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Synthesis and physical properties of polyurethanes from saccharide-based polycaprolactones

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SUMMARY: Polyurethane (PU) sheets were prepared from glucose-, fructose- and sucrose-based polycaprolactones (PCL). The obtained saccharide-based PCL's were characterized by gel permeation chromatography, Fourier-transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The glass transition temperature, thermal degradation temperature, tensile strength, elongation and Young's modulus of the PU sheets were measured. The obtained results suggest that the molecular motion of PU's is enhanced with increasing fraction of PCL chains in PU molecules, and that at the same time the saccharide components act as hard segments.

Introduction

Biodegradable polyurethanes, which can be prepared from plant components such as cellulose, hemicellulose, saccharides and lignin, have been extensively studied [1~12]. The PU's prepared at our laboratory showed excellent mechanical and thermal properties. They were biodegraded by microorganisms when they were placed in soil [9]. In the present study, polycaprolactone (PCL) derivatives were newly synthesized from saccharides such as glucose (Glu), fructose (Fru) and sucrose (Suc). Polyurethane sheets were prepared from the above PCL derivatives by the reaction with diphenylmethane diisocyanate (MDI). The obtained saccharide-based PCL's were characterized with respect to chemical structure and molecular weight. Thermal and mechanical properties of prepared PU sheets were also studied.

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Experimental part

Sample preparation

Saccharide-based PCL's were synthesized by the polymerization of ε-caprolactone (ε-CL) which was initiated by each of the above mentioned saccharides (Glu, Fru and Suc). The amount of ε-CL was varied from 1 to 5 mols / each OH group of each saccharide. The polymerizations were carried out for 12 hr at 150 °C with the presence of a small amount of dibutyltin dilaurate (DBTDL). Polyurethane sheets were obtained by the following procedure. Saccharide-based PCL's were dissolved in tetrahydrofuran (THF). MDI was reacted with the above solution for 30 min at room temperature with stirring. The obtained prepolymer was cast on a glass plate and the solvent was evacuated in a desiccator under dry conditions. The obtained polyurethane sheet was cured at 120 °C for 2 hours.

Measurements

Gel permeation chromatography (GPC) was carried out using a Shimadzu RID-6A. Fourier-transformed infrared spectroscopy (FT-IR) was carried out using a Perkin Elmer 2000FT-IR and a JASCO FT/IR-5300. Nuclear magnetic resonance spectroscopy (NMR) was carried out using a Varian Gemini 300 BB. Thermogravimetry (TG) was carried out in nitrogen using a Seiko TG 220 at a heating rate of 10 °C / min. Differential scanning calorimetry (DSC) was performed using a Seiko DSC 220 at a heating rate of 10 °C / min under a nitrogen flow. Mechanical properties were measured using a Shimadzu Autograph AGS 500D.

Results and discussion

Chemical structure of saccharide-based polycaprolactones and prepared PU's

The obtained saccharide-based PCL' s were characterized by GPC, FT-IR and NMR. The average molecular weights were in the order of 10^3 from 1.3 to 4.9 in sucrose-based PCL's and from 0.8 to 3.0 in glucose- and fructose-based PCL's, corresponding well with the calculated values. Fig. 1 shows FT-IR spectra of glucose and glucose-based PCL (Glu-PCL). It can be seen that the absorption band at around 3410 and 3316 cm^{-1} corresponding to the hydroxyl group in glucose disappeared in Glu-PCL and the absorption bands at around 1732 and 1195 cm^{-1} and 1200 cm^{-1} corresponding to the ester group appeared.

Figs. 2 and 3 show ^1H- and ^{13}C-NMR spectra of sucrose-based PCL (Suc-PCL) with 4 mols of CL/OH. The spectra show the presence of CL chains attached to sucrose, although we could not calculate exactly the numbers of CL chains from the ^1H-NMR spectra, since the intensities of the peaks in the range from 4 to 6 ppm, which are assigned to protons in sucrose molecules, are too small in the S/N ratio of the measurements.

The core structure of prepared PU's consists of saccharide-based PCL's linked by urethane bonding. Accordingly, it can be assumed that the obtained PU's are essentially copolymers having three dimensional networks of urethane bonding which have saccharide-based PCL components. A schematic chemical structure of PU's derived from Suc-PCL is shown in Fig. 4, as an example of prepared PU's.

