

Thermal and Mechanical Properties of Semi-Interpenetrating Polymer Networks Composed of Diisocyanate-Bridged, Four-Armed, Star-Shaped ϵ -Caprolactone Oligomers and Poly(ϵ -caprolactone)

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ABSTRACT: Semi-interpenetrating polymer networks (S-IPNs) were prepared by the reactions of hydroxyl-terminated four-armed, star-shaped ϵ -caprolactone oligomers with degrees of polymerization per one oligocaprolactone chain (n s) of 3, 5, and 10 and 2,4-tolylene diisocyanate (TDI) in the presence of poly(ϵ -caprolactone) (PCL). In the dynamic mechanical analysis of the S-IPN [2,4-tolylene diisocyanate bridged hydroxyl-terminated four-armed, star-shaped ϵ -caprolactone oligomer (TH4CLO)/PCL], only one $\tan \delta$ peak was observed; its temperature increased with increasing TH4CLO content and with decreasing n value. Differential scanning calorimetric analyses of the TH4CLOs and TH4CLO/PCLs revealed that the TH4CLOs with n s of 3 and 5 were amorphous, whereas TH4CLO with an n of 10 was semicrystalline and that the crystallization of the PCL chain for TH4CLO/PCLs was more strongly disturbed with increasing TH4CLO content and decreasing n value. Although the tensile strength, modulus, and elongation at break of TH4CLO were much lower than those of PCL, those values increased with the n value. Although the tensile strength and modulus of the TH4CLO/PCLs decreased with increasing TH4CLO content, TH4CLO ($n = 3$)/PCL 50/50 showed the highest elongation at break (314%) among the S-IPNs because of the suppression of crystallization of the polycaprolactone chain. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Poly(ϵ -caprolactone) (PCL) is a biodegradable, semicrystalline, flexible polymer, which has low glass-transition and melting temperatures ($T_g \approx -60^\circ\text{C}$ and $T_m \approx 60^\circ\text{C}$, respectively)¹ and has similar mechanical properties to low-density polyethylene.² Its long-term degradation and intracellular resorption, associated with its hydrophobic character and high crystallinity (χ_c), has restricted its use as a biomaterial. However, PCL has recently attracted increasing attention as an implantable polymeric scaffold material for tissue engineering because of its superior moldability, stability in ambient conditions, and low cost.^{3,4} To achieve tailorable material properties for diverse tissue engineering applications and the regulation of cell behavior, blends of PCL with other biodegradable polymers, such as polysaccharide,^{5,6} poly(D,L-lactic-co-glycolic acid),^{7,8} and chitosan,⁹ and polymer networks containing oligocaprolactone or polycaprolactone chains have been investigated in past studies. With regard to the latter polymer network, crosslinked resins of poly(ϵ -caprolactone fumarate),^{10,11} the diacrylated product of

PCL diol,^{12,13} and the reaction product of diglycerol-initiated star-shaped oligo(ϵ -caprolactone) with maleic or itaconic anhydride¹⁴ have been reported. Recently, semi-interpenetrating polymer networks (S-IPNs) composed of PCL and crosslinked poly(propylene fumarate) (PPF) have also reported.¹⁵ The control of χ_c and the crosslinking density is very important in tuning the mechanical and surface physicochemical properties that regulate cell behavior for polymer networks and S-IPNs containing oligocaprolactone or polycaprolactone chains. In particular, the crystallization behavior of a linear semicrystalline polymer entangled in a network polymer of a S-IPN is a very interesting subject.

Recently, it has been reported that the crosslinking reaction of two kinds of four-armed, star-shaped ethylene glycol oligomers in water generates a high-strength hydrogel with homogeneous network.^{16–18} With regard to the S-IPNs containing star polymers or oligomers, Wu et al.¹⁹ reported an S-IPN hydrogel composed of a 21-armed star polymer and crosslinked poly(vinyl alcohol). However, an S-IPN-containing crosslinked

