

Synthesis of Novel Block Copolymers Containing Polyamide4 Segments and Control of Their Biodegradability

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ABSTRACT: Different novel copolymers, ABA-type block copolymers composed of polyamide4 as outer segments and polyoxyethylene as an inner segment and AB- and ABA-type block copolyamides containing polyamide4 and another hydrophilic polyamide derived from a bicyclic lactam, were synthesized by the anionic ring-opening polymerization of 2-pyrrolidone using the corresponding acyllactam-type macromolecular activators. The degradation rate of

both block copolymers containing polyamide4 segments in a composted soil was found to decrease with increasing content of the second segments, although they were also hydrophilic and/or biodegradable. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3492–3498, 2004

Key words: biodegradable; block copolymers; polyamides; nylon; crystallization

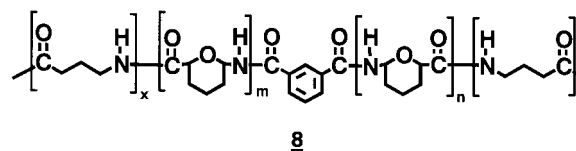
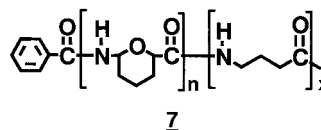
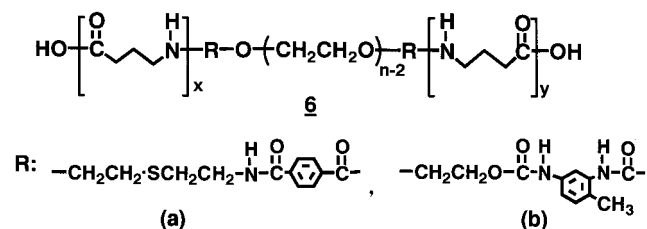
INTRODUCTION

Most artificial synthetic polymers are essentially hard to decompose under natural conditions. In particular the degradation of synthetic polyamides (nylons) is known to be generally slower than that of the corresponding synthetic polyesters through both biological and hydrolytic processes under neutral conditions.^{1–4} Mainly their high symmetrical molecular structures and strong hydrogen bonds in highly ordered crystalline morphology may bring about the high resistance to the degradation of polyamides. Therefore, only a few investigations of the biodegradation of nylons having relatively simple repeating units have been reported to date.^{5–9}

Recently polyamide4 (1) easily obtained by the anionic polymerization of 2-pyrrolidone (2) has been reported to degrade in composted soils and activated sludge.^{10–13} In the blend films composed of polyamide4 and polyamide6, only the polyamide4 portion degraded in the composted soils.¹³

Polyoxyethylene glycol (3) with narrow molecular weight distribution is commercially available and known to be soluble in water and to be biodegradable.^{14,15} A bicyclic lactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (4), can be polymerized anionically to give a hydrophilic polyamide (polyBOL, 5) under mild conditions, such as at room temperature in dimethyl

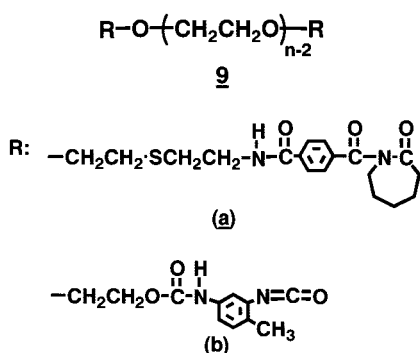
sulfoxide.^{16,17} PolyBOL (5) degraded in phosphate buffer solution (pH 7.5), although the degradation rate was not as high.¹⁰



Since microorganisms have a tendency to attack hydrophilic polymeric materials, the composites of polyamide4 (1) with these hydrophilic polymers (3 and 5) are expected to have significant influence upon their biodegradability. In the present work, different block copolymers of polyamide4 with polyoxyethylene and hydrophilic polyamide segments (6, 7, and 8, respectively) were synthesized and their degradability