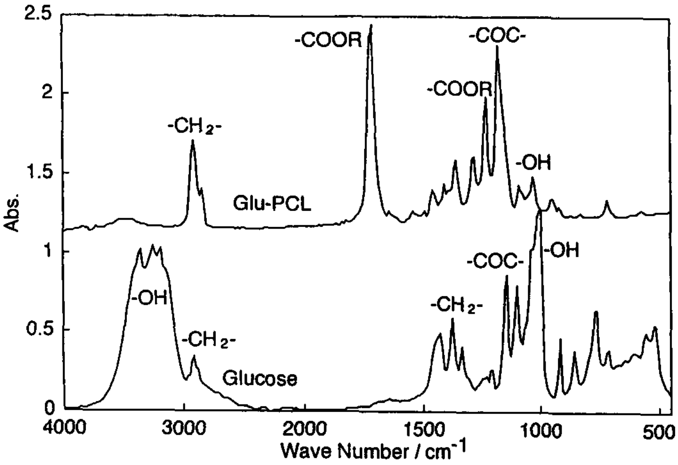

Fig. 1. FT-IR spectra of glucose and glucose-based PCL. R: glucose residue

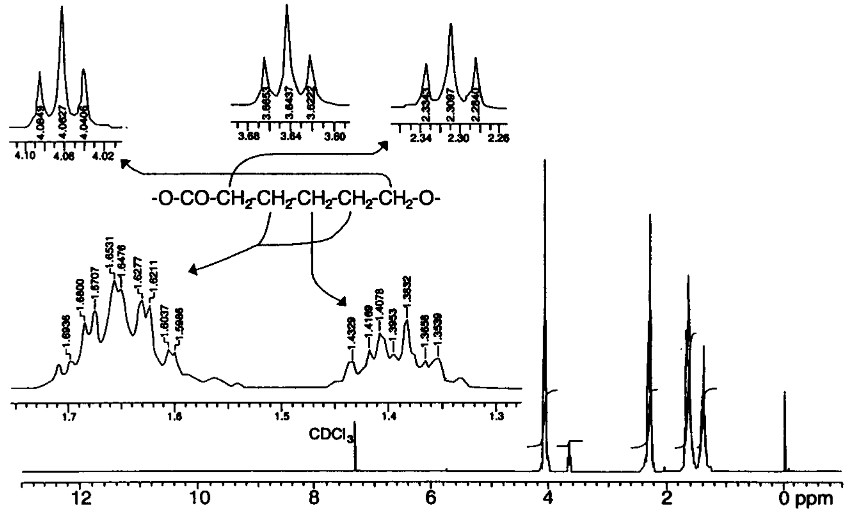

Fig. 2. ^{1}H-NMR spectra of sucrose-based PCL.

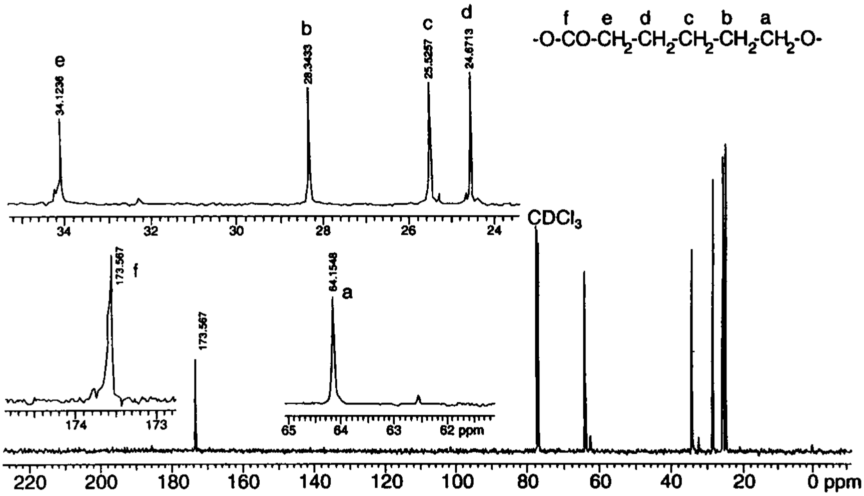

Fig. 3. ^{13}C-NMR spectra of sucrose-based PCL.