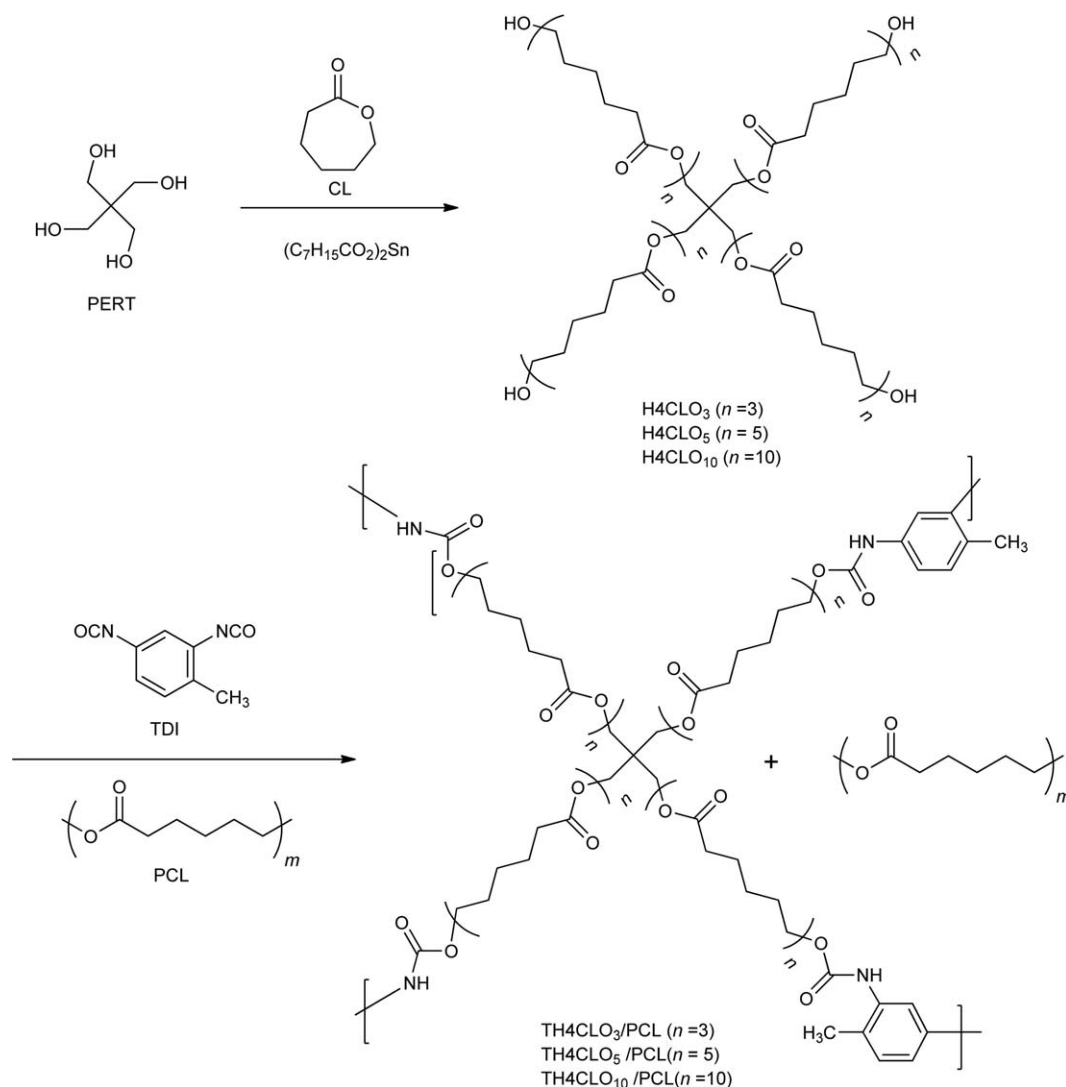


Figure 1. Synthetic scheme of the H4CLOs and TH4CLO/PCLs.

star polymer or oligomer and linear polymer has not yet been reported to the best of our knowledge. In this study, we dealt with homogeneous polymer networks [2,4-tolylene diisocyanate bridged hydroxyl-terminated four-armed, star-shaped ϵ -caprolactone oligomer (TH4CLOs)] prepared by the reactions of hydroxyl-terminated four-armed, star-shaped ϵ -caprolactone oligomers (H4CLOs) with the degrees of polymerization per one oligocaprolactone chain (n s) of 3, 5, and 10 and 2,4-tolylene diisocyanate (TDI). The thermal and mechanical properties of the TH4CLOs and S-IPNs of TH4CLO/PCL were investigated in relation to the crosslinking density and χ_c .

EXPERIMENTAL

Materials

Pentaerythritol (PERT), ϵ -caprolactone (CL), and TDI were purchased from Tokyo Chemical Industry Co., Ltd. Tin(II) bis(2-ethylhexanoate) [$Sn(Oct)_2$] was purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). 1,2-Dichloroethane was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). PCL [Cel Green P-H7, density = 1.14 g/cm^3 , melt flow rate (190°C ,

2.16 kg) = 1.7 g/10 min] was supplied from Daicel Co., Ltd. (Osaka, Japan). All of the reagents were used without further purification.

Syntheses of Hydroxyl-Terminated, Four-Armed, Star-Shaped ϵ -Caprolactone Oligomers (H4CLOs)

The synthesis of H4CLO has previously been reported by several groups.^{20–22} A typical synthetic procedure of H4CLO with a theoretical degree of polymerization of CL per one arm, n of 5 in this study was as follows: PERT (5.96 g, 43.8 mmol) and CL (100.0 g, 876 mmol) were put into a nitrogen-purged, three-necked flask. The mixture was heated to 150°C until complete dissolution of PERT was achieved, and then, $Sn(Oct)_2$ (1.00 g, 2.47 mmol) was added to the flask. After the evacuation and nitrogen-purging processes were repeated three times, the resulting mixture was stirred at 150°C under a nitrogen atmosphere for 24 h. To the cooled reaction mixture, we added hexane (300 mL) with stirring, and then, the supernatant was decanted off. This process was repeated three times, and the separated viscous liquid was dried at 40°C *in vacuo* to give H4CLO₅ (where the subscripted number represents the n value) as a colorless viscous

