Degradation of Several Polyamides in Soils

INTRODUCTION

Synthetic polyamides (nylons) are generally hard to be decomposed under natural environmental conditions either through biological or hydrolytic processes.[1-4] Their high resistance to degradation is caused mainly by the high symmetry of their molecular structures and strong interchain hydrogen bondings, which result in a highly ordered crystalline morphology. Therefore, several procedures for the weakening of these characteristics, such as the introduction of substituents in their repeating units, chemical modification, and even physical processing, are effective for the increase of their biodegradability.[1-6] However, the degradation of nylons having relatively simple repeating units has been scarcely reported up to date.[7] The present note is concerned with the degradability of three kinds of polyamides (**4**, **5**, and **6**) prepared from 2-pyrrolidone, ϵ-caprolactam, and a bicyclic lactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (**1**, **2**, and **3**, respectively), in several kinds of soils and in a phosphate buffer (see Scheme 1). The bicyclic oxalactam **3** (abbreviated BOL) has both five- and seven-membered lactam rings and its quasi-living anionic polymerization in dimethyl sulfoxide gives a monodisperse and well-defined novel polyamide having a tetrahydropyran ring in the repeating unit.[10-13]

EXPERIMENTAL

Reagents

Commercially available 2-pyrrolidone (**1**) was purified through the recrystallization of its monohydrate.[14] After the pyrolysis of the recrystallized monohydrate, water was removed by distillation from the mixture and subsequent azeotropy with xylene. The residual 2-pyrrolidone was first distilled under reduced pressure, and the main fraction was dried over 4 Å molecular sieves for several days in a high vacuum line twice, followed by redistillation *in vacuo*.

BOL (**3**) was prepared by the procedure reported earlier[12,13] and stored over phosphorus pentoxide *in vacuo* until use. The *N*-benzoyl derivative of **3** was prepared by the same methods as reported in previous articles.[15-17] Potassium pyrrolidonate was obtained as described in the literature.[18] Dimethyl sulfoxide (Me_2SO) was dried over calcium hydride in a high-vacuum line and distilled *in vacuo*. Acetone was distilled after drying over 4 Å molecular sieves.

Poly(ϵ-caprolactam) (**5**) provided by Teijin Co. (Japan) was purified by reprecipitation using 2,2,2-trifluoroethanol and acetone as a solvent and a precipitant, respectively: $[\eta]$, 1.17 dL/g in *m*-cresol at 25°C.

Preparation of Poly(2-pyrrolidone) (4)

All the following polymerization procedures were carried out in a high-vacuum line. Into a 100 mL three-necked, round-bottomed flask was added 28 mg of *N*-benzoyl derivative of **3**, which was subsequently dried *in vacuo* at room temperature for several hours. After the activator was dissolved in 10.4 g of 2-pyrrolidone, 301 mg of potassium pyrrolidonate was added and kept at 30°C for 24 h. The polymerization was terminated with a small amount of water. The resulting gross polymer was ground and immersed in water to remove the unreacted 2-pyrrolidone and the catalyst residue and dried *in vacuo:* Polymer yield, 3.87 g (37%); $[\eta]$, 2.48 dL/g in *m*-cresol at 25°C.

Preparation of PolyBOL (6)

Under dry nitrogen, 20.34 g of BOL, 7.4 mg of the *N*-benzoyl derivative of **3**, and 197 mg of potassium pyrrolidonate were dissolved in 64 g of Me_2SO in an ampule. After sealing, the ampule was kept at 25°C for 2 days. The polymerization mixture was poured into a large amount of deionized water. The resulting colorless polymer was collected by filtration, washed with fresh water several times, and dried *in vacuo:* Yield, 16.6 g (82%); $[\eta]$, 1.70 dL/g in *m*-cresol at 25°C.

Soil Burial Tests

Several pieces of films of polyamides (**4**, **5**, and **6**; weight, 50–65 mg; thickness, 60–70 μm, respectively) were buried in four kinds of soils: soil composted for more than 10 years in Nagoya University Farm (pH 7.5), noncomposted soil from the same farm (pH 5.9), and soil on the campus of Nagoya University (pH 4.5) and its sterilized soil (pH 4.5). They were kept in an atmosphere controlled at 80% relative humidity at 27°C. After an appropriate time, the weights of the recovered polyamides were determined. The molecular weights of the recovered **4** and **5** were estimated from the solution viscosity in 2,2,2-trifluoroethanol at 25°C, and that of **6**, by gel permeation chromatography.