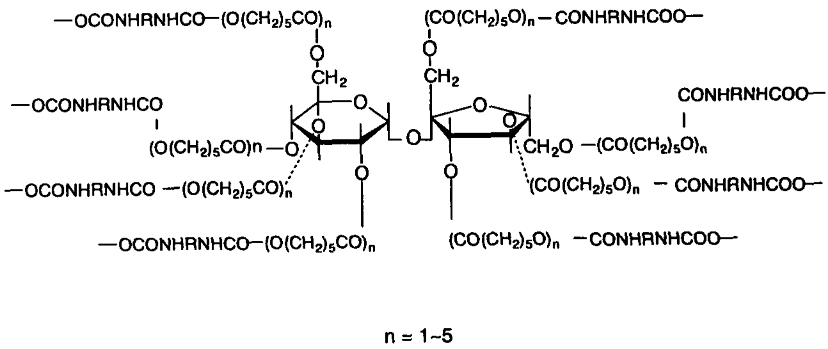

Fig. 4. Schematic chemical structure of PU derived from sucrose-based PCL's.

Thermal properties of PU's

Differential scanning calorimetry

Fig. 5 shows DSC curves of PU sheets derived from Glu-PCL with various CL/OH ratios from 1 to 5. A marked change in baseline due to glass transition was observed in each DSC curve. Glass transition temperature's (T_g's) were determined by the method reported previously[13]. T_g decreases with increasing CL/OH ratio in PU's, since caprolactone chains with saccharides act as soft segments in PU networks. This softening effect of caprolactone chains was enhanced progressively with increasing chain length of CL chains.

In the case of the DSC curve representing Glu-PCL with CL/OH ratio 5, a prominent exothermic peak due to cold crystallization of Glu-PCL and also a prominent peak of melting of crystals are observed at around - 20 and + 40 °C, respectively. The DSC curve representing Glu-PCL with CL/OH ratio 4, which was annealed at room temperature, also showed a melting peak around + 40 °C. The other PU's derived from Fru- and Suc-PCL's showed similar DSC results. The above results suggest that the PU's derived from the saccharide-based PCL's with CL/OH ratios over 4 have a crystalline region in the molecular structure.

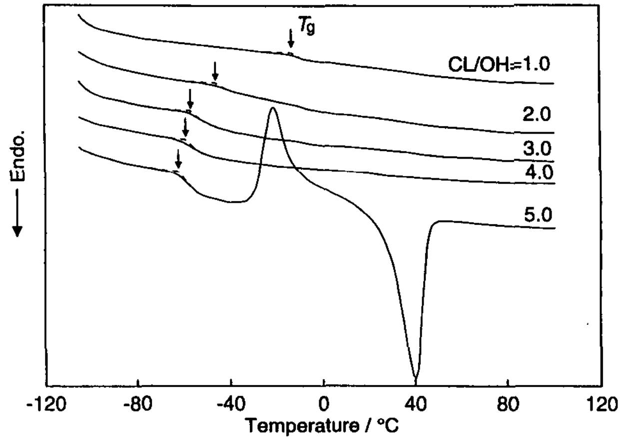

Fig. 5. DSC curves of PU's prepared from glucose-based PCL's with various CL/OH ratios.

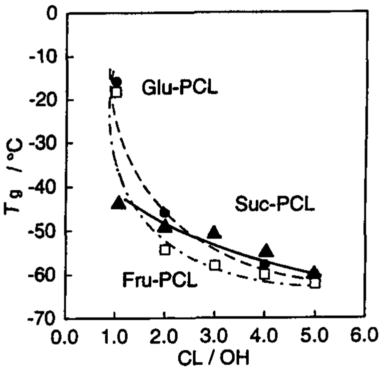

Fig. 6. Change of Tg's of PU's prepared from saccharide-based PCL's with various CL/OH ratios.

● : PU from glucose-based PCL

□ : PU from fructose-based PCL

▲ : PU from sucrose-based PCL

Fig. 6 shows the relationship between T_g's and CL/OH ratios of sugar-based PCL's in PU's. T_g decreased steadily with the CL content for all three types of PU's derived from glucose-, fructose- and sucrose-based PCL's. This can be attributed to a number of factors. The incorporation of saccharide-based PCL's into the PU structure leads to the enhancement of molecular motion of PU networks due to the flexible PCL chains attached to saccharides. The functionality of glucose and fructose is 5 and sucrose has a functionality of 8. The longer the PCL chain in PU molecules, the more flexible the main chain motion and the lower the *Tg*. In addition, the structure of saccharide which forms core structure affects *Tg*'s. Accordingly, the tendency of the decrease of *Tg*'s is different between the PU's derived from Glu- and Fru-PCL and those derived from Suc-PCL.

