Degradable Polyurethanes Synthesized from Poly(butylene succinate) polyol, Poly(ethylene glycol), and 4,4'-Methylenebis(cyclohexyl isocyanate)

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Most synthetic polymers usually have caused serious environmental problems since their disposals are not easily degraded in nature. The degradability problems of polymers may be resolved by using biodegradable polymers.[1] Aliphatic polyesters have been actively investigated since they seem to be one of the most promising degradable synthetic polymers.[2] As a result, some polyesters synthesized from diol and diacid, such as 'Bionolle' (Showa), 'Sky Green' (SK Chemicals), and 'Eslon' (Saehan), are commercially available.

Molecular weight of polyesters can be increased by employing proper catalysts and coupling reaction.[3] The increased molecular weight of polyesters usually leads to an increase in the certain mechanical properties, but biodegradability of the resulting polymers decreases. One of the strategies for enhancing biodegradability of the polyesters is incorporation of hydrophilic poly(ethylene glycol) (PEG) segments into the polymer backbone. Kim synthesized polyurethane from polyester polyol, ethylene glycol, and aromatic or aliphatic diisocyanate, and reported that polyurethane prepared from aliphatic diisocyanate shows higher degradation rate.[4] Polyesters prepared from succinic acid, 1,4-butanediol and PEG were reported by Nagata *et al.*[5] Polyesters containing PEG segments, such as poly(ethylene succinate)[6,7] and poly(ethylene terephthalate) copolymers,[8,9] were also reported.

It is interesting to study biodegradable polyurethanes prepared from biodegradable polymer polyols due to the typical mechanical characteristics of polyurethanes. Especially, we are interested in polyurethanes containing PEG since it has been frequently used as comonomers in preparing biodegradable polymers due to its biocompatibility and biodegradability.[10,11] However, such type biodegradable polyurethanes have not been reported yet in the literature.

Recently, we synthesized gas-permeable polyurethanes from poly(butylene succinate) polyol (PBS, number-average molecular weight $\overline{M}_n$ 1,000), PEG ($\overline{M}_n$ 200), and 4,4'-methylenebis(cyclohexyl isocyanate) (H_{12}MDI).[12] However, their hydrolytic degradation was not satisfactory due to a small hydrophilic PEG segment. Thus, we attempted to synthesize new polyurethanes from PBS ($\overline{M}_n$ 1,470), PEG ($\overline{M}_n$ 1,000), and H_{12}MDI. As a first attempt, any chain extender was not used for the synthesis with a hope that the resulting polymers may have moderate molecular weights since the biodegradability of polymers usually decreases with their molecular weights. Actually, we obtained polyurethanes with small molecular weights from the synthesis, but their characteristics may be valuable for further research on the same or similar type polyurethanes. This note describes briefly the synthesis and some general properties of the polymers.

