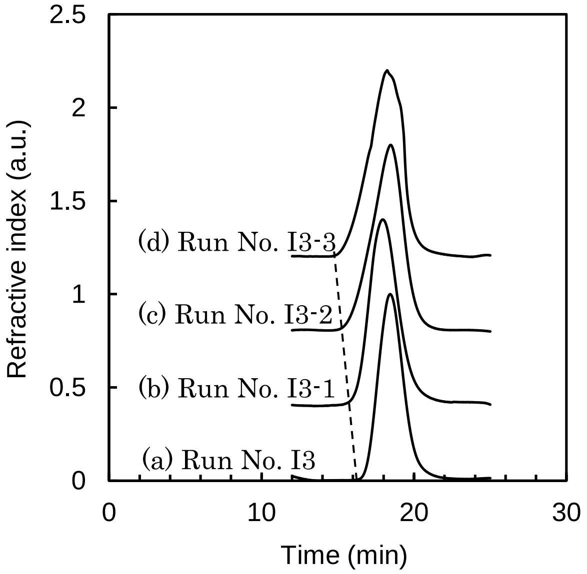


Figure 5-1 GPC profiles for azo-PA4 (Run No. I3) and separated polymerization products (Run No. I3-1, I3-2, I3-3 in Table 5-1).

To verify that the separated products were in fact the block copolymers consisting of both PA4 and PVAc chains, their ^{1}H NMR spectra were measured. A typical ^{1}H NMR spectrum of the separated products is shown in Figure 5-2. ^{1}H NMR (500 MHz, CH_3OH-d_4, d): methylene protons (a), (b), (c), and amide proton (d) of PA4: 2.40 (br, 2H, CH_2), 1.87 (br, 2H, CH_2), 3.26 (br, 2H, CH_2), 8.42 (br, 1H, NH), methyl (C) and methylene protons (A) of PVAc: 2.17–2.12 (br, 3H, CH_3), 1.96 (br, 2H, CH_2). The methine protons (B) partially overlap the hydroxyl proton of methanol-d_4 and appear as a shoulder at 4.99 ppm. There were no peaks for the microstructure based on random or alternating sequences of constitutional repeating units, whereas the simple peaks were observed independently and suggested that the separated copolymers contained both PA4 and PVAc chains.

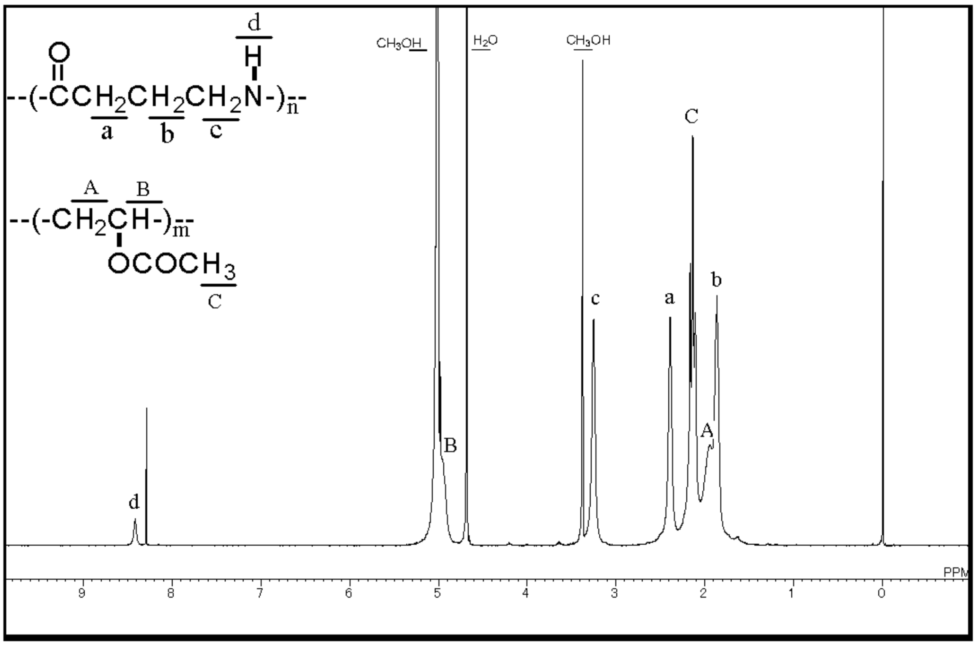


Figure 5-2 ^{1}H NMR spectrum of a separated polymerization product [polyamide 4-*block*-poly(vinyl acetate)].

The copolymer compositions were determined from the intensity ratio between a proton of the PA4 chain ([PRN]) and a proton of the PVAc chain ([VAc]) as follows. The integrated intensity of peak (c) provides the intensity of two protons of the PA4 repeating unit; hence, the intensity of one proton of the PA4 repeating unit is described by 0.5 × c. The intensity of peak (c) is equal to the intensity of both peaks (a) and (b), because they are all methylene protons. The integrated intensity of overlapping peaks (a + b + A + C) equals that of four protons (a + b) of the PA4 repeating unit and five protons (A1C) of the PVAc repeating unit; thus, the proton intensity of the PVAc repeating unit is described by $[(a + b + A + C) – (a + b)] \times 0.2$, namely $[(a + b + A + C) – (c \times 2)] \times 0.2$. Here, the overlapping peaks (a + b) are approximated by substituting c into a and b, respectively. Combining these expressions, the copolymer compositions were obtained from the following formula:

$[PRN] / [VAc] = (c \times 0.5) / [a + b + A + C – c \times 2) \times 0.2$,

which is the ratio of one proton intensity for the PA4 repeating unit to the PVAc repeating unit.

Based on the above facts such as the nearly unimodal shape of the GPC curves, simple peaks of the NMR spectra and preparation method, the isolated copolymers were regarded as mostly consisting of block copolymers, i.e., polyamide 4-*block*-poly(vinyl acetate).

Features of Polymerization

The polymerization tendency and properties were examined by synthesizing other members of the series of polyamide 4-*block*-poly(vinyl acetate)s using several azo-PA4 units with different molecular weights in a similar manner. The polymerization results are provided in Table 5-1. The total yields of the polymerization products (both the fractions that were soluble and insoluble in chloroform) based on the feed materials were relatively high at approximately 69–92 wt%. These high yields imply that VAc was polymerized efficiently by the azo-PA4 macromolecular initiator. The soluble and insoluble fractions could be separated by Soxhlet extraction with chloroform. The above purification results indicate that the insoluble fraction largely consisted of polyamide 4-*block*-poly(vinyl acetate).