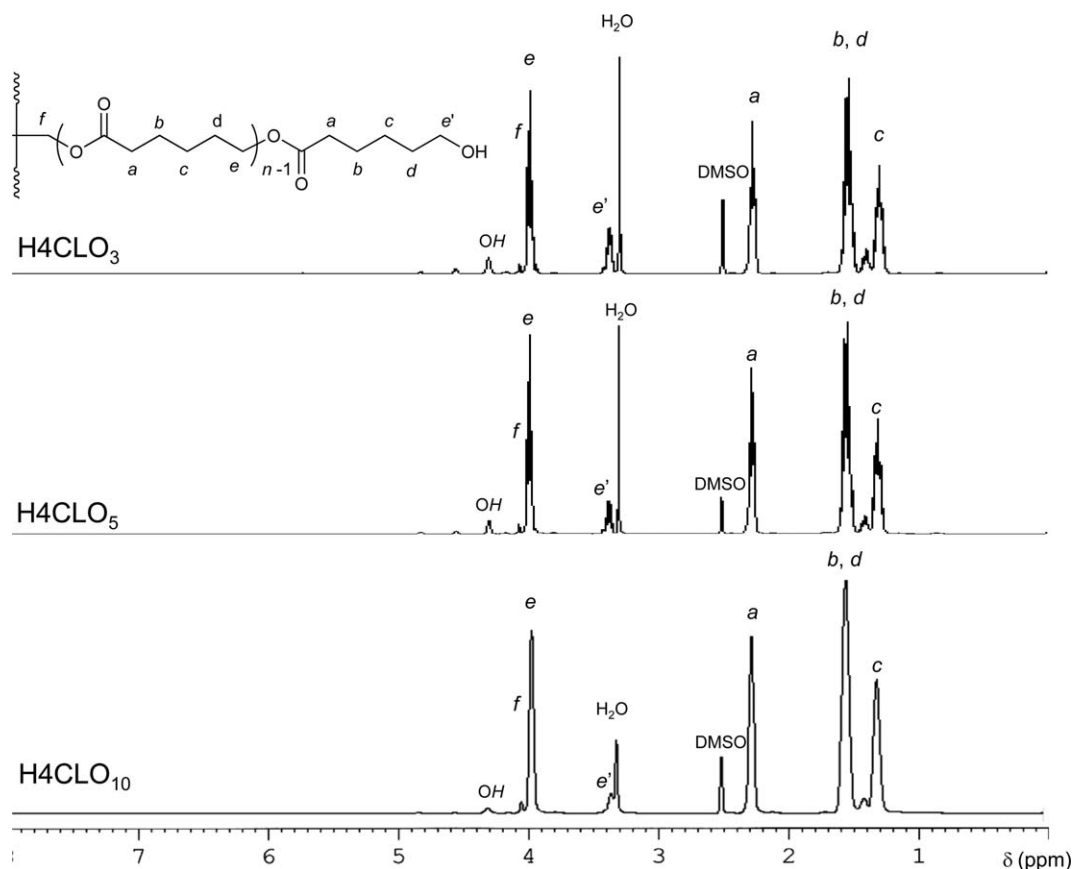


Figure 2. $^1\text{H-NMR}$ spectra of the H4CLO_n ($n = 3, 5, \text{ and } 10$) in hexadeuterated dimethyl sulfoxide.

liquid (yield = 93.2 g, 88.0%). The n measured by the $^1\text{H-NMR}$ method was 4.90.

H4CLO_3 was also obtained as a colorless viscous liquid (yield = 63.5 g, 76.1%) in a manner similar to the previous synthetic procedure except with the following values: PERT (7.54 g, 55.4 mmol), CL (75.9 g, 665 mmol), and $\text{Sn}(\text{Oct})_2$ (0.83 g, 2.04 mmol). H4CLO_{10} was also obtained as a colorless viscous liquid (yield = 50.6 g, 89.1%) in a manner similar to the previous synthetic procedure except with the following values: PERT (1.50 g, 11.0 mmol), CL (55.3 g, 484 mmol), and $\text{Sn}(\text{Oct})_2$ (0.50 g, 1.23 mmol). The values of n measured by the $^1\text{H-NMR}$ method for H4CLO_3 and H4CLO_{10} were 2.99 and 9.70, respectively. The n measured by the $^1\text{H-NMR}$ method was used for the calculation of the feed amount of the following reactions of H4CLO_n and TDI.

Preparation of Semi-IPNs of TH4CLO/PCL

A solution of H4CLO_5 (1.70 g, 0.716 mmol), TDI (0.25 g, 1.43 mmol), and PCL (1.95 g) in 1,2-dichloroethane (15 mL) was poured into a Petri dish (diameter: 75 mm) made of polytetrafluoroethylene. The molar ratio of OH/NCO in H4CLO/TDI was fixed at 1/1. The mixture was dried at 60°C for 24 h and then at 85°C for 12 h in an electric oven. The obtained $\text{TH4CLO}_5/\text{PCL}$ 50/50 film was peeled off from the Petri dish. Similarly, TH4CLO_3 , TH4CLO_5 , TH4CLO_{10} , $\text{TH4CLO}_3/\text{PCLs}$ (72/25, 50/50 and 25/75), $\text{TH4CLO}_5/\text{PCLs}$ (72/25 and 25/75),

$\text{TH4CLO}_{10}/\text{PCLs}$ (72/25, 50/50 and 25/75), and PCL films were prepared.