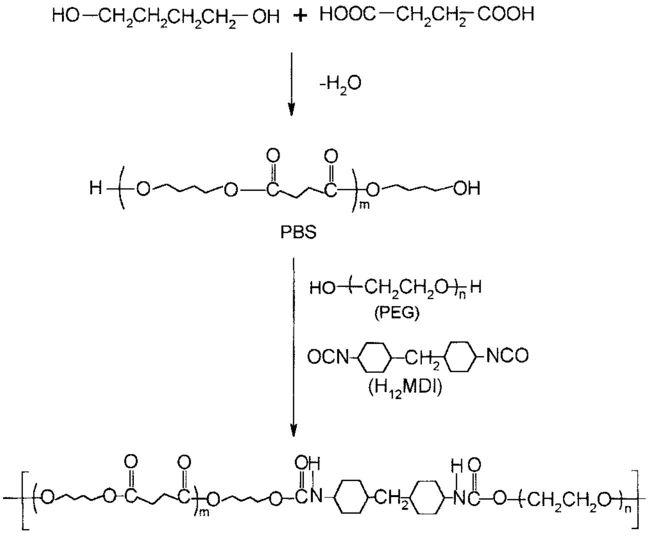
Experimental Section

Measurements. The chemical structures of the polymers were confirmed by analyzing the FT-IR and ^{1}H NMR spectra obtained from a JASCO FT-infrared spectrophotometer and JEOL-JMN 400 (400 MHz) spectrometer, respectively. The thermal transitions of the polymers were observed with differential scanning calorimetry (DSC, DuPont 2000). The average molecular weights of the polymers were estimated with gel permeation chromatography (Maxima 820) using polystyrene solution in chloroform as the calibration standard. The tensile strength and elongation at break were measured with a UTM (LLOYD Co.) at a strain rate of 2.5 mm/min. A wide angle X-ray diffraction was studied with a X-ray diffactometer (Rigaku Co., Cu target) at 40 kV and 20 mA.

Synthesis. The synthetic route to the new polyurethanes is shown in Scheme 1. PBS was prepared by employing the known procedure with some modifications. Briefly, a mixture of 1,4-butanediol and succinic acid in a molar ratio of 1.2 : 1 was reacted in the presence of titanium(IV) isopropoxide (0.02 wt%) at 180 ^{o}C for 2 h under a nitrogen atmosphere. The mixture was further heated at 210-220 ^{o}C for 3 h under a vacuum for a deglycol reaction. The titrations for the measurement of the hydroxy and acid numbers were conducted on the basis of ASTM D 1957-63 and ASTM D 1980-67, respectively.

The PBS was dried at 70 ^{o}C and 50 torr for 24 h, and melt at 130 ^{o}C in a reaction flask, followed by the addition of an appropriate amount of PEG. H_{12}MDI was added at 120-130 ^{o}C under a nitrogen atmosphere. The mixture was heated in the presence of dibutyltin dilaurate (0.02 wt%) until the isocyanate peak in the FT-IR spectrum disappeared. Molar ratios of PBS/PEG/H_{12}MDI were 3/1/4, 2/1/3, and 1/1/2, yielding the corresponding polymer PU-1, PU-2, and PU-3, respectively.

Hydrolytic degradation. The film specimens (10 mm × 10 mm and about 50 μm in thickness) were placed in small bottles containing 10 mL of a 3% NaOH aqueous solution. The bottles were then incubated at 37 ^{o}C for 72 h. The films were then washed with distilled water and dried in a vacuum oven



Scheme 1. Schematic representation of a synthetic route to new polyurethanes.

at 60°C for 24 h. The % weight loss was calculated by subtracting the film weight from the initial weight, which was then multiplied by 100.

Results and Discussion

The $\overline{M}_n$ of PBS was calculated to be about 1,470, based on the hydroxy and acid values. The incorporation of PEG and PBS into the polyurethane chain via urethane linkage was confirmed from ^{1}H NMR and FT-IR spectra. The FT-IR spectrum of PU-2 shows the peaks of ester and urethane bonds while the peaks of $H_{12}MDI$ disappeared almost completely as shown in Figure 1. The proton resonance peaks at 4.05, 3.60, 2.58 ppm correspond to the protons of two methylene groups at 1,4-position of 1,4-butanediol unit, two methylene groups of PEG unit, and methylene groups of succinic acid unit, respectively (Figure 2). The expected ratio of the integrals for the NMR peaks at 4.05, 3.60, and 1.90-0.80 ppm (protons in the $H_{12}MDI$ unit and in the two internal methylene groups in the 1,4-butanediol unit)) is 1 : 1.53 : 2.19, and the measured ratio is 1 : 1.53 : 2.13 for PU-2. This result indicates that the molar composition ratios of the polymers determined by the ^{1}H NMR peak areas are in good agreement with the feed ratio of the comonomers employed for the polymerization.