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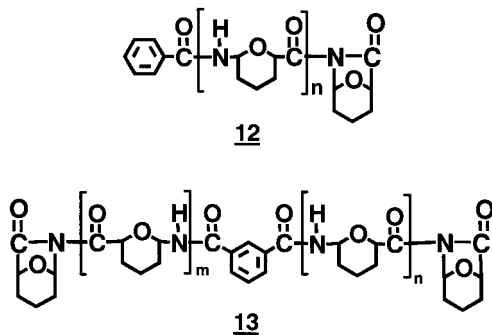
was compared with that of homopolyamide4 in the compost soil.



RESULTS AND DISCUSSION

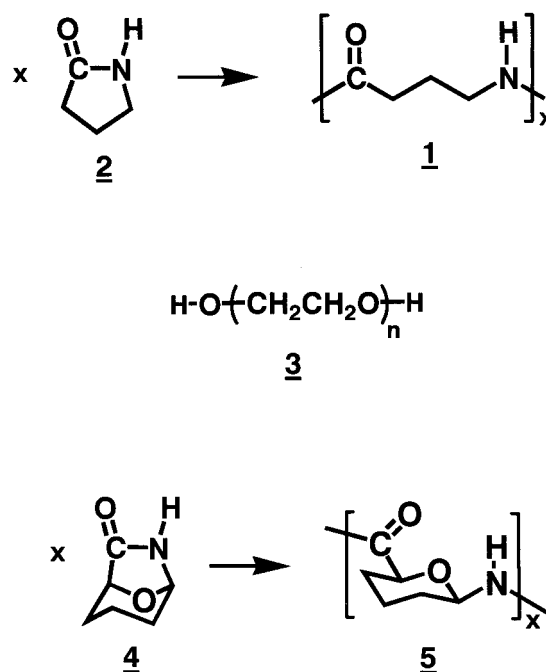
Synthesis of polyamide4-polyoxyethylene block copolymers (6)

The ABA-type block copolymers (6) composed of polyamide4 as outer segments and polyoxyethylene (M_n , 3.6×10^3 and 2.1×10^4) as an inner segment were prepared by the anionic polymerization of 2-pyrrolidone (2) using the polyoxyethylene carrying acylactam or isocyanate groups at both chain ends (9a and 9b) as macromolecular activators.



As shown in Scheme 2, 9a was prepared from commercially available polyoxyethylene glycol (3) with narrow molecular weight distribution according to the literature.¹⁸ The functionality defined as the average number of the functional groups per polyoxyethylene chain was estimated by spectroscopic analyses as described in the experimental section. Large excess of the reagents, mild conditions such a low temperature, and long reaction time were preferable for the quantitative conversion of each functional group at the chain ends.

The isocyanate-terminated polyoxyethylene (9b) of different molecular weight was also prepared by the reaction of 3 with an excess of 2,4-tolylene diisocyanate in a high vacuum line (Scheme 3).¹⁹ The average number of the isocyanate group introduced in a polyoxyethylene chain was determined from the content of the terminal biscarbamic acid ester group, de-



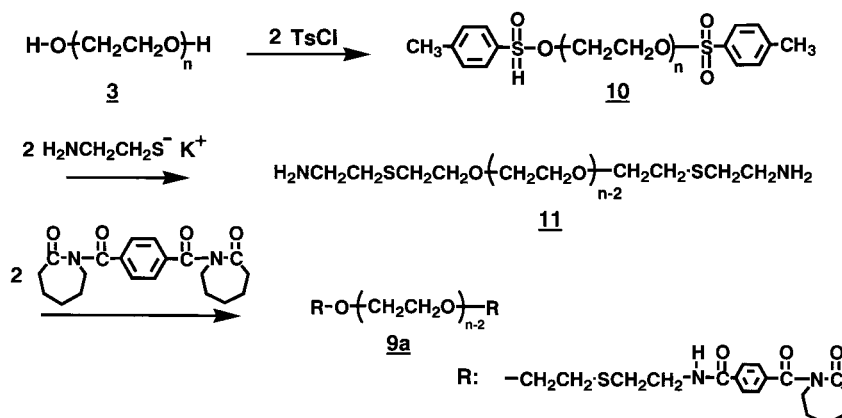
Scheme 1

terminated to be higher than 1.9 by UV spectroscopy after the treatment with ethanol.