Thermogravimetry

Fig. 7 shows TG and derivative TG (DTG) curves of PU's with various CL/OH ratios derived from Suc-PCL, measured in N_2. In the TG curves of PU's a small weight change is observed at around 100°C, which may be attributed to the evaporation of water from the samples in both N_2 and air. At a temperature higher than 500 °C, weight residues are observed in TG

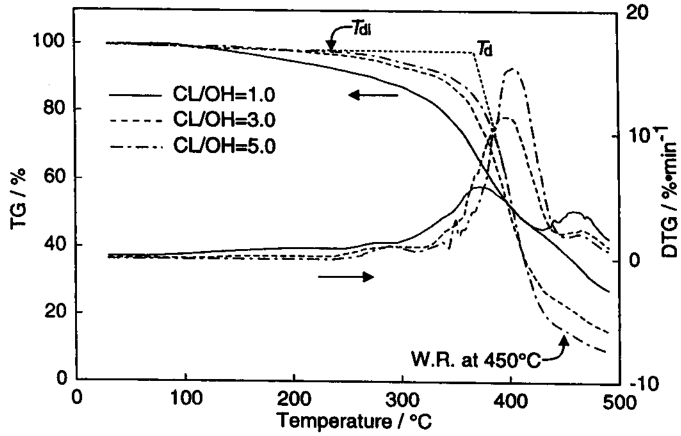

Fig. 7. TG and DTG curves of PU's prepared from sucrose-based PCL's with various CL/OH ratios.

curves measured in N_2. As seen in Fig. 7, the thermal decomposition occurred in almost a single step until a certain temperature (up to ca. 420 °C). This suggests that the degradation process occurring up to this temperature region can be attributed to the dissociation of urethane links between hydroxyl groups of PCL and isocyanate groups.

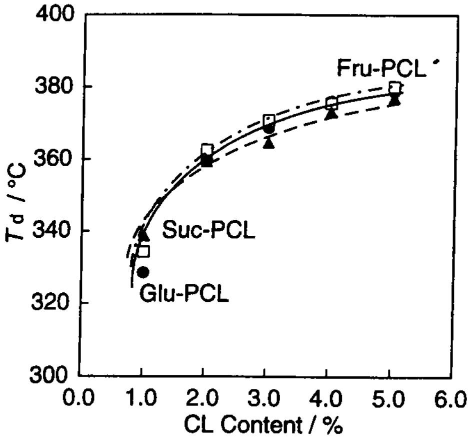

Fig. 8. Change of *T*d's of PU's prepared from saccharide-based PCL's with various CL/OH ratios.

● : PU from glucose-based PCL

□ : PU from fructose-based PCL

▲ : PU from sucrose-basedPCL

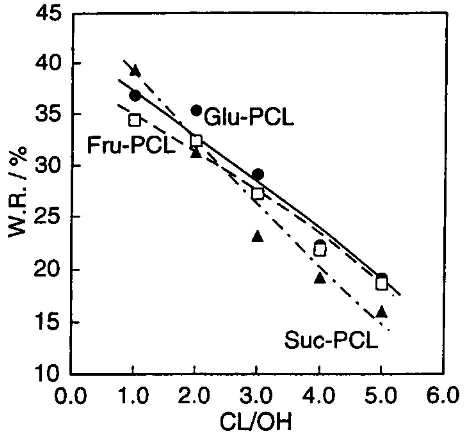

Fig. 9. Change of the weight residue at 450 °C of PU's prepared from saccharide-based PCL's with various CL/OH ratios.

● : PU from glucose-based PCL

□ : PU from fructose-based PCL

▲ : PU from sucrose-based PCL

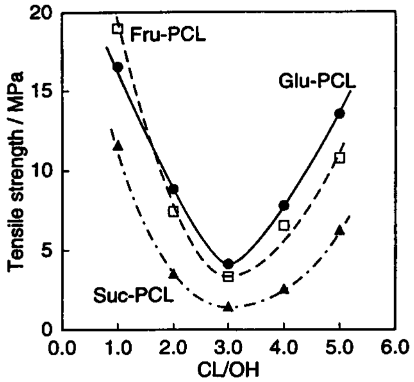

Fig. 10. Change of tensile strength of PU's prepared from saccharide-based PCL's with various CL/OH ratios.

● : PU from glucose based PCL

□ : PU from fructose-based PCL

▲ : PU from sucrose-based PCL

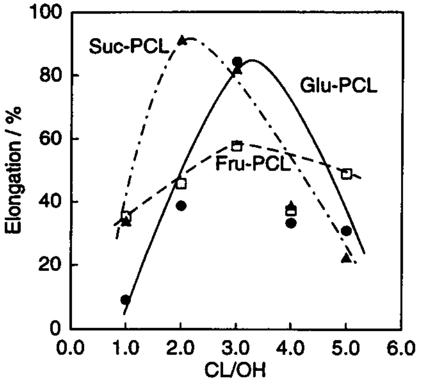

Fig. 11. Change of elongation of PU's prepared from saccharide-based PCL's with various CL/OH ratios.

