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SYNTHESIS AND ENZYMATIC DEGRADATION OF NYLON 66 COPOLYMERS WITH POLY(ETHYLENE GLYCOL)S

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ABSTRACT

Nylon 66 (N66) copolymers were prepared by melt polycondensation of adipic acid and hexamethylenediamine with 5–80 mol% poly(ethylene glycol) (PEG), where the molecular weight (MW) of PEG was 200–1000. The reduced specific viscosity of the copolymers was increased by the copolymerization. The crystallinity and melting temperature (T_m) of N66 components decreased with increasing PEG content, but T_m depression of copolymers at the same mole content decreased with increasing MW of PEG, suggesting that the copolymer structures are not of the random type but of the block type at the higher MW of PEG. The water absorption increased with increasing PEG content, and its increase was much higher at the higher MW of PEG. The enzymatic degradation was estimated by the weight loss of copolymer films in the buffer solution with and without a lipase at 37°C. The weight loss was enhanced appreciably by the presence of a lipase, and increased abruptly at higher PEG content, which was correlated to water absorption and the concentration of ester linkages. The enzymatic degradation of these N66 copol-

ymers was much higher than that of previously reported PET copolymers with PEG. The abrupt increase of weight loss by alkali hydrolysis was fairly comparable to that of water absorption.

INTRODUCTION

Continuing our studies on the introduction of biodegradation properties into nonbiodegradable synthetic polymers [1], we have now extended them to nylon. As is well known, nylon is a commercial polymer of low cost with superior thermal and mechanical properties, but nonbiodegradable except for its oligomers [2, 3]. Biodegradability could be obtained by incorporating degradable components into the backbone of nondegradable nylon chains. Nylon copolymers with poly(ethylene glycol) (PEG) have been developed as thermoplastic elastomers [4–6], but their biodegradability has been little examined.

In this study we prepared nylon 66 (N66) copolymers with PEG to obtain widely varying molecular weights (MW) and PEG contents. The effect of MW and PEG content on the structure and some thermal and physicochemical properties as well as the enzymatic degradation of copolymers was investigated systematically in comparison with poly(ethylene terephthalate) (PET) copolymers with PEG [1] reported previously.

EXPERIMENTAL

Monomers

Poly(ethylene glycol)s (PEGs) were obtained from Wako Pure Chemical Industries. The MWs of the PEGs used are shown in Table 1. PEGs and adipic acid were used as received. Hexamethylenediamine was distilled under reduced pressure.

Polymerization

N66 homopolymer was prepared by a melt polycondensation method. After a N66 salt had been melted at 220–225°C in a stream of nitrogen, it was heated at 275–280°C for 1 hour and then maintained at the same temperature for 3 hours in a vacuum of 0.1–0.5 torr.

Copolymers were also prepared by a melt polycondensation method. A mixture of 25 mmol adipic acid and 1.25–20 mmol PEG (depending on the copolymer composition) was heated at 200–205°C for 2 hours in a stream of nitrogen with a small amount of titanium isopropoxide as an esterification catalyst. Then 23.75–5 mmol hexamethylenediamine was added (total amount of HMDA and PEG were equimolar to that of adipic acid) and heated at 270–275°C for 1 hour and further heated at the same temperature for 3 hours in a vacuum of 0.1–0.5 torr. In the above polycondensation, agitation with a mechanical stirrer was applied for E1000 series copolymers.

TABLE 1. Reduced Specific Viscosity (η_{sp}/C) and PEG Content of Copolymers

Polymer code[a]	PEG, wt%	η_{sp}/C, dL/g
N66	—	0.78
E200-10	9	1.07
E200-20	16	1.52
E200-30	24	1.58
E200-40	31	1.58
E200-50	37	1.64
E200-60	43	1.96
E200-70	49	1.22
E200-80	54	1.21
E400-10	16	1.65
E400-20	28	1.71
E400-30	38	1.15
E400-40	47	1.36
E600-10	22	1.77
E600-20	37	1.15
E600-30	48	1.41
E600-40	57	1.37
E1000-5	19	1.18
E1000-10	32	2.22
E1000-20	50	1.19

[a]The number at the left is the MW of PEG comonomer and at the right is the PEG content (mol%) in the feed.