Since the thermodynamic polymerizability of 2-pyrrolidone (2) is not so high, the polymerization is preferable in bulk but not in solution.^{17,20} Fortunately the resulting polyoxyethylenes (9a and 9b) were soluble in 2 and convenient as macromolecular activators on the anionic polymerization of neat 2. They were dried by azeotropy with tetrahydrofuran in a high vacuum line before use, because they were hygroscopic.

The potassium *t*-butoxide-catalyzed anionic polymerization of 2 with the use of 9a with different molecular weights as activators proceeded in bulk at 30°C in a high vacuum line (see Table I). The reaction mixture became viscous and turbid after 5~10 min and then solidified. The conversion in the polymerization using 9a, of which the molecular weight was 2.1×10^4 , as an activator was lower than that in the homopolymerization using *N*-benzoyl-2-pyrrolidone. In the former polymerization, the resulting polymer may deposit from the polymerization system in relatively low conversion because of the low solubility in 2.

The potassium pyrrolidonate-catalyzed polymerization of 2 using 9b also proceeded in a similar way. Taking account of the results on the homopolymerization of 2, the influence of the catalysts and the end groups in the macromolecular activators upon the block copolymerization is inferred to be not so significant. However, all the procedures, including the preparation of 9b, its purification, and the polymerization of 2 using 9b as an activator, had been carried out in a high vacuum line, because of high sensitivity

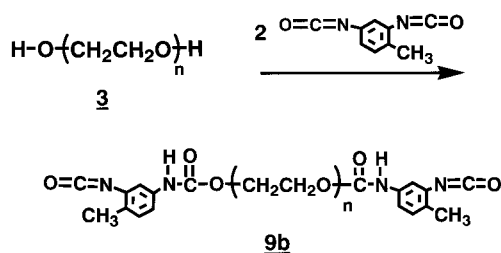


Scheme 2

of the isocyanate groups in **9b** to humidity.¹⁹ Therefore the acyllactam-type activator, **9a**, which can be easily handled in air, is more useful as a macromolecular activator for the preparation of the polyamide4-polyoxyethylene block copolymer (**6**).

The resulting block copolymer (**6**) was insoluble in water, although it contained the water-soluble polyoxyethylene segment. On the other hand **6** was soluble in *m*-cresol and 2,2,2-trifluoroethanol, which were common solvents for homopolyamide4 (**1**). In addition **6** was found to be soluble in *N,N*-dimethylacetamide (DMAC) mixed with 5 wt % of lithium chloride. Therefore the average molecular weight of **6** was estimated by gel permeation chromatography using the DMAC-lithium chloride mixture as an eluent to be 1.4 to 6.2×10^4 . The chromatography suggested that no homopolyoxyethylene derivative was contained in the isolated polymer.

The ¹H-NMR spectrum of the copolymer was recorded in 2,2,2-trifluoroethanol, in which three kinds of methylene signals (δ , 3.26, 2.26, and 1.82 ppm), an amide signal (δ , 7.21 ppm) due to the 2-pyrrolidone unit, and a methylene signal (δ , 3.68 ppm) due to the polyoxyethylene unit were observed. The copolymer composition was determined from the intensity ratio of these signals. The ¹³C-NMR spectrum in Figure 1 also shows that the copolymer contains both repeating units.