Measurements

$^1\text{H-NMR}$ spectra were recorded at room temperature on a Bruker AV-400 (400 MHz) with hexadeuterated dimethyl sulfoxide as a solvent and tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were recorded at room temperature in the range from 4000 to 500 cm^{-1} on a Shimadzu FTIR 8400s by the attenuated total reflectance method. The IR spectra were acquired with 50 scans at a resolution of 4 cm^{-1} . Dynamic mechanical analysis (DMA) of the rectangular plates ($40 \times 8 \times 0.5\text{ mm}^3$) was performed on a Rheograph Solid instrument (Toyo Seiki Co., Ltd., Tokyo, Japan) under an air atmosphere with a chuck distance of 20 mm, a frequency of 1 Hz, and a heating rate of $2^\circ\text{C}/\text{min}$ on the basis of ISO 6721-4:1994. The differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer Diamond DSC instrument under a helium atmosphere. To eliminate the thermal history of the samples (8–12 mg), the samples were heated from -100 to 100°C at a heating rate of $20^\circ\text{C}/\text{min}$, held at that temperature for 3 min, and then cooled to -100°C at a cooling rate of $100^\circ\text{C}/\text{min}$. After the sample was held at -100°C for 3 min, the second heating scan was monitored at a heating rate of $20^\circ\text{C}/\text{min}$ to determine T_g , cold crystallization temperature (T_c), heat of crystallization (ΔH_c), T_m , and heat of

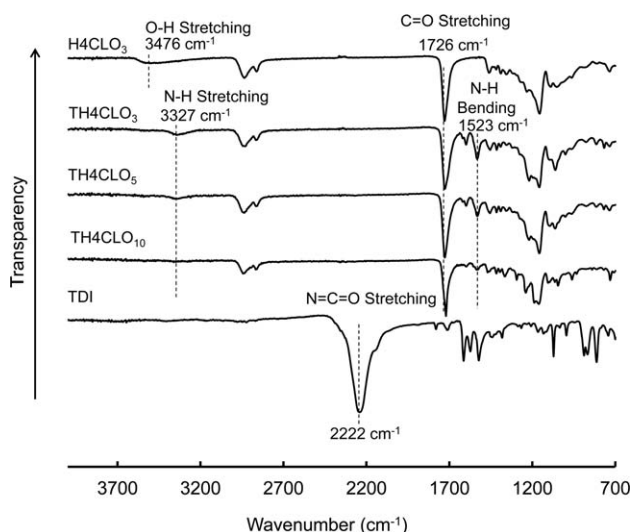


Figure 3. FTIR spectra of the TH4CLOs as compared with those of H4CLO₃ and TDI.

fusion (ΔH_m). Tensile testing of the rectangular specimen (length = 40 mm, width = 5 mm, thickness = 0.5 mm) was performed at 25°C with a Shimadzu Autograph EZ-S on the basis of the standard method for testing the tensile proper-

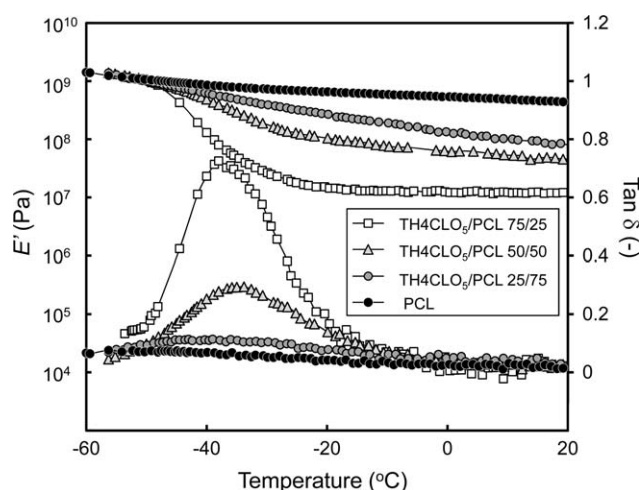


Figure 4. DMA curves of TH4CLO₅/PCL (25/75, 50/50 and 75/25) and PCL.