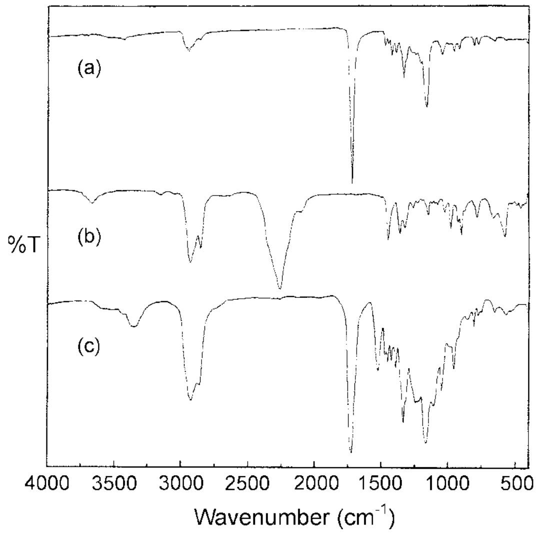


Figure 1. FT-IR spectra of (a) PBS, (b) $H_{12}MDI$, and (c) PU-2.

Table 1 shows the average molecular weight, melting transition temperature (T_m), melting transition enthalpy (ΔH_m), tensile strength, and elongation at break of the polyurethanes. The average molecular weights of the polymers are pretty low. This result may be explained by considering a few factors. The measured hydroxy and acid values of PBS were 76.3 and 6.1, respectively, indicating that the concentration of undesirable carboxyl group in PBS is still appreciable. Any chain extender was not employed in the synthesis, and the polymers can be regarded as prepolymers whose molecular weights are usually low. Thus, this result suggests that a proper chain extender should be used in order to moderately increase the molecular weight of this type polyurethanes.

The T_m of PU-1, PU-2, and PU-3 are about 102, 98, and 94 °C, respectively, which are lower than that of PBS (109 °C) as shown in Figure 3. The ΔH_m of the polymers decreases progressively as the PBS content in the polymers decreases. This result suggests that the melting transition of the polymers may arise from the PBS segments and the crystallization of the PBS segments can be lowered by the incorporation them into the polyurethane backbones.[4,5] A wide angle X-ray diffraction experiment reveals that two peaks appear at 2θ values of 19 and 23° for PBS, PU-1, PU-2, and PU-3, but intensities of the peaks for the three different polyurethanes are lower and broader than those for PBS (Figure 4). The 2θ

Table 1. The number- and weight average molecular weight ($\overline{M}_n$, $\overline{M}_w$), melting transition temperature (T_m), melting transition enthalpy (ΔH_m), PEG and PBS content (wt%), tensile strength, and elongation at break of synthesized polymers. The DSC data were obtained from the second heating scanned thermograms of samples which had been rapidly quenched with liquid nitrogen after melting. The heating scan rate was 10 °C/min

	Molar ratio of PBS/PEG/$H_{12}MDI$	$\overline{M}_n$	$\overline{M}_w$	Tm (°C)	ΔH_m (cal/g)	PEG wt%	PBS wt%	Tensile strength (kg/mm^2)	Elongation at break (%)
PBS	–	1,470		109	24.0	–			
PU1	3/1/4	9,150	29,900	102	13.0	16.0	68.2	0.95	8
PU2	2/1/3	12,000	31,700	98	9.7	25.8	58.5	1.25	21
PU3	1/1/2	8,140	23,000	94	7.3	39.4	44.6	0.75	4