Journal of Applied Polymer Science, Vol. 54, 1579–1583 (1994)

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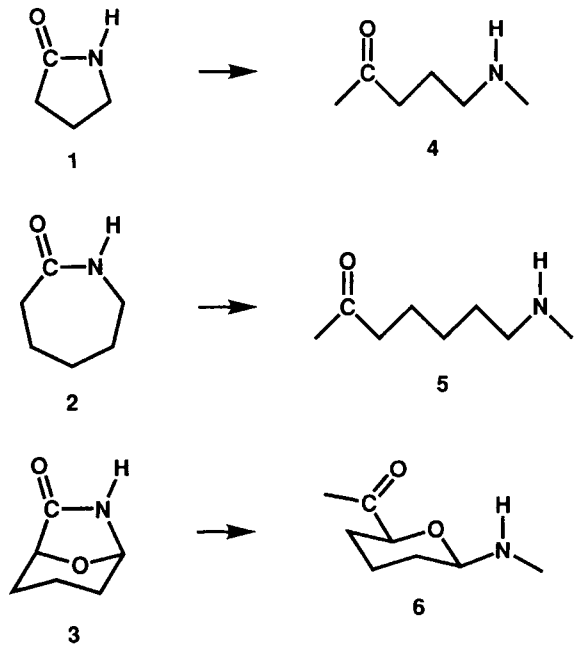

Scheme 1

Hydrolysis Test in a Phosphate Buffer

Each film of polyamide (**4**, **5**, and **6**; weight, 50–65 mg; thickness, 60–70 μm, respectively) was immersed in a phosphate buffer controlled at pH 7.5 in each testing tube and kept at 27°C. The weights and the molecular weights of the recovered polyamides were determined by the same methods as used in the soil burial tests.

Characterization

Gel permeation chromatograms were measured with a JASCO Model BIP-1 high-performance liquid-chromatograph apparatus (column, Shodex KF 803 → 804, 8ϕ × 600 mm; solvent, Me_2SO). PolyBOL of low dispersity[10,11] was used for the standard. Microscopic photographs of the polyamide films were taken with a Carl Zeiss photomicroscope III (magnification, 16 × 1.25 × 10).

RESULTS AND DISCUSSION

The results for the burial tests of polyamide films in the soil composted for more than 10 years (pH 7.5) are shown in Figure 1(A). The weight of the recovered poly(2-pyrrolidone) **4** was found to decrease with the burial time and disappeared within 4 months, although the weights of the other polyamides did not reduce. Figures 2 and 3 show that the apparent change of the film of **4** after the burial tests is conspicuous and there are many pores in the film. In contrast, the shape of the other two polyamide films did not change.

As shown in Figure 1(B), the molecular weight of the recovered **4** was almost the same as that of the original one. Therefore, the degradation of **4** in this soil should have proceeded heterogeneously from the surface of the film. On the other hand, a decrease of the molecular weight of the recovered **6** was observed, although its weight loss was almost negligible during the burial test. In the case of the film of **5**, not only the weight but also the molecular weight did not change in this soil.

Hydrolysis tests of the polyamides (**4**, **5**, and **6**) were

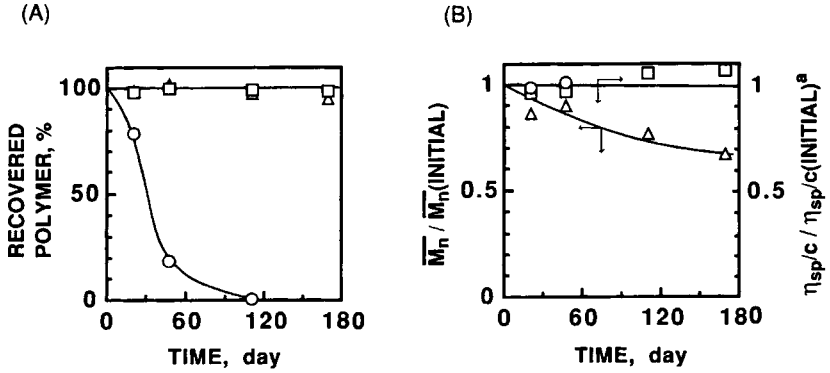

Figure 1 Changes in (A) the weights and (B) the molecular weights of the films of the polyamides (**4**, **5**, and **6**) after the soil burial test (relative humidity, 80%, 27°C). The soil was composted for more than 10 years in the university farm (pH 7.5). Polyamide: (○) **4**; (□) **5**; (△) **6**. (a) Viscosity number in 2,2,2-trifluoroethanol (1 g/100 mL, 25°C).