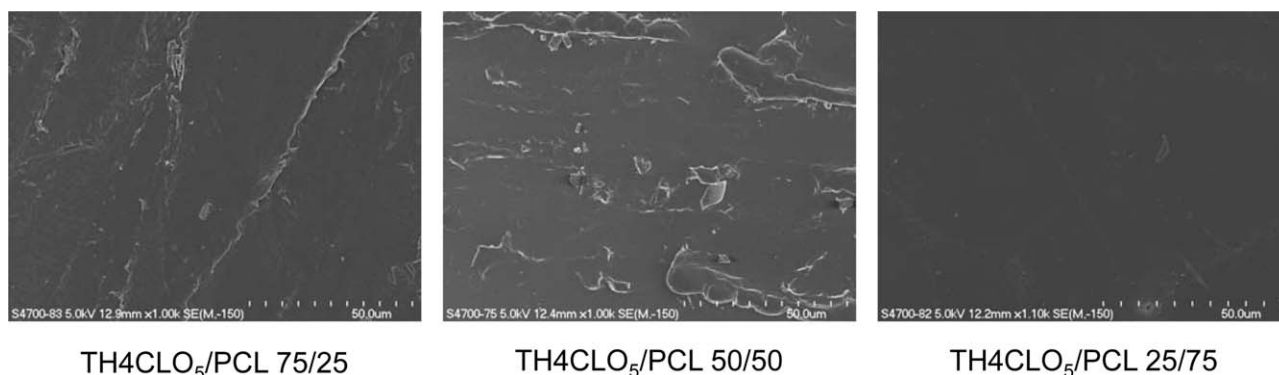


Figure 5. FESEM images of TH4CLO₅/PCL (25/75, 50/50, and 75/25).

Table I. DMA Data for the TH4CLO/PCLs and PCL

Sample	Tan δ peak temperature (°C)	E' (MPa)	
		-20°C	0°C
TH4CLO ₃ /PCL 75/25	-19.0	110	9.8
TH4CLO ₃ /PCL 50/50	-22.6	268	110
TH4CLO ₃ /PCL 25/75	-32.0	305	113
TH4CLO ₅ /PCL 75/25	-38.7	15.2	12.2
TH4CLO ₅ /PCL 50/50	-35.4	105	62.0
TH4CLO ₅ /PCL 25/75	-40.3	272	133
TH4CLO ₁₀ /PCL 75/25	-42.8	263	140
TH4CLO ₁₀ /PCL 50/50	-44.9	347	235
TH4CLO ₁₀ /PCL 25/75	-48.9	452	343
PCL	-56.3	656	540

ties of plastics [JIS K7161:1994 (ISO527-1:1993)]. The span length and testing speed were 25 mm and 5 mm/min, respectively. Five specimens were tested for each set of samples, and the mean values and the standard deviation were calculated. The morphology of the cured resins was observed by field emission scanning electron microscopy (FESEM) with a Hitachi S-4700 machine (Hitachi High-Technologies Corp., Tokyo, Japan).

RESULTS AND DISCUSSION

Characterization of H4CLO and TH4CLO

H4CLOs with the theoretical ns of 3, 5, and 10 were synthesized by the ring-opening polymerization reactions of CL initiated by PERT in the presence of Sn(Oct)₂ (Figure 1). Figure 2 shows the ¹H-NMR spectra of the H4CLOs ($n = 3, 5, \text{ and } 10$). The ¹H signals of repeating methylene units adjacent to a carbonyl group (a , $-\text{COCH}_2-$, δ 2.29 ppm) and those of the terminal methylene units connected to hydroxyl groups (e' , $-\text{CH}_2\text{OH}$, δ 3.38 ppm) were quite distinguishable for the ¹H-NMR spectra of H4CLOs. From the integral ratio of these proton signals, the ns for the H4CLOs ($n = 3, 5, \text{ and } 10$) were calculated to be 2.99, 4.90, and 9.70, respectively. The calculated n values were found to be in good agreement with the theoretical values, which were solely predictable from the feed CL/hydroxyl ratios.

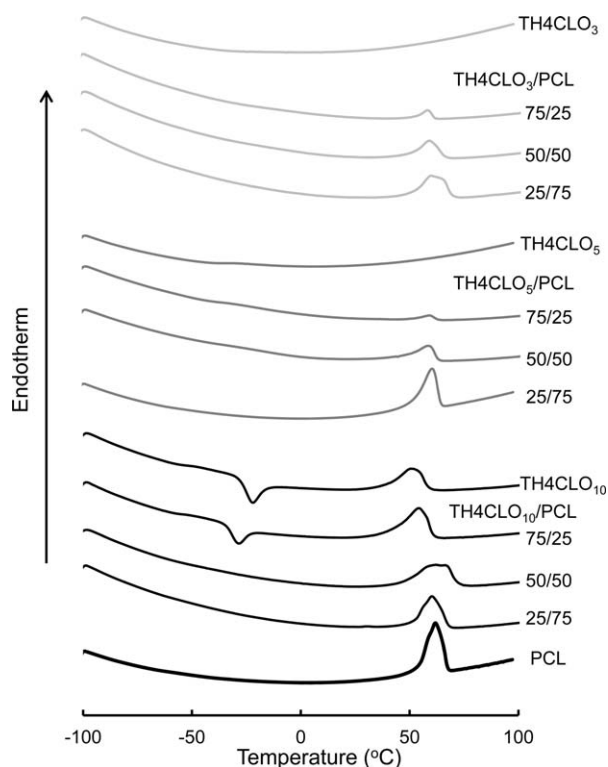


Figure 6. Second-heating DSC curves of the TH4CLOs, TH4CLO/PCLs, and PCL.