Scheme 3

Synthesis of block copolyamides composed of polyamide4 and bicyclic lactam-derived polyamide segments (**7** and **8**)

The anionic polymerization of the bicyclic lactam (**4**) proceeds under mild conditions in a homogeneous phase, which is desirable for suppressing possible side reactions, to give the polyamide with an acyllactam-type growable chain end (**12**).^{16,17} In this work, the polyamide with acyllactam groups at both chain ends (**13**) was also prepared in the anionic polymerization of **4** with the use of *N,N'*-isophthaloylbis-(8-oxa-6-azabicyclo[3.2.1]octan-7-one) as an activator.

The polyamide-type activators (**12** and **13**) were soluble in 2-pyrrolidone (**2**) and conveniently provided for its anionic polymerization using potassium *t*-butoxide as a catalyst. The polymerization proceeded in a similar way with the potassium pyrrolidonate-catalyzed polymerization described in our previous article.¹⁶

The resulting block polyamides (**7** and **8**) were soluble not only in common solvents for polyamides such as *m*-cresol and 2,2,2-trifluoroethanol, but also in the mixture of aprotic polar solvents with lithium halides such as DMAC-LiCl (5 wt %), although both homopolyamides were insoluble in the mixed solvent.

Degradation test of block copolymers in a composted soil

The films of block copolymers (**6** and **7**) were obtained by casting from their 2,2,2-trifluoroethanol solution and buried in a composted soil gathered from the same university farm as in our previous work.^{10,13}

As shown in Figure 2, the weight of the film of the polyamide4-polyoxyethylene block copolymer decreased during the burial test in a similar way as that of the homopolyamide4. However, the former degradation rate was significantly lower than that of the homopolyamide4, which suggested that content of

TABLE I
Anionic Ring-Opening Polymerization of 2-Pyrrolidone with the Use of Polyoxyethylene Activators at 30°C^a

2-Pyrrolidone (g)	Polyoxyethylene activator		Catalyst	Time (h)	Conversion (%)	Weight fraction of polyamide	<i>E</i> ^b	<i>M_n</i> ^c × 10 ⁻⁴	<i>M_w</i> / <i>M_n</i> ^c	
	End Group	<i>M_n</i> (mol %)								
6.4	9a	Acylactam	3,600 (0.1)	<i>t</i> BuOK	24	47	0.92	0.88	1.8	1.45
6.5	9a	Acylactam	3,600 (0.1)	<i>t</i> BuOK	72	61	0.92	0.90	6.2	1.37
10.8	9a	Acylactam	21,000 (0.02)	<i>t</i> BuOK	24	10	0.70	0.31	3.8	1.47
8.8	9b	Isocyanate	3,500 (0.26)	K-Pydm	24	84	0.90	0.91	3.7	1.41
16.2	9b	Isocyanate	22,000 (0.02)	K-Pydm	72	16	0.89	0.35	4.6	1.38
5.9	— ^d	Acylactam	189 (0.1)	<i>t</i> BuOK	24	41	1.00	—	8.3 ^e	—
10.4	— ^d	Acylactam	189 (0.1)	K-Pydm	24	37	1.00	—	7.5 ^e	—

^a Catalyst, 2 mol %/monomer; temperature, 30°C.

^b Efficiency of block copolymerization estimated from the weight ratio of polyoxyethylene in copolymer to activators fed initially.

^c By GPC in DMAC with 5 wt % of lithium chloride.

^d *N*-Benzoyl-2-pyrrolidone.

^e Estimated from the intrinsic viscosity in *m*-cresol at 25°C.²¹

only 10 wt % of the polyoxyethylene segment decreased degradation rate seriously. In addition the degradation rate seems to decrease with increasing the molecular weight of the polyoxyethylene segment.

Taking account of high solubility of polyoxyethylene in water, we expected that the resulting block copolymer (**6**) was more hygroscopic and degraded faster than the homopolyamide4 (**1**) before the experiments. However the degradation rate determined in the experiments was found to contradict the above hypothesis. Therefore the moisture sorption isotherms of **6** with different molecular weights were examined at 25°C and compared with that of homopolyamide4 (**1**). As summarized in Figure 3, the amount of water adsorbed on **6** was much lower than that of **1**, which also suggested that the above hypothesis should be revised.