Film Preparation

Copolymers were cast from hexafluoroisopropanol solution, which is a good solvent that hardly causes the hydrolysis of these copolymers. The N66 homopolymer and the E200-10 copolymer shown in Table 1 were melt-pressed and then quenched in ice water. The prepared films were dried at room temperature in vacuo for 24 hours and stored in a dry desiccator.

Characterization

The reduced specific viscosities of 1% solutions of polymers in *m*-cresol were measured at 30°C. Infrared spectra (IR) were recorded on a thin film. Differential thermal analysis (DTA) was performed on the melt-quenched samples at a heating rate of 10°C/min in a nitrogen atmosphere. Wide-angle x-ray scattering (WAXS) was performed on the film samples with nickel-filtered CuKα radiation. Water absorption was measured by immersing the film in water at 30°C for 24 hours followed by removing surplus surface water with a filter paper and then immediately weighing.

In Vitro Degradation

The film specimen (20 mm × 20 mm and about 120 μm thickness) was placed in a small bottle containing 10 mL of 1/15 mol phosphate buffer solution (pH 7.2) with and without 20 mg of *Rhizopus delemar* lipase (fine grade from Seikagaku Kogyo Co.). The bottle then was incubated at 37°C on standing for various times. After incubation the film was washed with water and dried overnight at room temperature in vacuo. The degree of degradation was estimated from the weight loss expressed by mol/m^2, which was calculated by dividing g/m^2 by the average MW of the repeating unit in the copolymer [1].

Alkali Hydrolysis

Alkali hydrolysis of copolymers was conducted by the same procedure given above in enzymatic degradation in a 1/200 N sodium hydroxide aqueous solution at 30°C for 4 hours.

RESULTS AND DISCUSSION

Table 1 shows the reduced specific viscosities (η_{sp}/C) of the copolymers prepared. The η_{sp}/C increases with copolymerization, which may be caused by the incorporation of longer PEG chains and/or an increase of the hydrodynamic volume. All copolymers obtained have a MW high enough to form a tough and flexible film.

The structure and composition of the resulting copolymers were confirmed from their nitrogen content by elemental analysis and infrared spectroscopy. The monomer feed ratio agreed well with the compositions of the copolymers. Figure 1

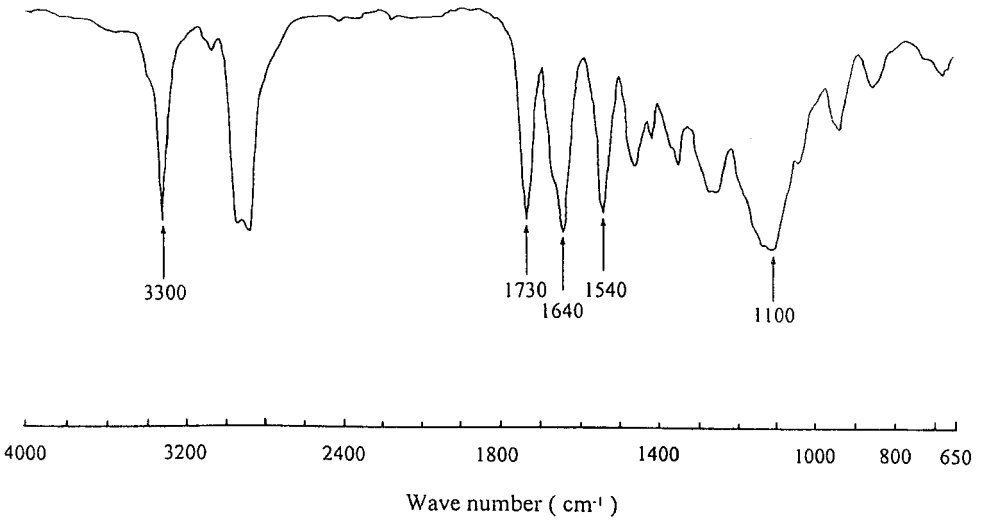

FIG. 1. IR spectrum of E600-40 copolymer.