Figure 3 shows the FTIR spectra of the TH4CLOs ($n = 3, 5,$ and 10) compared with those of H4CLO₃ and TDI. The absorption band of O—H stretching vibrations for H4CLO₃ at 3476 cm^{-1} and that of the NCO stretching vibrations at 2222 cm^{-1} for TDI disappeared for TH4CLO₃. New absorption bands of the N—H stretching vibrations and N—H bending vibrations appeared at 3327 and 1523 cm^{-1} for TH4CLO₃,

respectively. These results suggest that the reaction of the hydroxyl group of H4CLO₃ and the isocyanate group of TDI proceeded smoothly to generate the polymer network bridged by urethane linkages. As the absorption band of the C=O stretching vibrations of the urethane bond overlapped at 1726 cm^{-1} with that of the C=O stretching vibrations of the original ester bond, we could not identify it a new, separated absorption band. A similar trend was observed for TH4CLO₅ and TH4CLO₁₀. Also, the reactions of the H4CLOs and TDI in the presence of PCL also proceeded smoothly to give the TH4CLO/PCLs (25/75, 50/50, and 75/25).

Properties of H4CLO/PCL

Figure 4 shows DMA curves of TH4CLO₅/PCL and PCL. TH4CLO₅ was so soft that a good DMA curve was not obtained. TH4CLO₅/PCL (25/75, 50/50, and 75/25) showed only one $\tan \delta$ peak, whose height weakened with increasing PCL content. All of the TH4CLO/PCLs showed similar trends; this implied that PCL was completely miscible with TH4CLO in the amorphous region and that the content of amorphous components related to the glass transition decreased with the increasingly high crystalline PCL content. The $\tan \delta$ peak temperatures increased with increasing TH4CLO content and with decreasing n value for all of the TH4CLO/PCLs, except for TH4CLO₃/PCL 50/50 (Table I). In the case of PCL and TH4CLO/PCL with a PCL content higher than 50 wt %, the $\tan \delta$ peak was very weak and broad because of the high χ_c . The storage modulus (E') at a temperature not less than -20°C for TH4CLO/PCLs increased with PCL content (Table I). Figure 5 shows the FESEM micrographs of the surface of 25/75, 50/50, and 75/25 TH4CLO₅/PCL. Although some cracks or defects arose when the 25/75 and 50/50 films were peeled off, all of the samples did not show any microphase separation; this indicated that the PCL chain was twined in the network of TH4CLO₅. Also,

Table II. DSC Parameters for the TH4CLOs, TH4CLO/PCLs, and PCL

Sample	T_g ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	ΔH_c (J/g)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	Estimated ΔH_m (J/g) ^a	χ_c (%) ^b
TH4CLO ₃	—	—	—	—	0	0	0
TH4CLO ₃ /PCL 75/25	—	—	—	58.0	7.4	16.5	15.1
TH4CLO ₃ /PCL 50/50	—	—	—	58.7	22.1	33.1	16.4
TH4CLO ₃ /PCL 25/75	—	—	—	59.8	43.1	49.6	31.9
TH4CLO ₅	-41.4	—	—	—	0	0	0
TH4CLO ₅ /PCL 75/25	-41.6	—	—	58.7	4.3	16.5	3.2
TH4CLO ₅ /PCL 50/50	—	—	—	58.4	25.7	33.1	19.0
TH4CLO ₅ /PCL 25/75	—	—	—	60.1	48.1	49.6	35.6
TH4CLO ₁₀	-48.7	-22.3	-43.2	50.6	45.4	45.4	33.6
TH4CLO ₁₀ /PCL 75/25	-50.1	-28.9	-38.3	54.0	48.9	50.6	40.0
TH4CLO ₁₀ /PCL 50/50	—	—	—	62.1	49.6	55.8	46.0
TH4CLO ₁₀ /PCL 25/75	—	—	—	60.1	60.1	60.9	44.5
PCL	(-63.0)	—	—	61.8	66.1	66.1	49.0

^a Estimated $\Delta H_m = (\text{Weight fraction of TH4CLO}_n) \times (\Delta H_m \text{ of TH4CLO}_n) + (\text{Weight fraction of PCL}) \times (\Delta H_m \text{ of PCL})$.

^b $\chi_c = (\Delta H_m / \Delta H_m^c) \times 100$.