The degradation rate of the AB-type block copolyamide (**7**) was also lower than that of homopolyamide4 (**1**) as shown in Figure 4. Such results indicate

that about 10 wt % of the polyBOL segment contained in the block copolymer decreased the degradation rate.

In our previous work,¹⁶ the moisture adsorption of similar AB-type block copolyamides (**7**) was examined and the amount of water adsorbed on the block copolyamides was unexpectedly lower than not only that on homopolyamide4 (**1**) but also that on polyBOL at high relative humidity. In addition, both films of homopolyamide-4 and the AB-type block copolyamides (**7**) obtained by casting from their 2,2,2-trifluoroethanol solution were examined to be amorphous, and the crystallinity of the latter was proved to increase during the adsorption of water from the X-ray diffraction and thermal analyses.¹⁶ Since the glass transition point of polyamides is known to decrease below room temperature with the adsorption of water, the high hygroscopicity of the polyBOL domain is inferred to decrease its glass transition point. The high mobility of the water-adsorbed polyBOL domain distributed into the polyamide-4 domain may enhance the rearrangement and crystallization of the polyamide-4 segment.

Consequently the composites of **1** with small amount of hygroscopic segments such as polyoxyethylene and polyBOL by the block copolymerization may provide a convenient method for control of the degradation rate of **1** in a composted soil.

EXPERIMENTAL

Reagents

Commercially available 2-pyrrolidone (**2**) was purified through the recrystallization of its monohydrate from ethyl acetate.²² The monohydrate was pyrolyzed and the resulting water was removed by the distillation and the subsequent azeotropy with xylene. The residual 2-pyrrolidone was distilled under reduced pres-

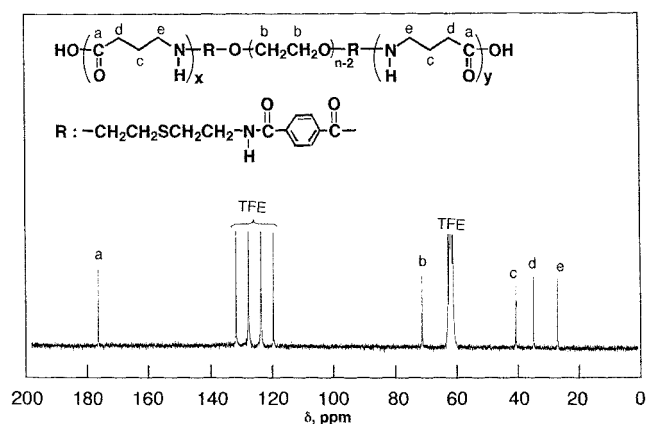


Figure 1 ¹³C-NMR spectrum of polyamide4-polyoxyethylene block copolymer (solvent, 2,2,2-trifluoroethanol, D₂O lock, tetramethylsilane, room temperature, 67.8 MHz).

TABLE II
Anionic Ring-Opening Polymerization of 2-Pyrrolidone with the Use of Hydrophilic Polyamide Having Acyllactam Groups at One or Both Chain Ends as an Activator at 30°C^a

2-Pyrrolidone (g)	Polyamide activator		Time (h)	Conversion (%)	Weight fraction of polyamide4	$M_n \times 10^{-4}$
	M_n	(mol %)				
14.1	12	3,600	72	51	0.92	4.7
16.2	12	8,900	72	62	0.85	6.2
12.4	13	7,300	24	47	0.90	4.7

^a Catalyst, potassium *t*-butoxide, 2 mol %/monomer; temperature, 30°C.