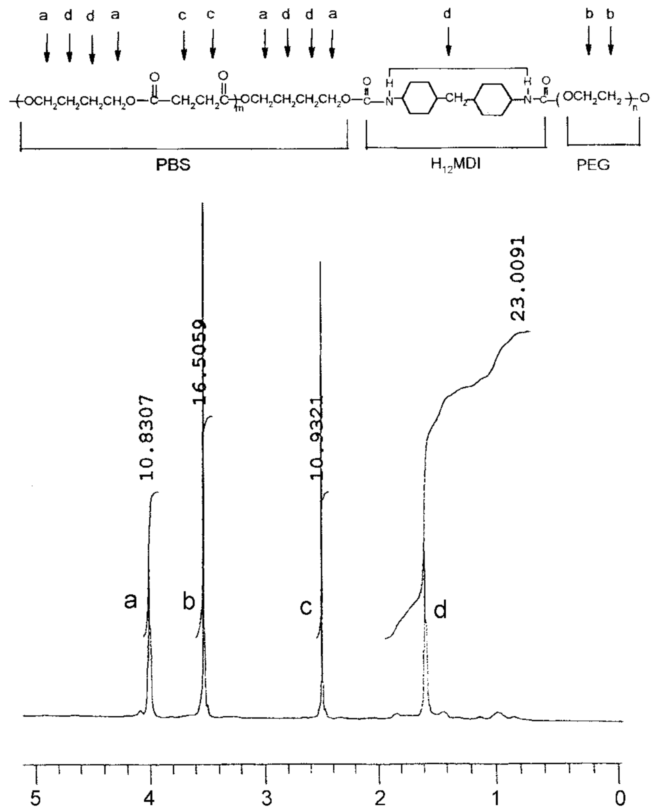


Figure 2. ^{1}H NMR spectrum of PU-2 where the molar feed ratio of PBS, PEG, and H_{12}MDI is 2/1/3.

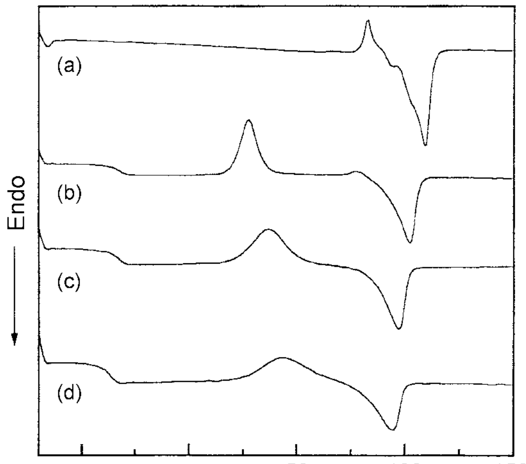


Figure 3. DSC thermograms of (a) PBS, (b) PU-1, (c) PU-2, and (d) PU-3. All of the thermograms were obtained from the second heating scans and the scan rate was 10 °C/min.

values of PEG were somewhat different from those of PBS and the polyurethanes. This results confirms that the crystallinity and the melting transition of the polymers arise from the PBS segments.

Thin films (thickness, 50 μm) of the polyurethanes were easily prepared, while those of PBS could not be prepared since the PBS was too brittle due to the low molecular weight. The tensile strength and elongation at break of PBS with much higher molecular weight ($\overline{M}_n$ 20,000, $\overline{M}_w$ 74,000) were reported to be 1.59 kg/mm^2 and 42%, respectively.[5] On the other hand, those of PU-2 are 1.25 kg/mm^2 and 21%, respectively. These values of PU-2 are somewhat smaller than those of the such high molecular weight PBS, but this result suggests that the mechanical properties of this type polyurethanes can be enhanced and even much greater than those of the conventional PBS by increasing the molecular weight.

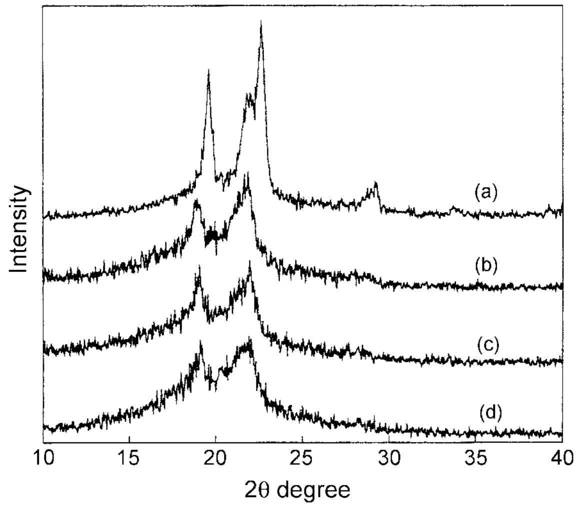


Figure 4. X-ray differaction pattern of (a) PBS, (b) PU-1, (c) PU-2, and (d) PU-3.