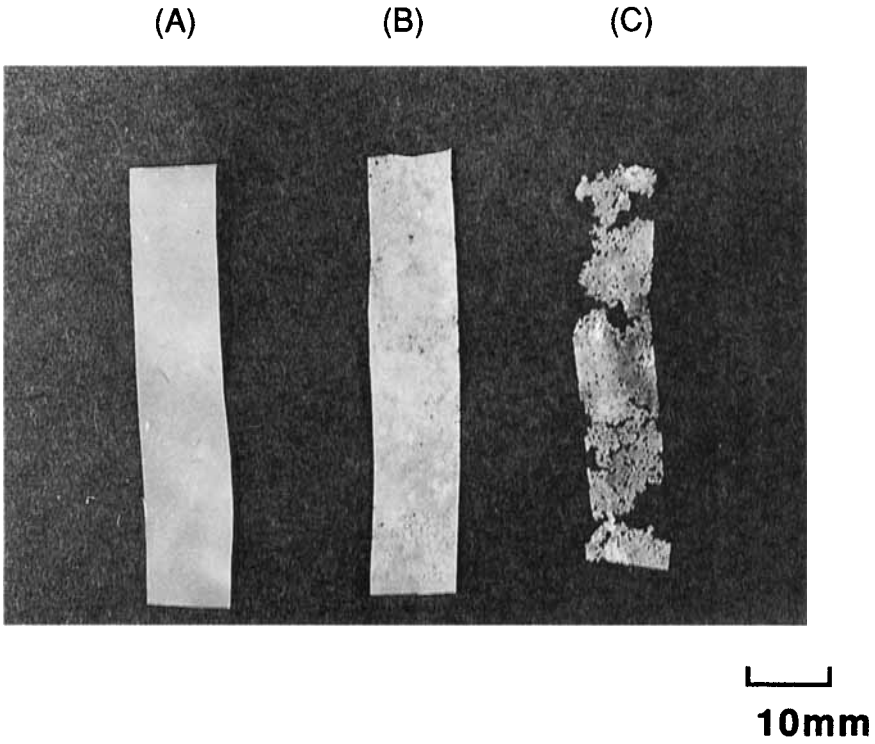

Figure 2 Photographs of the films of polyamide **4** before and after the soil burial test as shown in Figure 1: (A) 0 days; (B) 21 days; (C) 48 days.

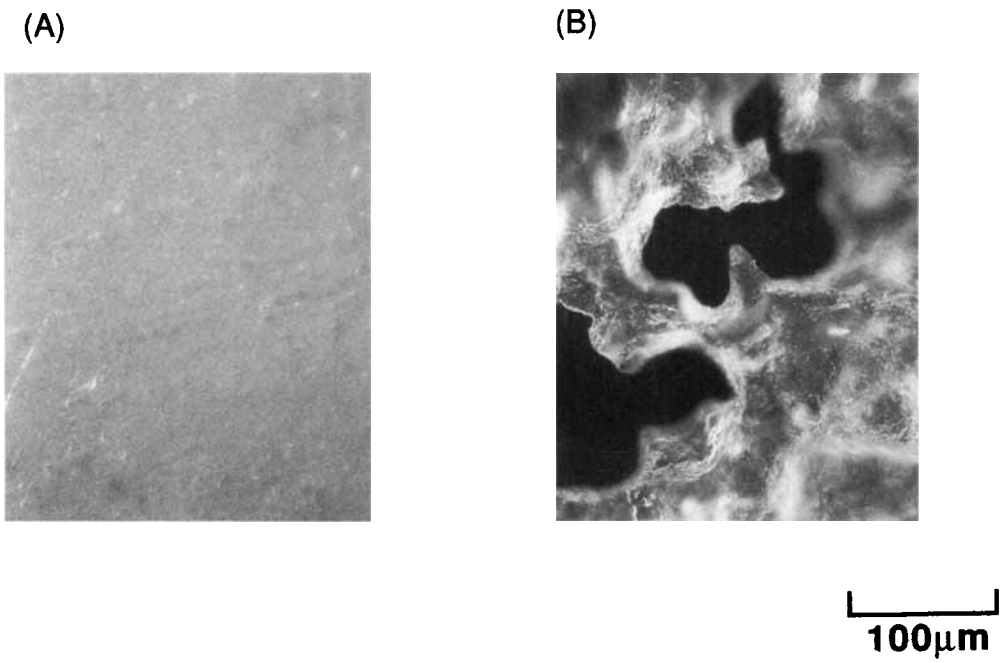

Figure 3 Microscopic photographs of the films of polyamide **4** before and after the soil burial test as shown in Figure 1: (A) 0 days; (B) 48 days.