shows the IR spectrum of the E600-40 copolymer sample. The characteristic absorptions of amide groups appear at 3300, 1640, and 1540 cm^{-1}. In addition, the formation of a new ester bond in the copolymer is clearly seen by the intensive absorption of the ester carbonyl group at 1730 cm^{-1}. The C—O—C ether antisymmetric stretching absorption due to the PEG component appears at around 1100 cm^{-1}.

Figure 2 shows DTA curves of melt-quenched samples for the E400 series of copolymers with varying PEG content. The glass transition temperature (T_g) decreases below room temperature due to copolymerization of the flexible PEG content. The melt temperature (T_m) of the N66 component decreases with increasing PEG content, suggesting that the crystal growth of N66 chains is disturbed by the incorporation of PEG chains.

Figure 3 shows DTA curves of melt-quenched samples for 20 mol% copolymers with varying MWs of PEG. T_m decreases with the copolymerization of PEG. However, it is noted that the T_m depression of copolymers decreases with an increasing MW of PEG. This suggests that the copolymer structures are not of the random type but of the block type at higher MWs of PEG. This may be caused by the poor miscibility of nylon and the PEG component [6], which is enhanced with an increasing MW of PEG. Similar behavior has been observed for PET copolymers with a higher MW of PEG [1]. The endothermic peak at 29°C for E1000-20 copolymer is due to melting of the crystallized PEG chains.

The WAXS curves of the E400 series copolymers and 20 mol% copolymers are shown in Figs. 4 and 5, respectively. The crystallinity gradually decreases with

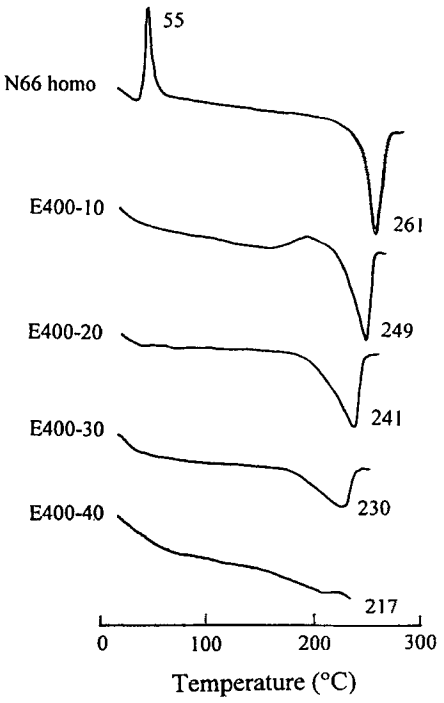

FIG. 2. DTA curves of melt-quenched samples for E400 series copolymers.

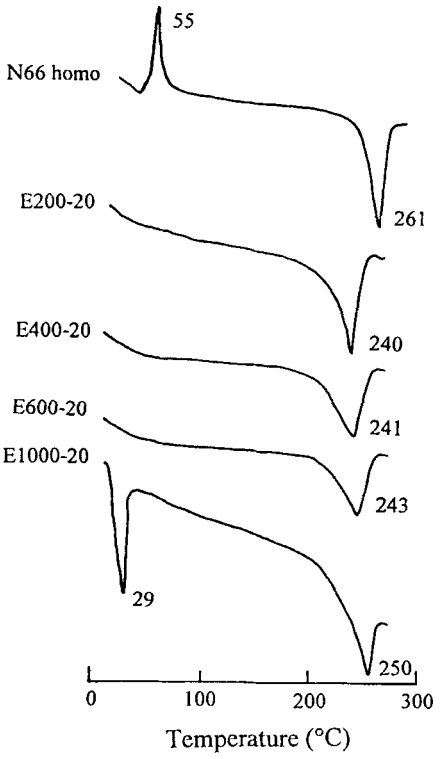

FIG. 3. DTA curves of melt-quenched samples for 20 mol% copolymers.