There are several possible approaches to assess the biodegradability of polymers,[13] but the hydrolytic degradation of the polymers in alkaline solutions was performed as the initial test. The weight loss of the Eslon ($\overline{M}_n$ 40,000, $\overline{M}_w$ 70,000), PU-1, PU-2, and PU-3 during the incubations in 3% NaOH aqueous solutions at 37 °C for 72 h was estimated to be 31, 70, 77, and 90%, respectively. Hydrolysis of polymers in aqueous solutions is usually facilitated by the hydrophilicity of the polymers because water can more efficiently penetrate into the polymers.[14,15] This order of the hydrolytic degradation rate of the polyurethanes is corresponding to the order of the hydrophilicity of the polymers, confirming that the degradation of the polyurethanes is affected by the hydrophilic PEG content. The slower degradation rate of the Eslon is presumably due to the high molecular weight and high crystallinity as well as the absence of the hydrophilic PEG segments.

In summary, polyurethanes were synthesized from two different polyols of PBS and PEG in the absence of chain extender. The T_ms of the polymers were lower than that of PBS because the crystalline domains of PBS segments are responsible for the melting transition and affected by the polymer backbones. The polyurethanes showed some degree of tensile strength and elongation even though their molecular weights are relatively small. They underwent very rapid degradation in alkaline aqueous solutions. This result suggests that the degradable polyurethanes with superior mechanical properties can be prepared from polyols of PBS along with PEG as long as the molecular weight is increased to some extent. Currently, we are attempting to synthesize this type polyurethanes by employing a chain extender in order to increase their molecular weight, and the result will be reported in the near future.

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References

1. Vasnev, V. A. *Polymer Science. Ser. B* **1997**, *30*, 474.
2. Dahlmann, J.; Rafler, G.; Rafler, K.; Mehlis, B. *British Polym. J.* **1990**, *23*, 235.
3. Fujimaki, T. *Polym. Degrad. Stab.* **1998**, *59*, 209.
4. Kim, Y.-D.; Kim, S. C. *Polym. Degrad. Stab.* **1998**, *62*, 343.
5. Nagata, M.; Kiyotsukuri, T.; Takeuchi, S.; Tsutsumi, N.; Sakai, W. *Polym. Int*. **1997**, *42*, 33.
6. Albertsson, A. C.; Ljungquist, O. J. *J. Macromol. Sci. Chem.* **1986**, *A23*, 411.
7. Albertsson, A. C.; Ljungquist, O. J. *Acta Polym.* **1988**, *39*, 95.
8. Reed, A. M.; Gilding, D. K. *Polymer* **1981**, *22*, 499.
9. Nagata, M.; Kiyolsukuri, S.; Minami, T.; Tsutsumi, N.; Sakai, W. *Polym. Int.* **1996**, *39*, 83.
10. Kawai, F. *Crit. Rev. Biotechnol.* **1987**, *6*, 273.
11. Kawai, F.; Enokibara, S. *J. Ferment. Bioeng.* **1996**, *82*, 575.
12. Oh, H.-J.; Kim, W.-Y.; Jeong, Y.-S.; Lee, Y.-S. *Bull. Korean Chem. Soc.* **2000**, submitted.
13. Andrady, A. L. *Rev. Macromol. Chem. Phys*. **1994**, *C34*, 25.
14. DiBenedetto, L. J.; Haung, S. J.; Cameron, J. A. *Polym. Mater. Sci. Eng.* **1987**, *57*, 404.
15. Haung, S. J.; Roby, M. S.; Macri, C. A.; Cameron, J. A. In *Biodegradable Polymers and Plastics*; Vert, M., Feijen, J., Albertsson, A., Scott, G., Chiellini, E., Eds.; Royal Chemical Society: 1992; p 147.