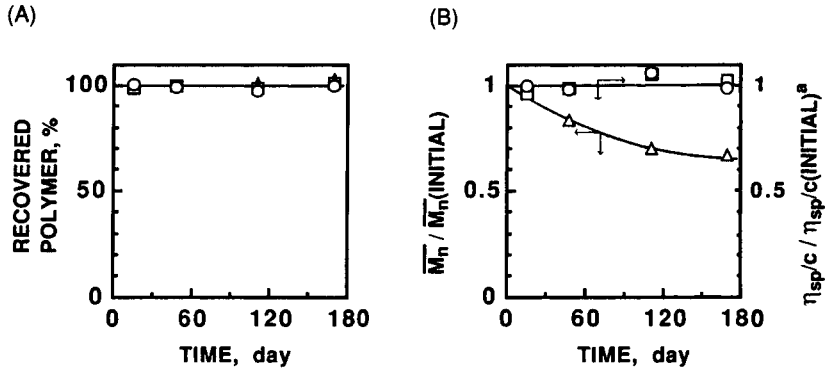

Figure 4 Changes in (A) the weights and (B) the molecular weights of the films of the polyamides (**4**, **5**, and **6**) immersed in a phosphate buffer at 27°C.

carried out in a phosphate buffer, in which the pH value was 7.5 (see Fig. 4). Although weight loss was not detected in any of the films, the molecular weight of **6** was found to decrease during the immersion. In addition, the rate of decrease of its molecular weight is noteworthily similar to that in Figure 1. Therefore, the degradation of the film of **6** in the soil probably occurs through hydrolysis. On the contrary, the heterogeneous degradation of the film of **4** in the soil can be speculated to have proceeded through biological processes, not through hydrolysis.

The polyamide films were also buried in other soils. Figure 5 shows the results in the soil, which has not been composted for more than 10 years, in the same university farm (pH 5.9). In the case of the film of **4**, weight loss was observed and the decrease of the molecular weight of the recovered film was negligible again. Its degradation rate seems to be lower than that in the composted soil, but the degradation process may be similar to that in the composted soil.

In the noncomposted soil, the molecular weight of the film of **6** was found to decrease more quickly than in the composted soil, and weight loss was also observed. These results show that the hydrolysis of **6** takes place easily in the acidic condition. Taking into account that **6** has an acetal–amide bond in the repeating unit, these results should be reasonable.

The molecular weight of the film of **5** was determined to reduce in the noncomposted soil, although this was not observed in the composted soil. The hydrolysis rate of **5** is lower than that of **6**.

In the soil gathered in the university campus (pH 4.5), hydrolysis of the films of **6** and **5** was observed as well as in the soils in the farm, as summarized in Table I. The degradation rates of **5** and **6** in the sterilized soil gathered in the campus were almost the same as those in the corresponding unsterilized one, respectively, which suggests that the degradation of **6** and **5** in the soil proceeded through their hydrolytic process. On the other hand, the film of **4** did not change in the campus soils. Therefore, there must be some microorganisms or bacteria, which degrade the film of **4**, in the soils in the university farm, but not in the campus soil. Search for such microorganisms and the analysis of the degradation mechanism will be the subjects of future investigation.

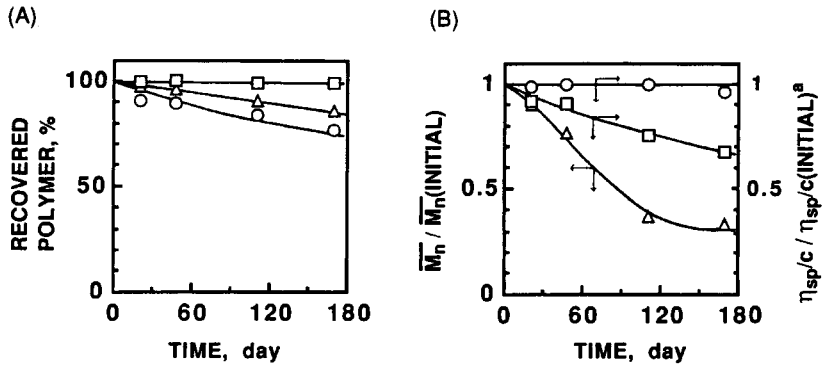

Figure 5 Changes in (A) the weights and (B) the molecular weights of the films of the polyamides (**4**, **5**, and **6**) recovered after the soil burial test (relative humidity, 80%, 27°C). The soil has not been composted for more than 10 years in the university farm (pH 5.9).