Table 5-1 Results of radical polymerization of vinyl acetate by azo-PA4 initioator

Run No.	Azo-polyamide 4 [I] (g) ; (mmol)	Vinyl acetate (g) ; (mmol)	Feed ratio [PRN] / [VAc]	Total yield (%)	Soluble part in $CHCl_3$ (g) ; (%)	Insoluble part in $CHCl_3$ [P] (g) ; (%)	Increments [P] – [I] = VAc unit (g) ; (mmol)	Polymer composition from increments [PRN] / [VAc] (mol%)	Polymer composition from NMR [PRN] / [VAc] (mol%)	*M*n $\times 10^{-3}$ b)	*M*w $\times 10^{-3}$ b)	*M*w / *M*n b)
I1 a)										13.1	21.9	1.68
I1-1	0.50 ; 5.88	0.49 ; 5.69	50.8 / 49.2	88.9	0.09 ; 9.1	0.79 ; 79.8	0.29 ; 3.37	64 / 36	56 / 44	16.5	46.8	2.85
I1-2	0.50 ; 5.88	1.48 ; 17.19	25.5 / 74.5	84.8	0.29 ; 14.6	1.39 ; 70.2	0.89 ; 10.34	36 / 64	32 / 68	20.6	104.0	5.05
I1-3	0.50 ; 5.88	2.93 ; 34.03	14.7 / 85.3	81.6	0.79 ; 23.0	2.01 ; 58.6	1.51 ; 17.54	25 / 75	23 / 77	25.8	136.7	5.29
I2 a)										15.8	26.9	1.70
I2-1	0.50 ; 5.88	0.49 ; 5.69	50.8 / 49.2	91.9	0.10 ; 10.1	0.81 ; 81.8	0.31 ; 3.60	62 / 38	56 / 44	20.4	56.6	2.78
I2-2	0.50 ; 5.88	1.48 ; 17.19	25.5 / 74.5	90.5	0.50 ; 25.3	1.29 ; 65.2	0.79 ; 9.18	39 / 61	37 / 63	36.7	117.7	3.20
I2-3	0.50 ; 5.88	2.97 ; 34.50	14.6 / 85.4	83.0	1.07 ; 30.8	1.81 ; 52.2	1.31 ; 15.22	28 / 72	26 / 74	27.3	133.0	4.86
I2-4	0.50 ; 5.88	4.45 ; 51.69	10.2 / 89.8	91.1	2.20 ; 44.4	2.31 ; 46.7	1.81 ; 21.02	22 / 78	20 / 80	19.7	163.7	8.32
I3 a)										17.8	31.5	1.77
I3-1	0.50 ; 5.88	0.50 ; 5.81	50.3 / 49.7	73.0	0.07 ; 7.0	0.66 ; 66.0	0.16 ; 1.86	76 / 24	64 / 36	24.3	62.2	2.56
I3-2	0.50 ; 5.88	1.50 ; 17.42	25.2 / 74.8	73.5	0.45 ; 22.5	1.02 ; 51.0	0.52 ; 6.04	49 / 51	42 / 58	21.5	79.7	3.72
I3-3	0.50 ; 5.88	3.00 ; 34.85	14.4 / 85.6	73.1	0.98 ; 28.0	1.58 ; 45.1	1.08 ; 12.55	32 / 68	28 / 72	23.2	106.8	4.60
I4 a)										18.3	33.8	1.85
I4-1	0.50 ; 5.88	0.50 ; 5.81	50.3 / 49.7	77.0	0.11 ; 11.0	0.66 ; 66.0	0.16 ; 1.86	76 / 24	58 /42	21.7	74.3	3.43
I4-2	0.50 ; 5.88	2.25 ; 26.14	18.4/ 81.6	69.8	0.76 ; 27.6	1.16 ; 42.2	0.66 ; 7.67	43 / 57	32 / 68	25.7	99.7	3.88
I4-3	0.50 ; 5.88	3.00 ; 34.85	14.4 / 85.6	69.4	1.10 ; 31.4	1.33 ; 38.0	0.83 ; 9.64	38 / 62	29 / 71	21.8	114.6	5.26
I5 a)										18.1	36.6	2.02
I5-1	0.50 ; 5.88	1.49 ; 17.31	25.4 / 74.6	76.9	0.46 ; 23.1	1.07 ; 53.8	0.57 ; 6.62	47 / 53	40 / 60	25.5	97.7	3.83
I5-2	0.50 ; 5.88	2.23 ; 25.90	18.5 / 81.5	78.7	0.94 ; 34.4	1.21 ; 44.3	0.71 ; 8.25	42 / 58	33 / 67	24.7	110.9	4.49
I5-3	0.50 ; 5.88	4.47 ; 51.92	10.2 / 89.8	82.3	2.48 ; 49.9	1.61 ; 32.4	1.11 ; 12.89	31 / 69	27 / 73	34.9	142.1	4.07

a) Original azo-PA4 initiator for radical polymerization.

b) Determined by GPC. The eluent was hexafluoroisopropyl alchohol, and the standard was poly(methyl methacrylate).

As mentioned above, the ^{1}H NMR analysis provided the copolymer compositions; however, these compositions can also be estimated by obtaining the weight change by subtracting the weight of the amount of azo-PA4 that was used from the weight of the insoluble fraction. The weight difference obtained in this way provides the increments of the VAc units in polyamide 4-*block*-poly(vinyl acetate). Although several data points for the content lie to low, the content obtained from the weight increments were largely in agreement with that obtained from the ^{1}H NMR spectra. The reason for the lower ratio of VAc units seems to be the removal of block copolymers with a high content of VAc units by Soxhlet extraction. The validity of the estimated copolymer compositions was verified by plotting the compositions obtained from the increments and those obtained from the ^{1}H NMR spectra, as shown in Figure 5-3. The VAc content obtained from the weight increment above ca. 70 mol% coincides approximately with the composition obtained from ^{1}H NMR; however, below ca. 70 mol%, the composition obtained from the weight increment deviated from the straight dotted line. The reason for the deviation seems to be that the accuracy with which the recovered amount of copolymer strongly affects the weight increments of the copolymer in situations when the copolymer compositions are low in VAc content. For example, consider the case of Run Nos. I3-1 and I3-3: assuming that the recovery loss is 0.01 g, the errors are 6.3% (from 0.01/0.16 ×100) for the increments of 0.16 g of I3-1 and 0.9% (from 0.01/1.08×100) for the increments of 1.08 g of I3-3, respectively.