● : PU from glucose-based PCL

□ : PU from fructose-based PCL

▲ : PU from sucrose-based PCL

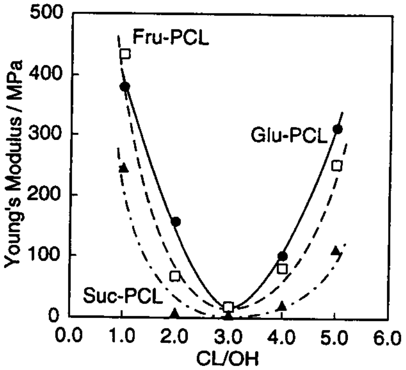

Fig. 12. Change of Young's modulus of PU's prepared from saccharide-based PCL's with various CL/OH ratios.

● : PU from glucose-based PCL

□ : PU from fructose-based PCL

▲ : PU from sucrose-based PCL

As shown in Fig. 8, T_d's of PU's increased from ca. 320 °C to 380 °C with increasing CL / OH ratio. From this result, it is considered that the dissociation of the urethane linkage formed between the isocyanate group and the OH group of PCL with increased chain length seems to occur with more difficulty than that formed between the isocyanate group and the OH group of saccharides.

Fig. 9 shows the relationship between the weight residue and the CL/OH ratios in PU's derived from saccharide-based PCL's. There appears to be almost a linear relationship between the residue at 450 °C and the CL/OH ratio, suggesting that the saccharides constitute a significant part of the residual products. This indicates that the thermal decomposition of these PU's is to a fairly large extent caused by the dissociation of isocyanate groups and hydroxyl groups of PCL.

Mechanical Properties

Fig. 10 shows the change of tensile strength of the prepared PU's with increasing CL / OH ratio. The tensile strength of PU's decreases with increasing CL / OH ratio and reaches a minimum when the CL / OH ratio is 3. The tensile strength becomes larger again with increasing CL / OH ratio when this value exceeds 3. On the other hand, as shown in Fig. 11, the elongation of PU's increases with increasing CL / OH ratio and reaches a maximum when the CL / OH ratio is 3, although the maximum values are different in PU's derived from different saccharide-based PCL's. The elongation becomes smaller again with increasing CL / OH ratio when this value exceeds 3.

As shown, in Fig. 12, Young's modulus of PU's showed a similar tendency as observed in the change of tensile strength of the prepared PU's with increasing CL / OH ratio. Young's modulus of PU's decreases with increasing CL / OH ratio and reaches a minimum when the CL / OH ratio is 3. Young's modulus becomes larger again with increasing CL / OH ratio when this value exceeds 3.

The above facts suggest that PCL chains attached to the OH groups of saccharides act as a soft segment in PU molecules when CL / OH ratio is below 3. However, the PCL molecular chains form a crystalline region when CL /OH ratio is over 3 and the PU matrix becomes rigid. As recognized from Figs. 10, 11 and 12, the sucrose-containing PU's have lower tensile strength, higher elongation and lower Young's modulus than the other samples. Since sucrose contains fewer OH groups per unit of mass than glucose and fructose, the sucrose PU's have lower crosslinking density. Also, since the NCO/OH ratio was kept constant, the PU's derived from the Suc-PCL have lower MDI content than the corresponding PU's derived from the Glu- and Fru-PCL.

Conclusions

(1) T_g's decreased with increasing CL / OH ratio. This suggests that the PCL chains act as a soft segment in the amorphous region of PU molecules. It was found that the PU's derived from the saccharide-based PCL's with CL/OH ratios over 4 have a crystalline region in the molecular structure.

(2) T_d's of PU's increased with increasing amounts of PCL chains in PU's. The dissociation of the urethane linkage formed between the isocyanate group and the OH group of PCL with increased chain length seems to occur with more difficulty than that formed between the isocyanate group and the OH group of saccharides.

(3) The tensile strength of PU's decreased with increasing CL / OH ratio and reached a minimum when the CL / OH ratio was 3. The tensile strength became larger with increasing CL / OH ratio when this value exceeded 3. Young's modulus of PU's showed a similar tendency. The above facts suggest that PCL attached to the OH groups of saccharides act as a soft segment in PU molecules when CL / OH ratio is below 3. However, the PCL molecular chains form a crystalline region when CL /OH ratio is over 4 and the PU matrix becomes rigid.

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