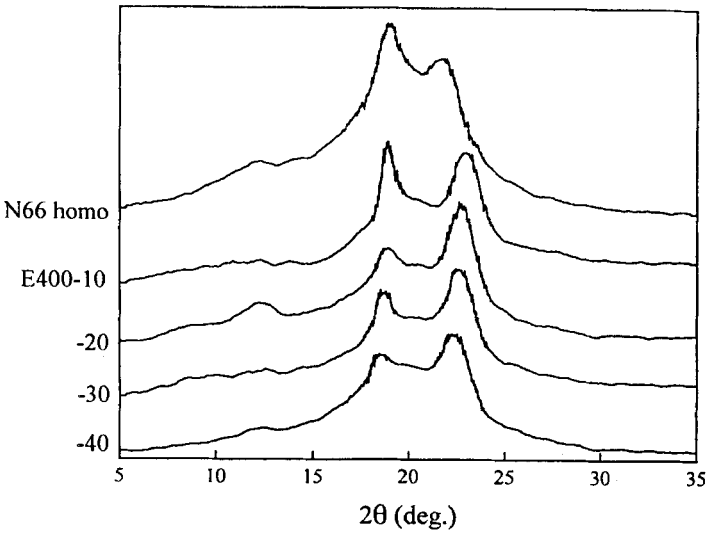

FIG. 4. WAXS curves of E400 series copolymers.

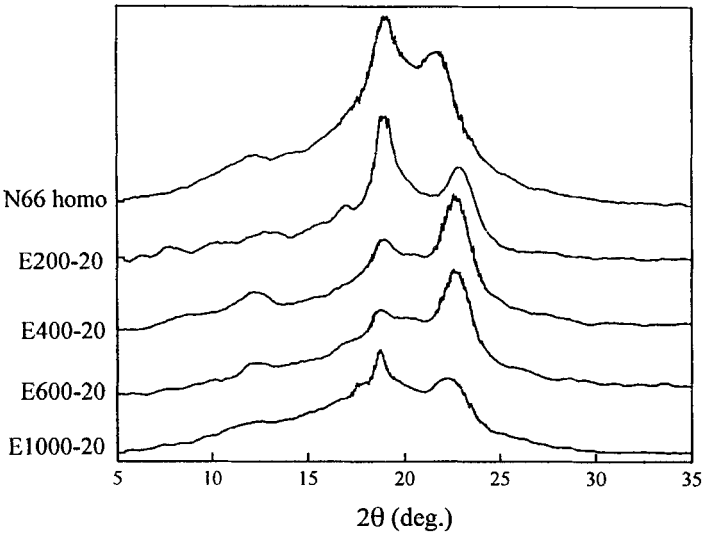

FIG. 5. WAXS curves of 20 mol% copolymers.

increasing PEG content for the E400 series copolymers, which can be explained by a decrease in the crystallization of the N66 component due to the incorporation of PEG chains. This result is consistent with the fact that the melting peak areas of copolymers decrease with increasing PEG content, as shown in Fig. 2. The crystallinity also decreases for 20 mol% copolymers with an increasing MW of PEG. The relatively small but sharp diffraction peak around 18° for E1000-20 copolymer seems to be due to the PEG crystal which had two sharp diffraction peaks at 18 and 22°. This appearance of the diffraction peak corresponds well to that of the melting peak at 29°C in the DTA curve for this copolymer shown in Fig. 3.

Figure 6 shows the water absorption of various copolymers against the PEG content by wt%. The water absorption increases with increasing PEG content, and it also increases with increasing MW of PEG at the same mole content of PEG. It is noteworthy that the water absorption increases abruptly at a higher wt%, and it also increases with increasing MW of PEG at the same wt%. Similar behaviors have been observed for PET copolymers with PEG [1].