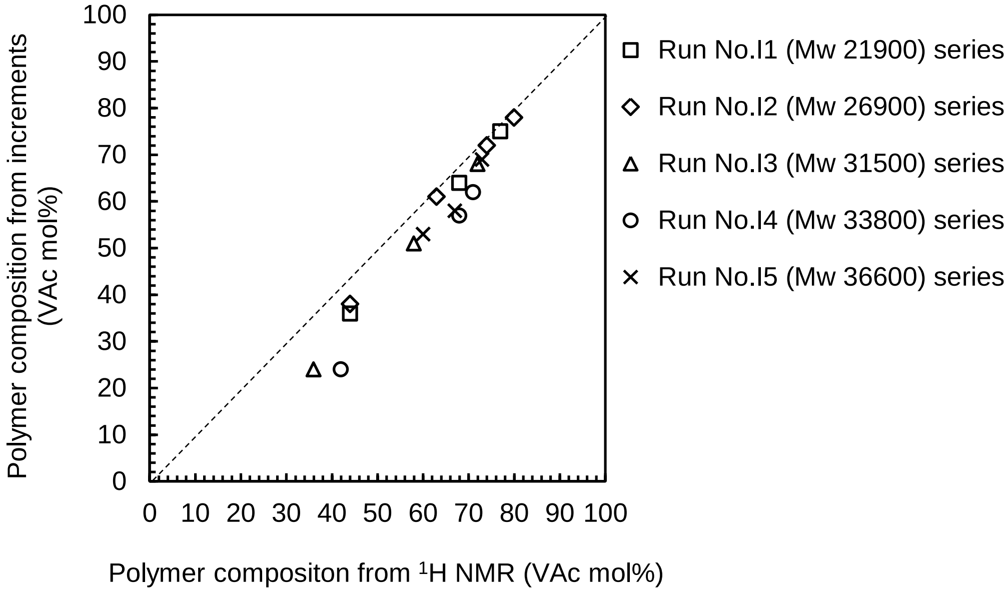


Figure 5-3 Polymer composition from increments against polymer composition from ^{1}H NMR for polyamide 4-*block*-poly(vinyl acetate).

The dependence of the weight-average molecular weights (*M*w) on the increments for the copolymers is shown in Figure 5-4. The data also included the *M*w of each original azo-PA4 before polymerization for reference. Although the data points show some scatter, the *M*w of the copolymers increases monotonically with the increments of the insoluble fractions. In contrast, the increments do not depend on the number-average molecular weight (*M*n). This irregularity against *M*n was a result of the sensitivity of the low-molecular-weight component in the copolymers. The approximate relationships for copolymers containing an azo-PA4 unit with a range of different molecular weights are shown in comparison to the straight dotted lines (Run No. I1 series and Run No. I5 series), which correspond to the *M*w of the original azo-PA4. The dependence of the molecular weights on the increments of the insoluble fractions provides further evidence for the formation of the block copolymers. For the *M*w and the molecular weight distribution (*M*w/*M*n) shown in Table 5-1, the *M*w increased as the feed quantity of VAc was increased for azo-PA4 and polydispersity broadened as the *M*w was increased. The increase in the feed quantity of VAc led to a relative increase in the concentration of the produced copolymers, because the same quantity of solvent was used, which caused the viscosity in the polymerization system to increase. Increasing the viscosity increases the *M*w because of the autoacceleration effect. There is also the possibility that chain transfer occurred on the copolymers to form a partially branching structure. Besides, cleavage of azo-PA4 continuously generates radicals throughout the polymerization process. Therefore, the polymerization systems simultaneously contain copolymers of various molecular weights to broaden the polydispersity.

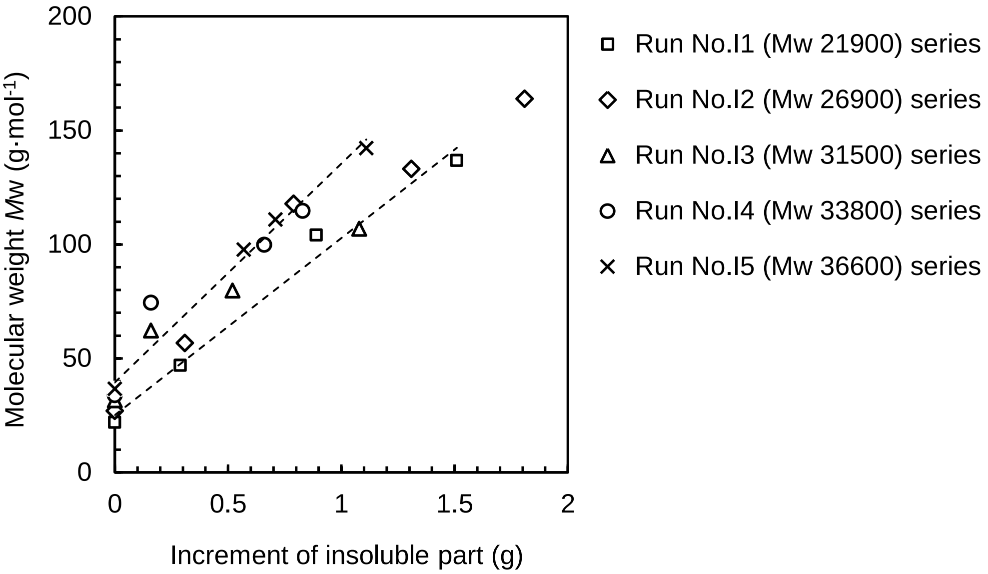


Figure 5-4 Relationship between the molecular weight and weight increment for polyamide 4-*block*-poly (vinyl acetate).

The relationship between the feed ratios of the monomer and polymer compositions was clarified by plotting the compositions against the feed ratios, as shown in Figure 5-5, in which the straight dotted line is fitted by using linear approximation. As seen in the figure, the polymer composition varied linearly with the feed ratio of the monomers and could therefore be controlled by the feed ratio. The VAc unit content of the copolymers is smaller than that in the original feed. The reason for the difference is that PVAc was formed partially by chain transfer and removed during the Soxhlet extraction process. Compared to the higher-molecular-weight azo-PA4 (*M*w 36600) polymers, the lower-molecular-weight azo-PA4 (*M*w 21900) polymers tended to form copolymers containing a slightly higher number of VAc units. Those with a lower molecular weight appeared to achieve the radical polymerization of VAc more efficiently.

