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Synthesis and Properties of Poly(ϵ -caprolactone)-based Poly(ester-urethane)s Having Quaternary Ammonium GroupsYuushou NAKAYAMA^{*1}, Naoki MATSUBARA^{*1}, Ryo TANAKA^{*1}, Zhengguo CAI^{*1*2}, Takeshi SHIONO^{*1}, Hiroyuki SHIRAHAMA^{*3} and Chikara TSUTSUMI^{*4}

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ϵ -Caprolactone (CL) was polymerized by using *N*-methyldiethanolamine as an initiator followed by chain extension with hexamethylene diisocyanate afforded PCL-based poly(ester-urethane)s (PCLUs) with equally spaced tertiary amine groups. Treatment of the PCLUs with iodomethane converted tertiary amine groups to quaternary ammonium groups to give cationic ionomers. The thermal and mechanical properties of the obtained polymers were investigated.

N-メチルジエタノールアミン (NMDA) を開始剤として Sn(Oct)₂ 存在下で ϵ -カプロラクトン (CL) の開環重合を行うことにより、主鎖の中央に三級アミノ基を導入した両末端水酸化ポリ CL (PCL) を合成した。生成したポリマーを単離することなく、引き続きヘキサメチレンジイソシアナートを加えることによって鎖拡張反応を行い、等間隔に三級アミノ基を有するポリ (エステル *e*-ウレタン) (PEU) を合成した。得られた PEU を CH₃I で処理することによって PCL ベースのカチオン性アイオノマーを合成した。その結果、アイオノマー化前後で熱的性質はほとんど変化せず、引っ張り試験における破断伸びが増加しアイオノマー化により靱性が向上する傾向が見られた。

Key Words

Poly(ϵ -caprolactone), Polyurethane, Ionomer

1. Introduction

Because of recent environmental problems, biodegradable polymers are focusing attentions. Aliphatic polyesters such as poly(ϵ -caprolactone) (PCL) and poly(L-lactide) (PLLA) have been known as representative biodegradable polymers¹⁾²⁾. PLLA is also known as a bio-based polymer³⁾. Although PCL is made from oil, a recent report have indicated possibility of the production of PCL from biomass⁴⁾. Improvements of the properties of these polymers have widely been studied⁵⁾⁶⁾.

An effective method to improve the mechanical properties of polymers is introduction of small amounts of ionic groups (usually no more than 15%), and the resulting materials are called ionomers⁷⁾⁸⁾. Several ionomers based on aliphatic polyesters have been reported^{9)~15)}.

We have recently synthesized poly(ester-urethane)s based on PLLA from one-pot synthesis via polymerization of L-lactide with *N*-methyldiethanolamine (NMDA) followed by chain extension of the resulting PLLA-diols with hexamethylene diisocyanate (HMDI)¹⁶⁾. The PLLA-based poly(ester-urethane)s with tertiary amine groups (PLLAU) were treated with iodomethane (MeI) to form PLLA-based cationic ionomers. The thermal, mechanical, hydrophilic, and biodegradation properties of the obtained polymers were investigated. In comparison with PLLA homopolymer, the obtained PLLAUs exhibited much higher elongation at break. Moreover, the MeI-treatment of the neutral PLLAUs effectively improved their tensile modulus and hydrophilicity. To our knowledge, this type of PCL-based poly(ester-urethane) has not been reported.

In this study, similar cationic ionomers based on PCL

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Scheme 1 Preparation of PCL-based ionomers

were synthesized (Scheme 1), and their properties were studied.

2. Experimental

2.1 General remarks

All the manipulations were carried out under an atmosphere of pure and dry nitrogen, using standard Schlenk techniques. *N*-Methyldiethanolamine (NMDA) (99%, Aldrich), ϵ -caprolactone (CL) (Daicel Chemical Industries) and 1,6-hexamethylene diisocyanate (HMDI) (98%, Aldrich) were distilled under vacuum and preserved on molecular sieves 4A. Tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) (95%, Aldrich) was diluted by dry-toluene and used as a solution (77 $\mu\text{mol}/\text{ml}$). Toluene was purified by distillation from sodium-benzophenone. Iodomethane (99.5%, Wako) was used without further purification. Dehydrated tetrahydrofuran (THF) was purchased from Kanto Chemical Co.

2.2 Synthesis of PCLUs containing equally spaced tertiary amine groups

A typical procedure: A dry-toluene solution of the catalyst $\text{Sn}(\text{Oct})_2$ (77 $\mu\text{mol}/\text{ml}$, 0.42 ml) was added to a solution of CL (3.3 ml, 3.1 mmol) and NMDA (90 μl , 790 μmol) in toluene (30 ml) at 100 $^{\circ}\text{C}$. After 24 h, the solution was cooled to 60 $^{\circ}\text{C}$, and HMDI (152 μl , 946 μmol) was added. The mixture was stirred at 60 $^{\circ}\text{C}$ for 5 h and then poured into methanol. The precipitated polymer was collected by centrifugation and dried in vacuo.