Figure 7 shows the weight loss of E600-40 copolymer against degradation time at 37°C. The weight loss increases with time, attaining approximately equilibrium after 3 days, and it is enhanced appreciably by the presence of a lipase. For PET copolymers with PEG, the effect of a lipase on degradation was smaller [1]. The reason for this enhanced effect of a lipase for N66 copolymers may be because they contain aliphatic ester linkages between adipic acid and PEG, which is favorable for enzymatic degradation. Figure 8 shows the weight loss of various copolymers against the PEG content degraded at 37°C for 5 days by wt%. Weight loss increases with increasing PEG content, and it increases with increasing the MW of PEG at the same mole content of PEG. It is noted that weight loss increases abruptly at the higher PEG content, which corresponds well to the water absorption shown in Fig. 6. Higher water absorptions must be favorable for the degradation of films. How-

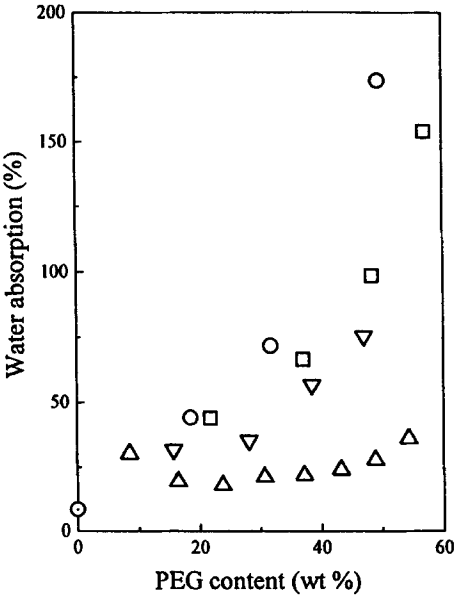

FIG. 6. Water absorption of copolymers against PEG content by weight percent. (△) E200; (▽) E400; (○) E600; (□) E1000.

ever, water absorptions are higher for E1000-20 (173.6%) than for E600-40 (153.8%), and higher for E600-30 (98.4%) than for E400-40 (75.4%). On the contrary, the weight loss is higher for E600-40 (37.3 mmol/m^2) than for E1000-20 (15.3 mmol/m^2), and for E400-40 (22.0 mmol/m^2) than for E600-30 (19.1 mmol/m^2). A similar result has been observed for PET copolymers with PEG. The higher

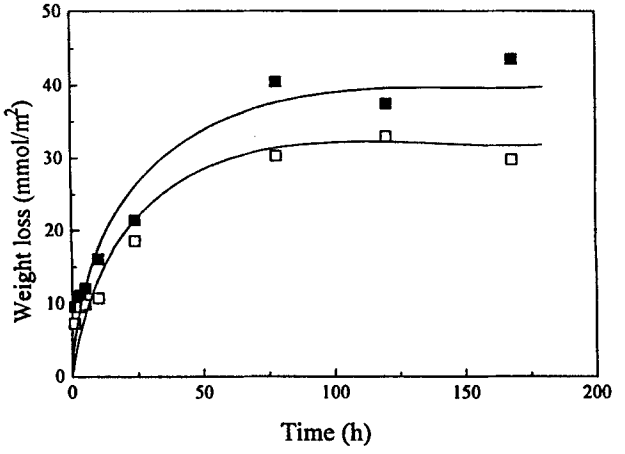

FIG. 7. Weight loss of E600-40 copolymer against degradation time in buffer solution with (■) and without (□) a lipase at 37°C.