Table I Degradation Tests of Polyamides in Several Soils and a Phosphate Buffer[a]

	4		5		6	
	H	B	H	B	H	B
Composted soil in farm (pH 7.5)	−	+++	−	−	+	−
Noncomposted soil in farm (pH 5.9)	−	+	+	−	++	−
Unsterilized soil in campus (pH 4.5)	−	−	+	−	++	−
Sterilized soil in campus (pH 4.5)	−	−	+	−	++	−
Phosphate buffer (pH 7.5)	−		−		+	

[a] H, hydrolysis; B, biodegradation. Degree of degradation: +++, > 50% for 30 days; ++, > 50% for 90 days; +, < 50% for 90 days; −, degradation was negligible for 90 days.

The authors are grateful to Prof. Shigekata Yoshida and Assoc. Prof. Toru Tashiro of Nagoya University for providing the composted and noncomposted soils from the Nagoya University Farm and to Prof. Makoto Kimura of Nagoya University for his helpful discussion on the results of the soil burial tests.

REFERENCES

1. S. J. Huang, in *Comprehensive Polymer Science,* G. Allen and J. C. Bevington, Eds., Vol. 6 (Volume Eds.: G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt), Pergamon Press, Oxford, 1989, Chap. 21, p. 597.
2. D. F. Williams, in *Comprehensive Polymer Science,* G. Allen and J. C. Bevington, Eds., Vol. 6 (Volume Eds.: G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt), Pergamon Press, Oxford, 1989, Chap. 22, p. 607.
3. A.-C. Albertsson and S. Karlsson, in *Comprehensive Polymer Science,* G. Allen and J. C. Bevington, Eds., First Suppl. (Volume Eds.: S. L. Aggarwal and S. Russo), Pergamon Press, Oxford, 1992, Chap. 13, p. 285.
4. S. J. Huang, in *Encyclopedia of Polymer Science and Technology,* H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Eds., Wiley, New York, 1986, Vol. 2, p. 220.
5. R. W. Lenz, *Adv. Polym. Sci.,* **107,** 1 (1993).
6. H. Nakata, H. Yamane, Y. Kimura, and T. Kitao, *Polym. Prepr. Jpn.,* **40,** E 1166 (1991).
7. T. Aikawa, T. Ohtsuka, K. Sanui, Y. Kurusu, and A. Sato, *Kobunshironbunshu,* **45,** 347 (1988).
8. J. Huguet, M. Boustta, and M. Vert, *Makromol. Chem. Macromol. Symp.,* **47,** 345 (1991).
9. Y. Ban, M. Rikukawa, K. Sanui, and N. Ogata, *Kobunshironbunshu,* **50,** 781 (1993).
10. K. Hashimoto, T. Sugata, S. Imanishi, and M. Okada, *J. Polym. Sci. Part A Polym. Chem.,* **34,** 1619 (1994).
11. K. Hashimoto, H. Sumitomo, and A. Washio, *J. Polym. Sci. Part A Polym. Chem.,* **27,** 1915 (1989).
12. K. Hashimoto and H. Sumitomo, *Macromolecules,* **13,** 786 (1980).
13. H. Sumitomo and K. Hashimoto, *Macromolecules,* **10,** 1327 (1977).
14. M. Taniyama, T. Nagaoka, K. Takada, and K. Sanuyama, *Kogyou Kagaku Zasshi (Jpn),* **65,** 415 (1965).
15. K. Hashimoto, H. Sumitomo, and M. Kawasumi, *Polym. Bull.,* **11,** 121 (1984).
16. K. Hashimoto, H. Sumitomo, and M. Kawasumi, *Polym. J.,* **17,** 1045 (1985).
17. K. Hashimoto, H. Sumitomo, and H. Shinoda, *Polym. J.,* **20,** 321 (1988).
18. H. Sekiguchi, *Bull. Soc. Chim. Fr.,* 1827 (1960).

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Received April 13, 1994
Accepted May 5, 1994

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