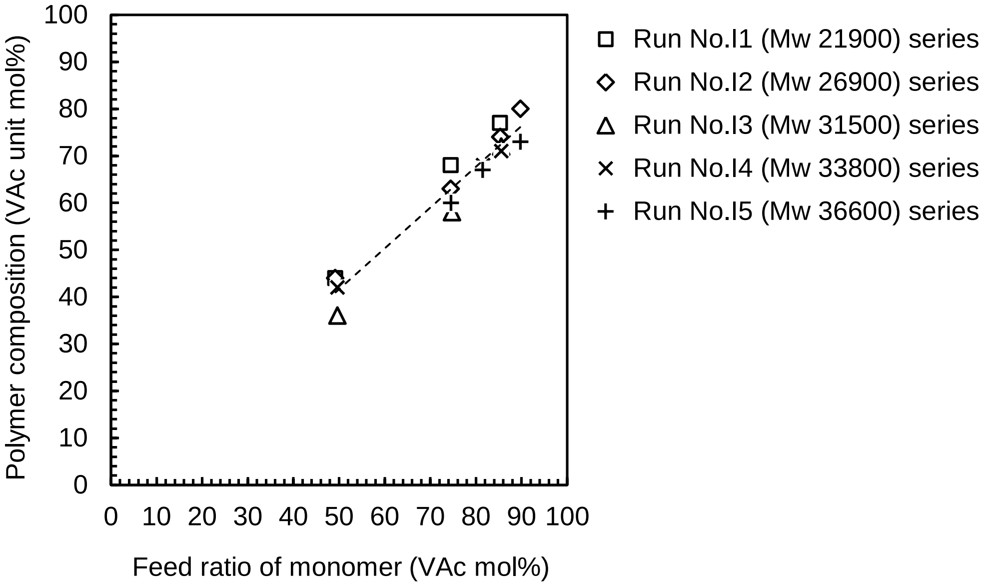


Figure 5-5 Polymer composition of polyamide 4-*block*-poly(vinyl acetate) against feed ratio of monomers.

Thermal and Mechanical Properties

Table 5-2 summarizes the thermal and mechanical properties, namely the melting point (*T*m), heat of fusion (*ΔH*m), and tensile strength and elongation at break, along with the compositions and molecular weights obtained by characterizing the block copolymers.

Table 5-2 Thermal and mechanical properties of various polyamide 4-*block*-poly(vinyl acetate) copolymers

Run No.	Copolymer composition from NMR [PRN] / [VAc]	$M\text{n}\times10^{-3}$ b)	$M\text{w}\times10^{-3}$ b)	$M\text{w} / M\text{n}$ b)	$T\text{m}$ ($^{\circ}$C)	$\Delta H\text{m}$ (J·g^{-1})	Tensile strength (MPa)	Elongation at break (%)
I1 a)		13.1	21.9	1.68				
I1-1	56 / 44	16.5	46.8	2.85	250.4	48	*** c)	*** c)
I1-2	32 / 68	20.6	104.0	5.05	248.2	28	13.8	146
I1-3	23 / 77	25.8	136.7	5.29	249.1	16	10.9	273
I2 a)		15.8	26.9	1.70				
I2-1	56 / 44	20.4	56.6	2.78	258.7	41	*** c)	*** c)
I2-2	37 / 63	36.7	117.7	3.20	259.7	26	21.5	155
I2-3	26 / 74	27.3	133.0	4.86	256.4	20	14.3	322
I2-4	20 / 80	19.7	163.7	8.32	259.1	13	12.5	374
I3 a)		17.8	31.5	1.77				
I3-1	64 / 36	24.3	62.2	2.56	260.4	48	20.9	18
I3-2	42 / 58	21.5	79.7	3.72	259.5	31	18.2	149
I3-3	28 / 72	23.2	106.8	4.60	259.7	23	15.7	204
I4 a)		18.3	33.8	1.85				
I4-1	58 /42	21.7	74.3	3.43	262.5	42	*** c)	*** c)
I4-2	32 / 68	25.7	99.7	3.88	260.9	22	17.6	255
I4-3	29 / 71	21.8	114.6	5.26	259.6	23	14.0	264
I5 a)		18.1	36.6	2.02				
I5-1	40 / 60	25.5	97.7	3.83	262.0	28	19.9	171
I5-2	33 / 67	24.7	110.9	4.49	259.6	25	17.5	258
I5-3	27 / 73	34.9	142.1	4.07	261.3	16	12.7	316

a) Original azo-PA4 initiator for radical polymerization.
b) Determined by GPC. The eluent was hexafluoroisopropyl alchohol, and the standard was poly(methyl methacrylate).
c) Good films were not obtained.

The thermal properties of the block copolymers were determined with DSC. Typical DSC thermograms of polyamide 4-*block*-poly(vinyl acetate) are shown in Figure 5-6. From the DSC traces, the melting points (*T*m ~ ca. 260°C) suggested that the block copolymers included PA4 blocks. The broad strong peaks indicate thermal decomposition of the copolymers (*Td* ~ ca. 300°C).

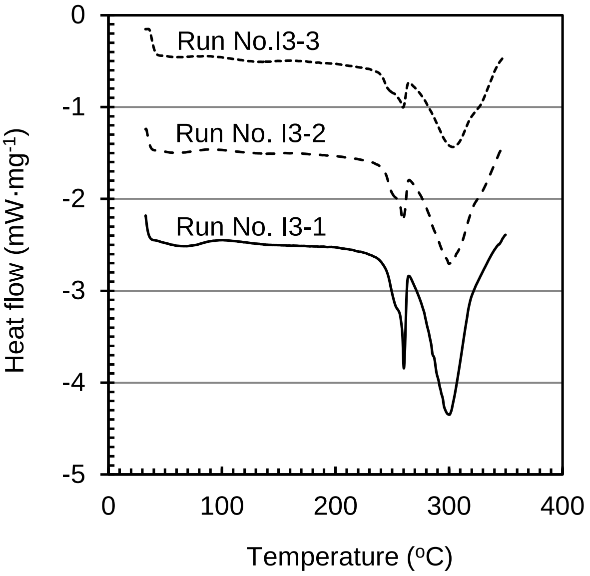


Figure 5-6 DSC thermograms of polyamide 4-*block*-poly(vinyl acetate).

The data in Table 5-2 indicate that the melting temperatures of PA4 blocks depend on the molecular weight of azo-PA4. For the lower-molecular-weight PA4 polymers (*M*w 21900), the average melting point is 249.2 ± 0.5°C, whereas it is 260.0 ± 0.3°C for those with higher molecular weight (*M*w 26900, 31500, 33800, 36600). The measurements also indicated that the melting points of the PA4 blocks were independent of copolymer composition, whereas the heats of fusion (*ΔH*m) were found to depend on the polymer composition and were approximately linear (Figure 5-7). The linear decrease in *ΔH*m with decreasing PA4 content shows that the polymers are almost block copolymers. The thermal properties, including the melting point and the linear relation between *ΔH*m and the compositions of the PA4 polymers, suggest that phase separation arises from both the PA4 and PVAc domains.