2.3 Preparation of cationic ionomer films (PCLU-Mel) by using iodomethane

A typical procedure: Iodomethane (1.0 ml) was added to a solution of PCLU (0.3 g) in THF (5.0 ml). After stirring at 30 $^{\circ}\text{C}$ for 10 h, the mixture was evaporated to dryness. Then, the residue was dissolved in chloroform (4.0 ml). The solution was placed into a 5 cm petri dish and dried in air

at room temperature for 3 days, followed by further drying in vacuo at room temperature for 1 day.

2.4 Degradation test in a Compost

Commercially available effective microorganism (EM) fermented solution (30 ml) containing *Rhodospirillum*, *Rhodopseudomonas*, *Pseudomonas*, *Micrococcus*, *Bacillus*, *Lactobacillus*, *Streptococcus*, *Saccharomyces*, *Aspergillus*, *Penicillium* etc. and theriaca syrup (40 ml) were added to 2000 ml of water, and this solution was sprayed on the mixture of rice hulls (5 kg) and rice bran (15 kg). Resulting material was wrapped with a polyethylene film and then dried in the shade for 1 day. The samples were sealed in polyethylene mesh and held in the resulting compost for a fixed time. The evaluation of the biodegradation was carried out by measuring the weight loss in the compost.

3. Results and Discussion

By using dimethylolpropionic acid (DMPA) as an initiator, CL was successfully polymerized in the presence of $\text{Sn}(\text{Oct})_2$ as a catalyst to give hydroxytelechelic PCLs (PCL-diols) (Table 1). The feed $[\text{CL}]_0/[\text{diol}]$ ratios, 40, 80, and 120, were employed. All the PCL-diols were obtained in almost quantitative yields. The molecular weights of the PCL-diols increased with increasing feed monomer to initiator

Table 1 Polymerization of ϵ -caprolactone initiated by NMDA in the presence of $\text{Sn}(\text{Oct})_2$

Run	$[\text{CL}]_0/[\text{I}]$	Yield (%)	$M_n^a \times 10^{-3}$	M_w/M_n^a
1	40	88	3.0	1.14
2	80	99	9.0	1.10
3	120	80	13.0	1.25

Polymerization conditions : $[\text{CL}]_0/[\text{Sn}(\text{Oct})_2] = 1000$, $[\text{CL}]_0 = 1.04$ M, Initiator (I) = NMDA, Temp = 100 $^{\circ}\text{C}$, Time = 24 h, Solvent = 2 ml of toluene. a)Determine by GPC calibrated with polystyrene standard.

ratio, while their molecular weight distributions were kept narrow ($M_w/M_n \leq 1.3$), indicating that the CL polymerization proceeded in a well-controlled fashion.

The PCL-based poly(ester-urethane)s (PCLUs) with tertiary amine groups were prepared from the ring-opening polymerization of CL by using NMDA as an initiator to generate PCL-diols in situ, followed by successive chain extension with HMDI (Table 2). The number following "PCLU" in the sample name means feed monomer to initiator ratio ($[CL]_0/[I]$). Comparison of Table 2 with Table 1 indicates that the PCLUs are composed of 7-20 PCL-diol chains, suggesting the successful chain extension. The 1H NMR spectra of the obtained PCLUs also supported the formation of the PCLUs with the expected structure.

The obtained PCLUs were treated with a large excess of iodomethane (MeI) in THF to produce the corresponding cationic ionomers. Fig. 1 shows the 1H NMR

spectra of the PCLU40 before and after MeI-treatment. The signals for the neutral NMDA moiety (f, g, and h) completely disappeared and new signals (f', g', and h') appeared at lower magnetic fields after MeI-treatment, indicating the complete conversion of the tertiary amine groups to quaternary ammonium groups by MeI-treatment.

Table 3 summarizes the thermal properties of the neutral and the MeI-treated PCLUs (PCLU-MeI). The glass transition temperature (T_g), melting temperature (T_m), and heat of fusion (ΔH_m) values were not significantly affected by MeI-treatment. On the other hand, 5% degradation temperature (T_{d5}) of the polymers tended to be lowered by MeI-treatment, indicating lower thermal stabilities of the PCLU-MeIs than those of the neutral PCLUs. This is in sharp contrast to the fact that the degradations of the PCLU-MeIs were slower than the corresponding PCLUs in compost at 45 and 60 °C (vide infra). We speculate that the iodide counter ion could cause nucleophilic attack to ester bonds to promote decomposition of the polymers at high temperature. The T_{d5} values of the PCLU-MeIs are still much higher than their T_m values (48-56 °C), indicating that the lower thermal stabilities of the PCLU-MeI might not limit their practical applications.