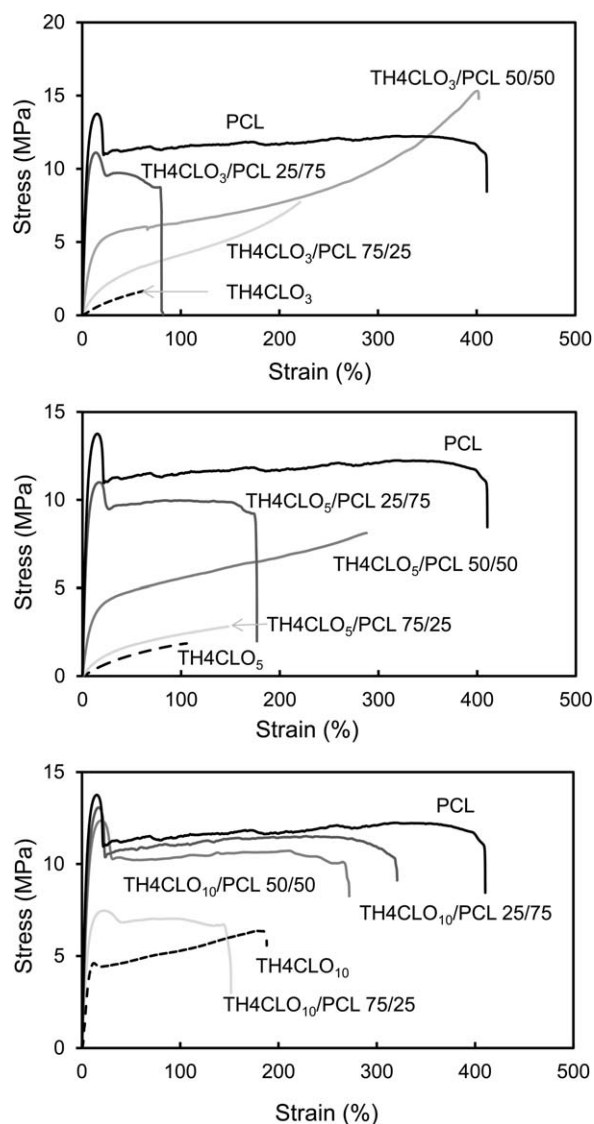


Figure 7. Stress–strain curves of the TH4CLOs, TH4CLO/PCLs, and PCL.

no phase separation was observed for the S-IPNs based on TH4CLO₃ and TH4CLO₁₀.

Figure 6 shows the second heating DSC thermograms for the TH4CLOs, TH4CLO/PCLs, and PCL. Table II summarizes the thermal parameters obtained from the DSC analysis. TH4CLO₃ and TH4CLO₅ showed neither a crystallization exothermic peak nor a melting endothermic peak, whereas TH4CLO₁₀ showed both peaks; this indicated that the former was amorphous, and the latter was semicrystalline. This result should be related to the fact that the crystallization of the oligocaprolactone chain is disturbed by decreasing degree of polymerization and by increasing crosslinking density. A similar suppression of crystallization of the oligocaprolactone chain by crosslinking was reported for the crosslinked poly(ϵ -caprolactone fumarate)s (PCLFs).¹⁰ All of the TH4CLO/PCLs and PCL showed both T_c and T_m . χ_c for TH4CLO/PCL was calculated from the ΔH_m value of TH4CLO/PCL with the following equation:

$$\chi_c(\%) = (\Delta H_m / \Delta H_m^c) \times 100$$

where ΔH_m^c (135 J/g) is heat of fusion of completely crystalline PCL.²³ The value of χ_c increased with increasing PCL content and n value of the TH4CLO component. Furthermore, the estimated heat of fusion (estimated ΔH_m), on the assumption that χ_c of each component of TH4CLO/PCL was the same as that of the single component (TH4CLO or PCL), was calculated by the following equation:

$$\begin{aligned} \text{Estimated } \Delta H_m = & (\text{Weight fraction of TH4CLO}_n) \\ & \times (\Delta H_m \text{ of TH4CLO}_n) + (\text{Weight fraction of PCL}) \\ & \times (\Delta H_m \text{ of PCL}) \end{aligned}$$

Thus, the deviation of the observed ΔH_m for TH4CLO/PCL from the estimated value implied the suppression and/or facilitation of the crystallization of polycaprolactone and oligocaprolactone chains by the blending of the two components. Actually, the observed ΔH_m was lower than the theoretical value for the TH4CLO₃/PCLs and TH4CLO₅/PCLs; this indicated that the crystallization of the PCL twined in the network of TH4CLO₃ and TH4CLO₅ was more strongly disturbed than that of control PCL. This result was very interesting compared with the already reported result that χ_c of PCL did not change in the PCL moiety in the S-IPN of crosslinked PPF and PCL.¹⁵ As a reason for the difference between the TH4CLO/PCL and crosslinked PPF/PCL, the following factors were considered: PCL was more easily twined with the network of TH4CLO than that of crosslinked PPF because TH4CLO itself contained an oligocaprolactone chain, and the regular network of TH4CLO based on a four-armed, star-shaped oligomer more effectively suppressed the crystallization of PCL. However, in the case of the TH4CLO₁₀/PCLs, the observed ΔH_m was almost same as the estimated value; this suggested that the crystallization of PCL twined in the network of TH4CLO₁₀ with a longer distance between the nearest crosslinking points than TH4CLO₃ and TH4CLO₅ was a little suppressed.

Figures 7 and 8 show the typical stress–strain curves and tensile properties for the TH4CLOs, TH4CLO/PCLs, and PCL, respectively. As PCL had the highest χ_c ($\chi_c = 49.0\%$), it showed the highest tensile strength and modulus. Also, PCL showed the highest elongation at break, probably because it contained an amorphous region of 51% composed to the twined linear polymer with a high molecular weight. However, as PCL was a semicrystalline polymer, it broke at an elongation of 410% after yielding at an elongation of 19.2% (Figure 7). The tensile strength, modulus, and elongation at break of TH4CLO increased with increasing n value and were still considerably lower than those of PCL. Although amorphous TH4CLO₃ and TH4CLO₅ broke at elongations of 62 and 106%, respectively, without a decrease in stress due to yielding, the semicrystalline TH4CLO₁₀ broke at an elongation of 188% after yielding at an elongation of 15%. The tensile strength and modulus of TH4CLO/PCLs decreased with increasing TH4CLO content as an approximate tendency (Figure 8). However, 50/50 TH4CLO₃/PCL and 50/50 TH4CLO₅/PCL showed a considerably high elongation at break of over 300%. Those samples showed stress–strain curves that resembled those of the amorphous