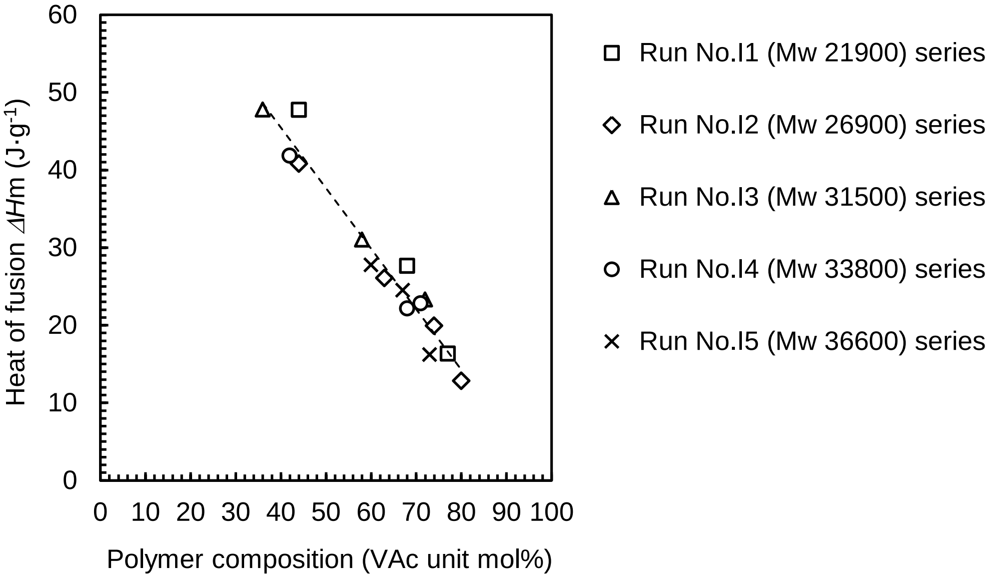


Figure 5-7 Heat of fusion against composition of polyamide 4-*block*-poly(vinyl acetate).

The solvent casting method was used to prepare films of polyamide 4-*block*-poly(vinyl acetate)s for mechanical testing by using the following method. Solutions of the polymer in 2,2,2-trifluoroethanol (ca. 10% w/v) were cast on glass Petri dishes, which were then covered. After gradual drying at atmospheric conditions for several days, films with an average thickness of ca. 100 mm were obtained. The block copolymers with a lower VAc content were so brittle that the good quality films could not be obtained. The good films were cut into rectangles (5 mm × 30 mm) and both ends of the rectangular specimens were fixed by square cardboard (25 mm × 25 mm) with a gauge distance of 10 mm. The specimens were thoroughly dried in a heated desiccator at 40–60°C under reduced pressure and then exposed to the atmosphere overnight before measurement of the mechanical properties.

Figure 5-8 (tensile strength) and Figure 5-9 (elongation at break) show the relation between these values and the copolymer compositions. The data for linear PA4 (*M*w 54600) and PVAc (*M*w 158200) were also included to enable comparison with the block copolymers. A straight solid line was fitted to the data of the block copolymers and the straight dotted line represents linear extrapolation on either side of the composition range. The tensile strength increased linearly with decreasing VAc content, thereby exhibiting increased strength for block copolymers compared to PVAc. The data at either end of the dotted line, i.e., at the intercepts with the axes for PA4 and PVAc, were in rough agreement with the measured values. As for the elongation at break, the block copolymers exhibited a larger elongation than PA4. An extrapolation of the straight dotted line showed that the elongation at break of the block copolymers approaches that of PVAc with increasing VAc content. In regard to the mechanical properties, the high tensile strength of the block copolymers is attributed to the hard segment domains of PA4 blocks and the large elongation at break is attributed to soft segment domains of PVAc blocks. In general, many blends of different polymers have low miscibility, and exhibit the disadvantages of both the polymers rather than displaying a synergetic effect in terms of the mechanical properties.[12,13] Therefore, the smooth continuous relation of the mechanical properties for different polymer compositions is a feature of the block copolymer, not the polymer blend.

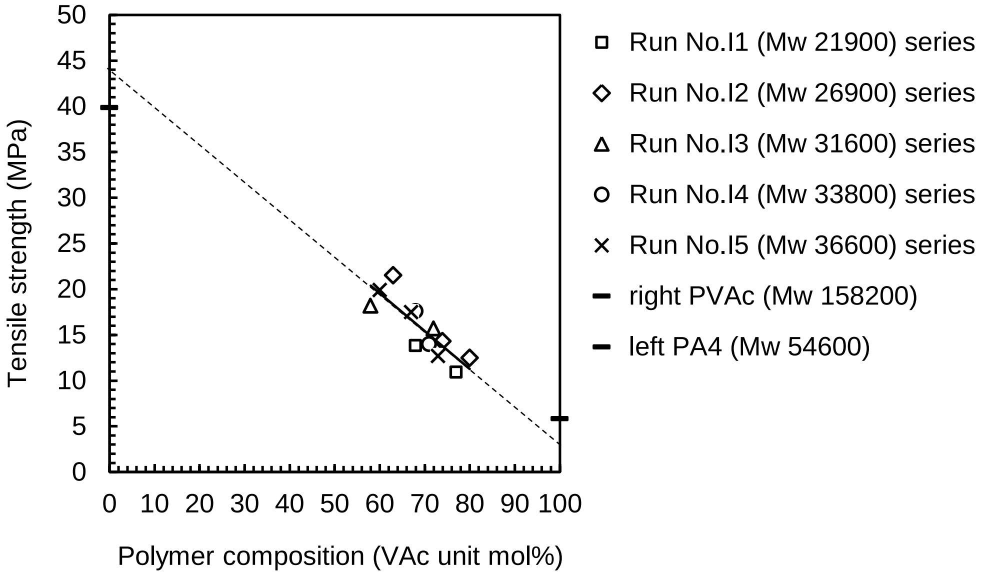


Figure 5-8 Tensile strength against composition of polyamide 4-*block*-poly(vinyl acetate).