Table 4 shows the mechanical properties of the PCLU and PCLU-MeI films recorded on a tensile testing machine. All the PCLUs and PCLU-MeIs showed much higher elongation at break values ($\sim 2000\%$) than that of PCL homopolymer (15%), indicating improved toughness of the PCLUs and PCLU-MeIs. Wang and coworkers

Table 2 Synthesis of the PCLUs with NMDA units

Sample	$[CL]_0/[I]$	Yield (%)	$M_n^{a)} \times 10^{-3}$	$M_w/M_n^{a)}$
PCLU40	40	98	59	1.6
PCLU80	80	>99	65	2.1
PCLU120	120	94	189	2.2

Polymerization conditions: $[CL]_0/[Sn(Oct)_2] = 1000$, $[CL]_0 = 0.50$ M, Initiator (I) = NMDA, Temp. = 100 °C, Time = 24 h, Solvent = 30 ml toluene. Chain extension conditions: $[HMDI]/[NMDA] = 1.2$, Temp. = 60 °C. a) Determined by GPC calibrated with polystyrene standards.

Fig. 1 1H NMR spectra of PCLU40 before and after treatment with MeI ($CDCl_3$, r.t.)

Table 3 The effect of ionomerization on thermal properties

Sample	$M_n \times 10^{-3}$	$T_{ds} (^{\circ}\text{C})^a$	$T_g (^{\circ}\text{C})^b$	$T_m (^{\circ}\text{C})^b$	$\Delta H_m (\text{kJ/kg})^b$
PCLU40	59	299.3	-64.1	48.4	68.6
PCLU40-MeI	—	275.1	-61.4	49.0	74.2
PCLU80	65	309.9	-63.7	51.8	87.7
PCLU80-MeI	—	292.6	-62.0	54.6	76.9
PCLU120	189	302.9	-62.1	53.7	60.1
PCLU120-MeI	—	294.7	-62.0	56.3	62.4

a) Determined by TG/DTA

b) Determined by DSC

Table 4 Mechanical properties of the PCLU and ionomer films

Sample	NMDA ^{a)} (mol%)	Tensile modulus (MPa)	Tensile strength ^{b)} (MPa)	Elongation at break ^{b)} (%)
PCLU40	2.4	900	31	2000
PCLU40-MeI	—	710	31	2500
PCLU80	1.2	1020	32	1900
PCLU80-MeI	—	620	28	2200
PCLU120	0.8	670	31	2100
PCLU120-MeI	—	740	36	2300
PCL ^{c)}	—	120	11	15

a) Theoretical values

b) Determined on an Orientic universal testing machine RTC-1210A

c) $M_n = 10000$ (*React. Funct. Polym.* 67, 798-806(2007))

reported poly(caprolactone-urethane) using 1,4-butanediol as an initiator, which exhibited elongation at break of 1000-1400% ¹⁷⁾. The present NMDA-containing PCLUs are more effectively improved than those without NMDA, this could come from the higher polarity of the former to enhance intermolecular interaction. The treatment of the PCLUs with MeI further improved the elongation, possibly due to aggregation of ionic groups in the polymer.

Biodegradation tests of the PCLUs and PCLU-MeIs

were performed in a compost at 45 °C (Fig. 2) and at 60 °C (Fig. 3). At 45 °C (lower than T_m), only PCLU40 showed significant weight loss after 28 days. At 60 °C (higher than T_m), all the samples exhibited significant weight-loss after 28 days. The degradation of PCLU40-MeI was slower than those of PCLU40 and PCL. Similar tendency was observed in the corresponding PLLA-based polyurethanes and their ionomers ¹⁶⁾. This could come from lower basicity and/or antibacterial activity of quaternary ammonium groups

Fig. 2 Biodegradation of the poly(ester-urethane)s in compost at 45 °C. Samples: PCLU40 (■), PCLU40-MeI (□), PCLU120 (○), PCLU120-MeI (■), PCL (×)

Fig. 3 Biodegradation of the poly(ester-urethane)s in compost at 60 °C. Samples: PCLU40 (■), PCLU40-MeI (□), PCLU120 (▲), PCLU120-MeI (△), PCL (×)

in comparison with tertiary amine groups. PCLU120 and PCLU120-MeI showed similar biodegradation behavior, possibly due to their very low NMDA content.

4. Conclusion

A series of PCLUs with equally spaced tertiary amine groups was successfully prepared by CL polymerization with NMDA as an initiator followed by chain extension with HMDI. The treatment of the obtained PCLUs with iodomethane converted tertiary amine groups to quaternary ammonium groups to form PCL-based cationic ionomers (PCLU-MeIs). Ionization of the PCLUs somewhat lowered their thermal stabilities and enhanced their elongation properties. These materials possess relatively soft and biodegradable nature and potentially antibacterial activity, which could be applied to biomedical applications such as absorbable scaffold, implants, and disinfectant apparatus.

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