sure, and the main fraction was dried over 4A molecular sieves for several days in a high vacuum line at least three times, followed by redistillation *in vacuo*. A bicyclic lactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (4), was prepared by the same method as described in the previous article.²³ To synthesize *N,N'*-isophthaloylbis(8-oxa-6-azabicyclo[3.2.1]octan-7-one), a mixture of 8.0 g of isophthaloyl dichloride with 15 mL of benzene was added dropwise to a solution of 10.0 g of 4 in a mixture of 9.3 mL of pyridine with 30 mL of benzene with stirring at room temperature for 1 day. The reaction mixture was poured into 300 mL of 2% hydrochloric acid aqueous solution and provided for the extraction with 300 mL of chloroform for three times. After the evaporation of the solvent, the crude product was recrystallized from a *n*-hexane-benzene mixed solvent: yield, 2.6 g(17%); mp, 173°C. *N*-Benzoyl-2-pyrrolidone,^{24,25} *N*-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one,²⁴ and *N,N'*-terephthaloylbis(ϵ -caprolactam)^{16,26} were prepared

from the corresponding lactams and acid chlorides by a similar method. Toluene-2,4-diisocyanate was distilled *in vacuo*, after being kept in a sealed flask for a week. Dimethyl sulfoxide, benzene, diethyl ether, and dichloromethane were distilled under reduced or atmospheric pressure after drying over calcium hydride, sodium metal, sodium metal, and calcium hydride, respectively. Commercially available potassium *t*-butoxide was divided into ampoules equipped with breakable seals in a dry box filled with dry nitrogen and kept *in vacuo* until use. Potassium pyrrolidonate was prepared according to the literature,²⁷ and stored *in vacuo* until use.

Conversion of hydroxyl groups in polyoxyethylene (3) to tosyl groups

According to the literature,²⁸ a solution of 7.0 g (0.35 mmol) of polyoxyethylene glycol (3, M_n : 2.0×10^4) in

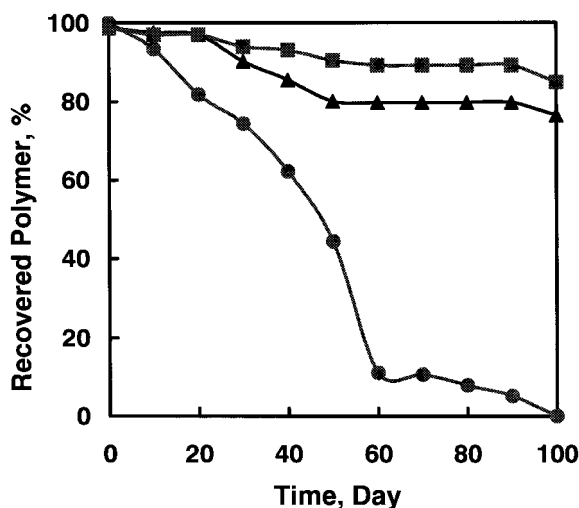


Figure 2 Change in weight of the films of the polymers after the burial test in the composted soil (relative humidity 80%, 25°C). ●, Polyamide4 (M_n , 4.7×10^4). ▲, Polyamide4-polyoxyethylene block copolymer (M_n of polyoxyethylene segment, 3.5×10^3 ; weight fraction of polyamide4 segment, 0.90). ■, Polyamide4-polyoxyethylene block copolymer (M_n of polyoxyethylene segment, 2.2×10^4 ; weight fraction of polyamide4 segment, 0.89).