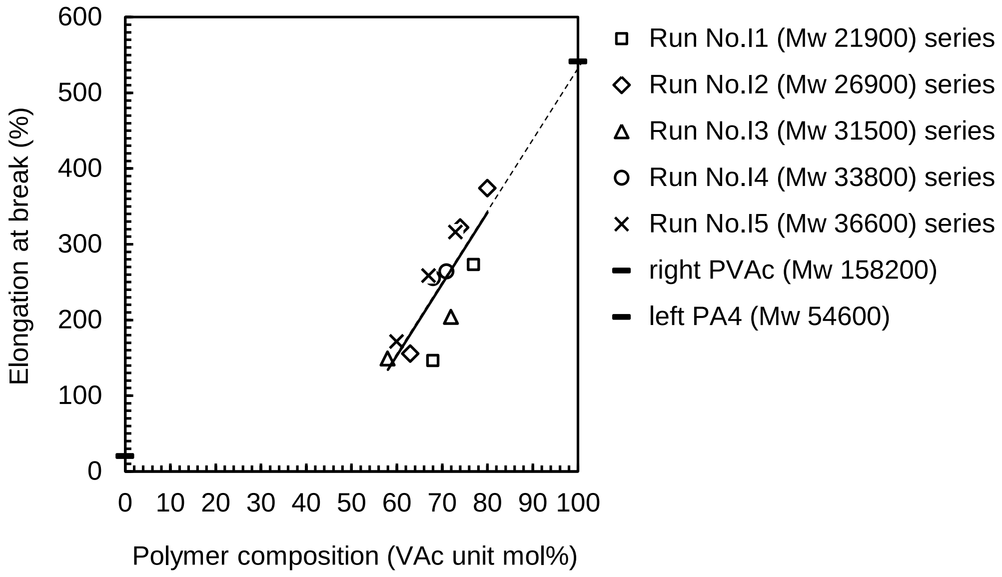


Figure 5-9 Elongation at break against composition of polyamide 4-*block*-poly(vinyl acetate).

Biodegradation

Polymer films prepared after three different polymerization runs (Run No. I3-1, I3-2, I3-3) were selected for the biodegradation test by an activated sludge. Figure 5-10 shows the time-course of the biodegradation results of these three block copolymers during a four week period. When only PA4 chains were biodegraded, the percent degree of biodegradation on the basis of three different PA4 compositions of polyamide 4-*block*-poly(vinyl acetate)'s ([PRN]/[VAc] = 28/72, 42/58, and 64/36) were 18%, 27%, and 59% over 28 days, respectively. PVAc blocks with abundant block copolymers tended to suppress the biodegradation of the PA4 blocks. This means that the linking between the PVAc and PA4 chains controls the biodegradation property.

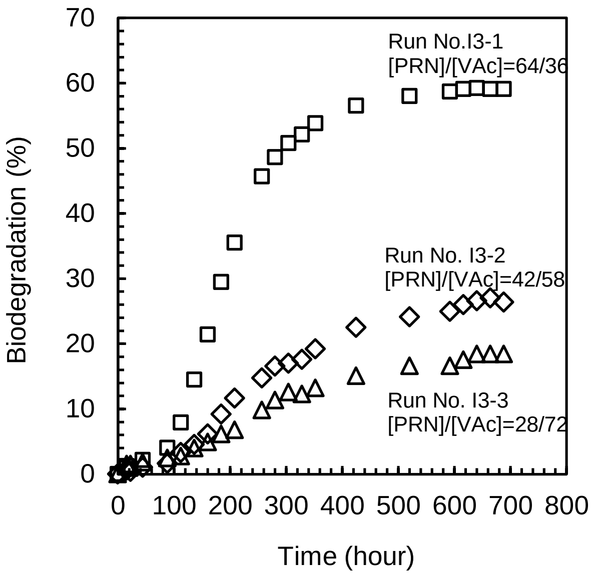
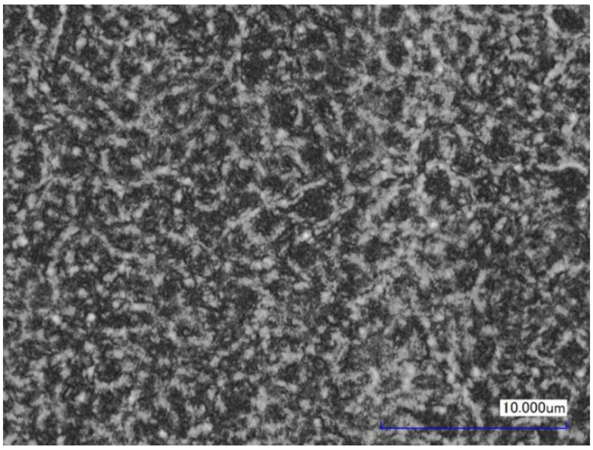


Figure 5-10 Time course of biodegradation for polyamide 4-*block*-poly(vinyl acetate) by an activated sludge.

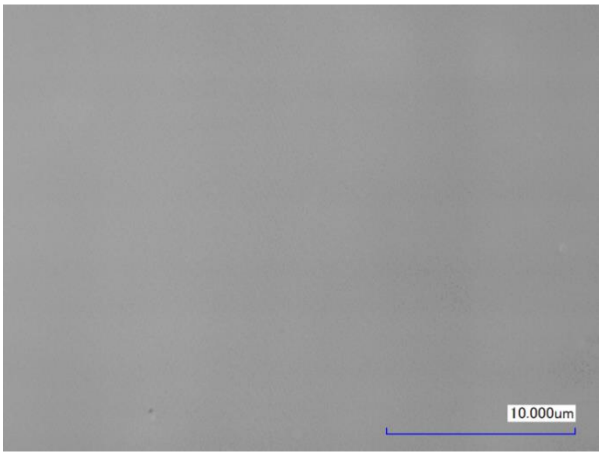
Morphology

The laser microscopic observation of the morphology of the original material was performed by preparing thin films by coating a 2,2,2-trifluoroethanol solution of the copolymers and homopolymers onto clean glass slides. Figure 5-11 shows the features of the free surfaces of the original PA4, PVAc, and polyamide 4-*block*-poly(vinyl acetate). For PA4, a granite pattern was observed that seems to be based on the crystalline and noncrystalline regions. For PVAc, no observable pattern or structure was found. As for polyamide 4-*block*-poly(vinyl acetate), a cellular wrinkled pattern was observed. From the above observation, it appeared that phase separation occurred for the block copolymers.

polyamide 4



poly(vinyl acetate)



polyamide 4-*block*-poly(vinyl acetate) (Run No. I3-2)

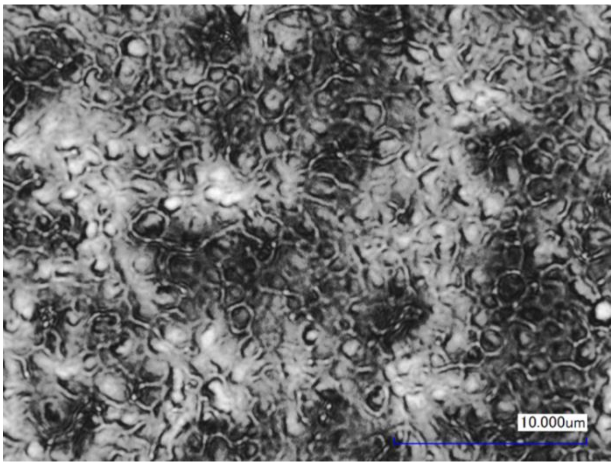


Figure 5-11 Laser micrographs of the free surface of polyamide 4, poly(vinyl acetate), and polyamide 4-*block*-poly(vinyl acetate).