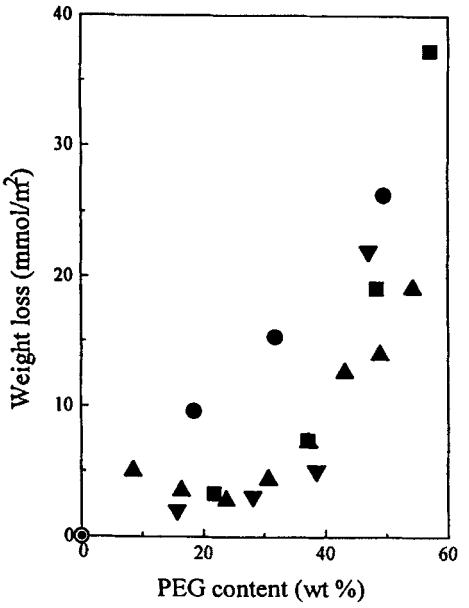

FIG. 8. Weight loss of various copolymers against PEG content degraded in buffer solution with a lipase at 37°C for 5 days by weight percent. (▲) E200; (▼) E400; (●) E600; (■) E1000.

weight losses of E600-40 and E400-30 could be due to the higher concentration of ester linkages between adipic acid and PEG. The weight losses are 4.4, 22.0, and 26.3 mmol/m^2 for E200-40, E400-40, and E1000-20, respectively, while that of PET copolymers with the corresponding MW and content of PEG degraded for 7 day under the same condition above was 0.55, 1.7, and 2.5 mmol/m^2, respectively [1]. This much higher weight loss of N66 copolymers than that of PET ones may be caused by not only the enhanced effect of a lipase on the degradation for the N66 copolymers shown above, but also the markedly higher water absorption for N66 copolymers than for PET ones as follows: The water absorption of N66 copolymers is 21.4, 75.4, and 173.6% for E200-40, E400-40, and E1000-20, respectively, while that of PET copolymers with the corresponding MW and content of PEG was 1.8, 3.4, and 7.5%, respectively [1].

Alkali hydrolysis of copolymers was carried out for comparison with enzymatic degradation. The weight loss in alkali solution is plotted against the PEG content by wt% in Fig. 9. An abrupt increase of weight loss at higher PEG content is observed, and its order is fairly comparable to that of water absorption at higher PEG content in Fig. 6, suggesting the effect of increased water absorption. We previously studied the enzymatic degradation of copolyesteramides from hexamethylene adipate (E66) and hexamethyleneadipamide (A66) and found that the weight loss for enzymatic degradation reached a maximum at 80 mol% of E66 and that for alkali hydrolysis reached a maximum at 60 mol% of A66. This suggested that alkali hydrolysis is affected by the content of the hydrophilic amide moiety which

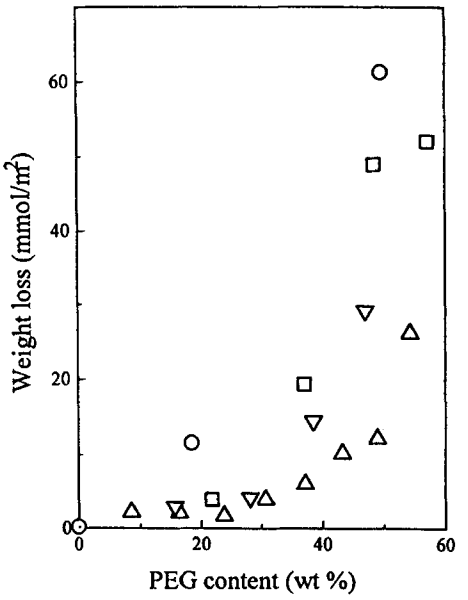

FIG. 9. Weight loss of various copolymer films against PEG content degraded in 1/200 N NaOH aqueous solution at 30°C for 4 hours by weight percent. Symbols are the same as in Fig. 6.

could accelerate the permeation of alkali aqueous solution into the film [7]. It is supposed from these results that alkali hydrolysis is more sensitive to water absorption than the concentration of ester linkages.

The above results show that enzymatic degradation is controlled mainly by water absorption as well as by the concentration of enzymatically degradable ester linkages. The former increases with an increase of the PEG content, and the latter increases with a decrease of the MW of PEG at the same PEG wt%. Thus, E600-40 copolymer is the most favorable copolymer for enzymatic degradation among the nylon copolymers studied.

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