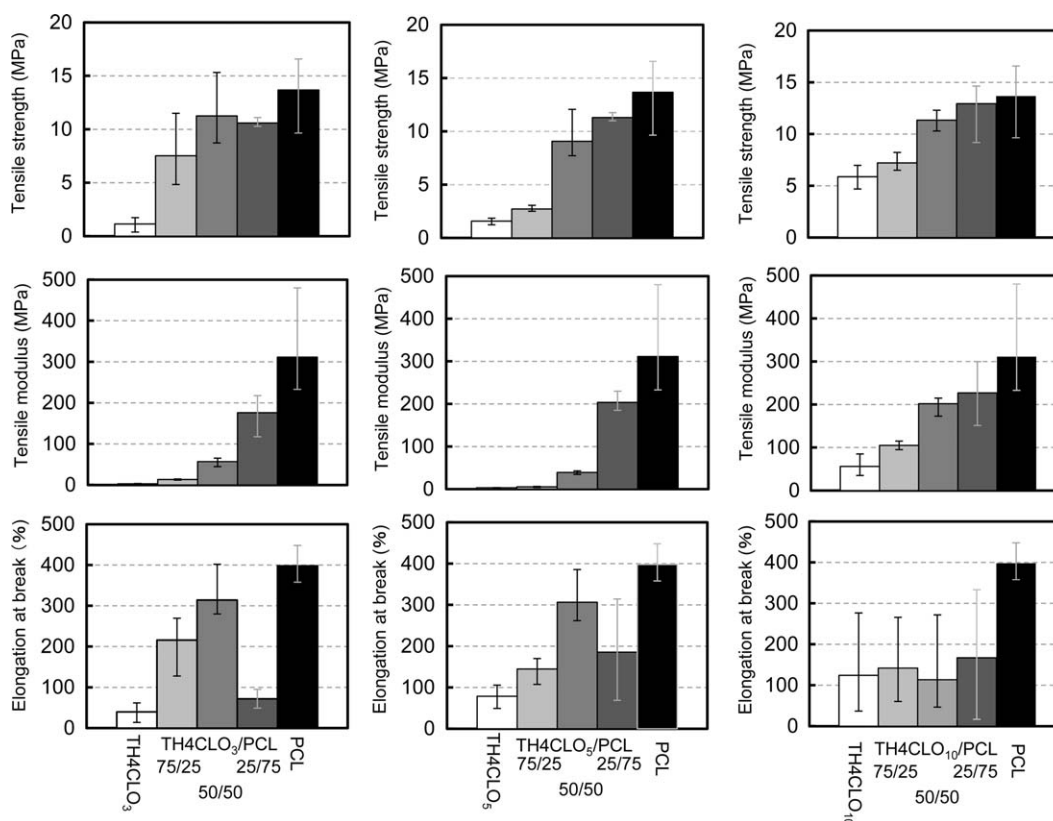


Figure 8. Tensile properties of the TH4CLOs, TH4CLO/PCLs, and PCL.

polymer and were in agreement with the DSC results in that the crystallization of the PCL component for 50/50 TH4CLO₃/PCL and 50/50 TH4CLO₅/PCL was considerably suppressed. In particular, 50/50 TH4CLO₃/PCL showed a significantly high tensile strength (11.2 MPa) and elongation at break (314%), although their values were a little lower than those of PCL (13.7 MPa, 400%).

CONCLUSIONS

The TH4CLOs and TH4CLO/PCLs ($n = 3, 5$, and 10) were prepared by the reactions of H4CLOs ($n = 3, 5$, and 10) and TDI in the absence and presence of PCL. The thermal and mechanical properties of the TH4CLOs and TH4CLO/PCLs were investigated and compared with those of PCL by means of DMA, DSC, and tensile testing. In the DMA curves of the TH4CLO/PCLs, only one $\tan \delta$ peak was observed, whose temperature increased with increasing TH4CLO content and with decreasing n value. The FESEM observation of the TH4CLO/PCLs revealed that there was no phase separation. The DSC analyses of the TH4CLOs and TH4CLO/PCLs revealed that the TH4CLOs ($n = 3$ and 5) were amorphous, whereas TH4CLO₁₀ was semi-crystalline, and that the crystallization of the polycaprolactone chain for TH4CLO/PCLs was more strongly disturbed with increasing TH4CLO content and decreasing n value. Although the tensile strength, modulus, and elongation at break of TH4CLO were much lower than those of PCL, those values increased with the n value. Although the tensile strength and modulus of TH4CLO/PCLs decreased with increasing TH4CLO

content, TH4CLO₃/PCL 50/50 showed the highest elongation at break (314%) among the S-IPNs because of its the suppression of the crystallization of the polycaprolactone chain.

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