This could be explained by the difference in the solubility parameter (δ) for PA4 and PVAc. According to the data in the literature, the average solubility parameters are 19.74 (δ calculated by using 19.62, 19.13, 20.93, 19.2, 18, 22.61, 19.2, 19.2)14) for PVAc and 23.96 (δ calculated by using 23.9, 24.02)15) for PA4, respectively. The difference between the solubility parameters of these two polymers is large ($\Delta\delta$=4.22). Furthermore, the intermolecular interaction between the two polymers is not strong because of the difficulty in forming mutual hydrogen bonds, and therefore, PVAc is not miscible with PA4. As the film was gradually formed and the disordered state was transformed into an ordered state, phase separation occurred due to immiscibility. The width of the wrinkles and the diameter of the cellular pattern were ca. 0.2 and 2 mm, respectively. The origin of the wrinkles and cellular pattern is not apparent but may be related to microphase separation rather than macrophase separation. This is because the pattern size order of macrophase separation is much more than mm order (>>mm).9,11) A possible interpretation of wrinkle formation on the free surface is the occurrence of shrinkage of the microphase separation structure of the film, presumably caused by the drying of the film.

5.4 Conclusions

Polyamide 4-*block*-poly(vinyl acetate)s were readily synthesized by using azo-PA4, which was prepared by a simple novel method. The composition and *M*w of the block copolymers, namely the content and degree of polymerization of the VAc unit, could be controlled by adjusting the feed ratio of the VAc monomers. The melting points of polyamide 4-*block*-poly(vinyl acetate)s originated from PA4 blocks and their heats of fusion varied linearly with the PA4 content of the block copolymers. The mechanical properties of the block copolymers showed continuous dependence on the composition. The tensile strength increased as the PA4 block content increased and the elongation at break increased with increasing PVAc block content. The biodegradation of polyamide 4-*block*-poly(vinyl acetate)s was monotonically dependent on the composition, and the percent degree of biodegradation decreased as the PVAc block content increased. Microscopic observation of the surface of the polyamide 4-*block*-poly(vinyl acetate) film showed that the morphology of the block copolymer film was quite different from that of both the PA4 and PVAc

5.5 References

1) Y. Yamashita, Y. Murase, K. Ito; *J. Polym. Sci. Polym. Chem. Ed* **1973**, *11*, 435.

2) J. Stehlicek, J. Sebanda; *Eur. Polym. J.* **1977**, *13*, 949.

3) J. Stehlicek, J. Sebanda; *J. Eur. Polym. J.* **1977**, *13*, 955.

4) T. Hirano, R. Amano, T. Fuji, K. Onimura, H. Tsutsumi, T. Oishi; *Polym. J.* **1999**, *31*, 864.

5) M. K. Lindemann; in *Polymer Handbook*, *4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grulke, Editos; Wiley: New York, **1999**; Section V, p 80.

6) R. L. Miller; in *Polymer Handbook*, *4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grulke, Editors; Wiley: New York, **1999**; Section VI, p 33.

7) E. A. Grulke; in *Polymer Handbook, 4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grulke, Editors; Wiley: New York, **1999**; Section VII, p 675.

8) E. B. Bradford, L. D. McKeever; *Prog. Polym. Sci.* **1971**, *3*, 109.

9) F. S. Bates; *Science* **1991**, *251*, 898.

10) T. Smart, H. Lomas, M. Massignari, M. V. Flores-Merino, L. R. Perez,G. Battaglia; *Nanotoday* **2008**, *3*, 38.

11) M. Ramanathan, S. B. Darling; *Prog. Polym. Sci.* **2011**, *36*, 793.

12) O. Nuyken, R. Weidner; *Adv. Polym. Sci.* **1986**, *73*/*74*, 145.

13) I. M. Campbell; in *Introduction to Synthetic Polymers*, *2nd ed.*; Oxford: New York, **2000**; p 195.

14) E. A. Grulke; in *Polymer Handbook*, *4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grullke, Editors; Wiley: New York, **1999**; Section VII, p 705.

15) E. A. Grulke; in *Polymer Handbook*, *4th ed.*; J. Brandrup, E. H. Immergut, E. A. Grullke, Editors; Wiley: New York, **1999**; Section VII, p 709.

Summary

This thesis presented the investigation of synthesis, properties, and biodegradation of aliphatic polyamides: composing unit of polyamide 6, polyamide 3, and polyamide 4. The aliphatic polyamides in this study demonstrated some attractive features due to amide linkage. The amide linkage was utilized in two standpoints: utilization of amide linkage incorporated into other polymer backbone and utilization of only amide linkage.

Utilization of amide linkage incorporated into other polymer backbone corresponds to the copolyesteramides in this study. The novel copolyesteramides: poly[L-lactic acid-*co*-(ε-caprolactam)] containing polyamide 6 unit and poly[acryl amide-*co*-(ε-caprolactone)] containing polyamide 3 unit were synthesized by using the new synthetic technique. With the commercial available polymers in this study's object, it is known that low biodegradability for poly(L-lactic acid), high hydrophobicity for poly(ε-caprolactone). The poly[L-lactic acid-*co*-(ε-caprolactam)] showed relatively high biodegradability in the standard activated sludge, regardless of the low biodegradability constituent: poly(L-lactic acid) and polyamide 6. The poly[acryl amide-*co*-(ε-caprolactone)] showed hydrolizability depending on amide linkage content for non-enzymatic hydrolysis nevertheless poly(ε-caprolactone) had difficulty for hydrolysis under the employing experimental conditions. The copolyesteramide also showed enzymatic hydrolizability for lipase and biodegradability for the activated sludge, regardless of the low enzymatic hydrolizability and biodegradability constituent: polyamide 3. The introducing amide linkage into their polymer backbone by copolymerization could be improved biodegradability or hydrolizability. Introducing amide linkage into the object aliphatic polyester had satisfactory effect on controlling of biodegradation, whereas the improvement of thermal and mechanical properties could not be achieved. With making use of their biodegradation and property, the copolyesteramides developed are thought to be applicable to a biodegradable plasticizer. The achievement of the improvement for the biodegradability and hydrophilicity is considered to be significant in these industrially produced polymers.