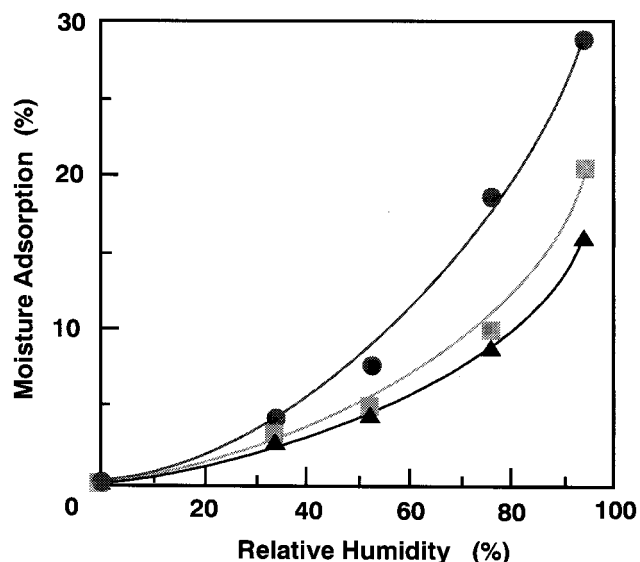


Figure 3 Moisture adsorption of various polymers at 25°C. ●, Polyamide4 (M_n , 4.7×10^4). ▲, Polyamide4-polyoxyethylene block copolymer (M_n of polyoxyethylene segment, 3.5×10^3 ; weight fraction of polyamide4 segment, 0.90). ■, Polyamide4-polyoxyethylene block copolymer (M_n of polyoxyethylene segment, 2.2×10^4 ; weight fraction of polyamide4 segment, 0.89).

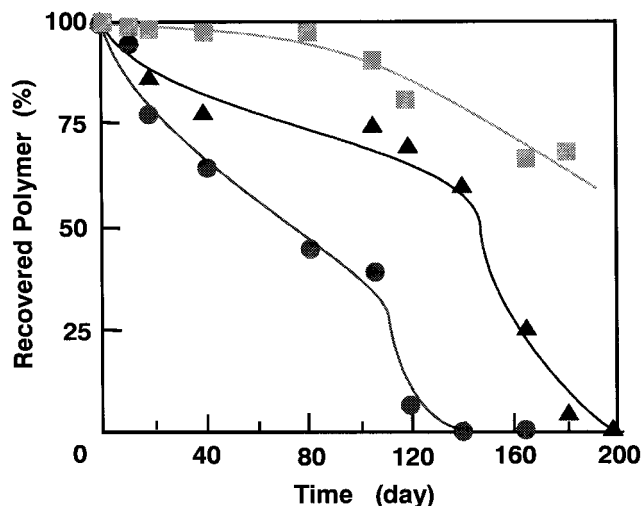


Figure 4 Change in weight of the films of the polymers after the burial test in the composted soil (relative humidity 80%, 25°C). ●, Polyamide4 (M_n , 4.7×10^4). ▲, Polyamide4-polyBOL block copolyamide (M_n of PolyBOL segment, 3.6×10^3 ; weight fraction of polyamide4 segment, 0.92). ■, Polyamide4-polyBOL block copolymer (M_n of polyBOL segment, 8.9×10^4 ; weight fraction of polyamide4 segment, 0.85).

35 mL of dichloromethane was added dropwise to a solution of 4.0 g (21.1 mmol) of tosyl chloride in a mixed solvent of 2.3 mL of pyridine with 35 mL of dichloromethane under dry nitrogen, and the reaction mixture was kept at 4°C with stirring for 8 days. Dichloromethane (9 mL) then was added to the reaction mixture, and 400 mL of diethyl ether was poured into the mixture, which was kept at 4°C overnight. Colorless precipitate then was collected by filtration, dissolved in 100 mL of ethanol in a heating bath, and reprecipitated in a cooling bath. The purified powder (10) was dried *in vacuo*: yield, 5.6 g (78%). The functionality (the number of tosyl groups per polyoxyethylene chain) was estimated to be 1.95 by using the extinction coefficient (ϵ_{\max} , 12,600) at the maximum wave length of *p*-methoxyethyl-*p*-toluenesulfonate (225 nm) in methanol.¹⁸

Preparation of amine-telechelated polyoxyethylene (11)

Potassium *t*-butoxide (0.69 g, 6.2 mmol) and 2-mercaptoethyl-ammonium chloride (0.41 g, 3.6 mmol) were dissolved in 42 mL of *t*-butanol-benzene (2 : 1 v/v) mixed solvent under dry nitrogen, and the solution was refluxed with stirring until it became turbid.²⁸ After a solution of 3.0 g of tosyl-telechelated polyoxyethylene (7) in 14 mL of benzene was added dropwise to the system, the mixture was refluxed for 5 h and subsequently stirred at room temperature for 20 h. The resulting precipitate was

removed by centrifugation and the supernatant solution was condensed under reduced pressure. The residue was dissolved in hot ethanol and the solution was kept at room temperature to obtain the yellowish precipitate, which was purified by reprecipitation in a dichloromethane-diethyl ether system. The resulting colorless powder was dried *in vacuo*: yield of amine-telechelated polyoxyethylene (11), 1.87 g (62%).

Preparation of polyoxyethylene telechelated with acyllactam groups (9a)

Under dry nitrogen, a solution of 11 (1.62 g, 0.08 mmol) in 35 mL of benzene was added slowly to a hot solution of *N,N'*-terephthaloylbis(ϵ -caprolactam) (2.22 g, 6.5 mmol) in 75 mL of benzene and refluxed for 48 h. After the reaction mixture was cooled, the precipitate was filtered out. The condensed filtrate was poured into 150 mL of deionized water and stirred for 1 h. The precipitate was removed by centrifugation and the supernatant was lyophilized. The resulting yellowish powder was purified by reprecipitation in a benzene (20 mL)-diethyl ether (1 L) system and the colorless polymer (9a) was dried *in vacuo*: yield, 1.46 g (69%). The functionality of the acyllactam group was estimated to be 1.94 by UV spectroscopy, in which *N*-(*p*-(*n*-butylcarbamoyl)benzoyl)- ϵ -caprolactam was used as a model compound (ϵ_{\max} , 13,600 at 237 nm).¹⁸

Anionic polymerization of 2-pyrrolidone (2) with the use of acyllactam-telechelated polyoxyethylene (9a) as an activator

In a high vacuum line, 0.28 g of 9a was added into a 100-mL round-bottom flask equipped beforehand with breakable ampules containing 2-pyrrolidone (2, 6.4 g) and potassium *t*-butoxide (0.17 g), respectively. After the flask was sealed, 2 was charged into the flask through the crushed breakable seal and 9a was dissolved in 2 with mechanical stirring. Potassium *t*-butoxide was added to the solution with stirring, and the flask was held in a bath controlled at 30°C. After the polymerization, the flask was opened under dry nitrogen, and 0.3 mL of acetic acid was added to the reaction mixture. The content was poured into a large amount of acetone and stirred for 1 day. The resulting colorless polymer was collected by centrifugation, washed with the mixture of acetone with water (5 : 1 v/v), and dried *in vacuo*: yield, 3.0 g (47%).

Soil burial test

The block copolymers (6 and 7) and homopolyamide4 (1) were dissolved in 2,2,2-trifluoroethanol, and the solutions were cast on flat glass plates and dried at room temperature to give corresponding films with

about 50- to 70- μm thickness. The resulting films were immersed and rinsed in deionized water and dried *in vacuo*. Several pieces of polyamide films (1 cm \times 5 cm) were buried in a composted soil, which was gathered from Nagoya University Farm and packed in containers made of polypropylene. The containers were kept in an atmosphere controlled at 80% relative humidity at 25°C. At an appropriate time, the films were recovered from the composted soil and washed with water. After drying *in vacuo*, they were weighed and used for their analyses.

Characterization

^1H - and ^{13}C -NMR spectra were recorded on a JEOL JNM-EX-270 Fourier transform high resolution spectrometer. Gel permeation chromatograms were taken with a JASCO model BIP-1 high-performance liquid chromatograph apparatus using Shodex KF803 and 804 columns (8 ϕ \times 600 mm) in DMAC containing 5 wt % of lithium chloride (flow rate, 0.2 mL/min). A monodisperse polyamide (5) was used as a standard.^{29,30}

Moisture sorption was determined gravimetrically at 25°C. The relative humidity was controlled by saturated aqueous solutions of appropriate inorganic salts.

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