On the other hand, utilization of only amide linkage corresponds to the polyamide 4 in this study. Modifying property and providing functionality for polyamide 4 were attempted with introducing the initiator's structure or functional group into polymer chain by making use of polymerization mechanism. For modifying property, the branched polyamide 4 was synthesized by ring-opening polymerization of 2-pyrrolidone with activated monomer mechanism. The melting point depended on the molecular weight and exhibited positive

molecular weight dependence. The molecular weight of ca. 40000 $g \cdot mol^{-1}$ was necessary to achieve high melting point of 265°C. The tensile strength for the branched polyamide 4 was higher than that for the linear polyamide 4 with same extent of molecular weight. The introducing branched structure achieved toughening of polyamide 4. The branched polyamide 4 readily biodegraded by a standard activated sludge in a similar manner as linear polyamide 4. The nitrogen component of the polyamide 4 was finally metabolized to nitrate ion. For providing functionality, the polyamide 4 containing azo group (azo-PA4) was synthesized by ring-opening polymerization of 2-pyrrolidone with activated monomer mechanism also. The azo-PA4 had initiation activity for radical polymerization of a variety of vinyl monomers (e.g. styrene, methyl methacrylate, vinyl acetate, etc.). The product for styrene/azo-PA4 polymerization system was identified as polyamide 4-*block*-polystyrene. In particular, radical polymerization of vinyl acetate using azo-PA4 and the product polyamide 4-*block*-poly(vinyl acetate) was examined in some detail. The melting point of the block copolymer was depended on the molecular weight of polyamide 4 chain. The heat of fusion of the block copolymer decreased linearly with increasing vinyl acetate unit content of polymer composition. The tensile strength decreased linearly with increasing vinyl acetate unit content of polymer composition, while the elongation at break increased linearly. The biodegradation% by the standard activated sludge depended on polymer composition, which was decreased with increasing vinyl acetate unit content. The block copolymer's thin film showed a cellular wrinkled pattern. It was speculated that micro phase separation in the film occurred. Unlike simple linear polymer chain, the introducing branching structure or azo group into the backbone has considerable promise as modifying properties or providing functionality to the polyamide 4. Thus the object polyamide 4 has several attractive features: biodegradability, availability of bio-based monomer, excellent physical properties, and facility of polymer structure design. The use of polyamide 4 will be possible in future application for biodegradable engineering plastics.

The study in this thesis demonstrated the usefulness for amide linkage utilization in a field of common biodegradable polymers. The utilization of polyamide 6 and polyamide 3 units exhibited the controlling of biodegradation in spite of their less biodegradation. The utilization of polyamide 4 unit exhibited possibility for a new biodegradable plastic. The aliphatic polyamides developed in this thesis have valuable aspects: controllable biodegradability, improved property and functionalization, and would be expected as a new material group in the common biodegradable plastics.

List of Publications

1. Synthesis of a new biodegradable copolyesteramide: poly(L-lactic acid-*co*-ε-caprolactam)
   Norioki Kawasaki, Atsuyoshi Nakayama, Yasukatsu Maeda, Kazuko Hayashi, Noboru Yamamoto, Sei-ichi Aiba
   Macromolecular Chemistry and Physics, **1998**, *199*, 2445-2451.

2. Studies on poly[acrylamide-*co*-(ε-caprolactone)]: synthesis,characterization and biodegradability
   Norioki Kawasaki, Atsuyoshi Nakayama, Takashi Higashi, Yasukatsu Maeda, Noboru Yamamoto, Sei-ichi Aiba
   Macromolecular Chemistry and Physics, **2001**, *202*, 2231-2238.

3. Synthesis, thermal and mechanical properties and biodegradation of branched polyamide 4
   Norioki Kawasaki, Atsuyoshi Nakayama, Naoko Yamano, Sahori Takeda, Yoshikazu Kawata, Noboru Yamamoto, Sei-ichi Aiba
   Polymer, **2005**, *46*, 9987-9993.

4. Synthesis of an azo macromolecular initiator composed of polyamide4 and its initiation activity for radical polymerization of vinyl monomers
   Norioki Kawasaki, Naoko Yamano, Sahori Takeda, Hisanori Ando, Atsuyoshi Nakayama
   Journal of Applied Polymer Science, **2012**, *126*, E425-E432.

5. Polyamide4-*block*-poly(vinyl acetate) via a polyamide 4 azo macromolecular initiator: thermal and mechanical behavior, biodegradation, and morphology
   Norioki Kawasaki, Naoko Yamano, Atsuyoshi Nakayama
   Journal of Applied Polymer Science, **2015**, *132*, 42466 (1-10).

Related Publications

1. Biodegradability of random and block copolymers of β-methyl-δ-valerolactone with α-pyrrolidone
   Norioki Kawasaki, Atsuyoshi Nakayama, Noboru Yamamoto, Sei-ichi Aiba
   Journal of Molecular Science (中国化学会分子科学学报), **1999**, *15-4 supplement*, 293-294.

雑誌

2. 「生分解性高分子材料を使用したケミカルリサイクルシステム」
   川崎典起, 中山敦好, 山本襄, 相羽誠一
   コンバーテック, **2001**, 29, 13-15.

3. 「バイオマスプラスチックポリアミド４」
   川崎典起, 山野尚子, 中山敦好
   工業材料, **2010**, 58, 58-59.

4. 「バイオベースポリアミド４の開発　バイオベースポリアミド４の物性と改質例」
   川崎典起, 山野尚子, 中山敦好
   プラスチックス, **2011**, 62, 27-31.

書籍

5. 「第24章　アミノ酸を原料としたバイオベースポリアミド４の開発」
   川崎典起, 中山敦好, 山野尚子, 竹田さほり
   植物由来プラスチックの高機能化とリサイクル技術, **2007**, 212-225.

特許

6. 特許3453600号（日本）2003年7月25日
発明人：川崎典起, 中山敦好, 山本襄, 相羽誠一
発明名称：特殊構造を有する２－ピロリドン重合体およびその製造方法

7. 特許3699995号（日本）2005年7月22日
発明人：川崎典起, 山本襄, 中山敦好、相羽誠一, 村木永之介, 指輪仁之
発明名称：ポリアミド４誘導体及びその製造法

8. 特許4150791号（日本）2008年7月11日
発明人：川崎典起, 中山敦好, 相羽誠一
発明名称：ポリアミド４誘導体、ポリアミド４を含むブロック共重合体及びその製造法

9. 特許5283058号（日本）2013年6月7日
発明人：川崎典起, 中山敦好, 山本襄、相羽誠一
発明名称：分岐構造を導入したポリアミド４共重合体及びその製造方法

10. 特許5729408号（日本）2015年4月17日
発明人：川崎典起, 中山敦好, 山本襄, 相羽誠一
発明名称：分岐構造を導入したポリアミド４共重合体及びその製造方法

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