Biodegradable and Photocurable Multiblock Copolymers with Shape-Memory Properties from Poly(ε-caprolactone) Diol, Poly(ethylene glycol), and 5-Cinnamoyloxyisophthalic Acid

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ABSTRACT: Biodegradable and photocurable multiblock copolymers of various compositions were synthesized by the high-temperature solution polycondensation of poly(ε-caprolactone) (PCL) diols of molecular weight (M_n) = 3000 and poly(ethylene glycol)s (PEG) of M_n = 3000 with a dichloride of 5-cinnamoyloxyisophthalic acid (ICA) as a chain extender, followed by irradiation by a 400 W high-pressure mercury lamp ($\lambda > 280$ nm) to form a network structure. The gel contents increased with photocuring time, reaching a level of over 90% after 10 min for all copolymers without a photoinitiator. The thermal and mechanical properties of the photocured copolymers were examined by DSC and tensile tests. In cyclic thermomechanical tensile tests, the photocured ICA/PCL/ PEG copolymer films showed good shape-memory properties at 37–60°C, with both shape fixity ratio and shape recovery ratio over 90% at a maximum tensile strain of 100–300%. The water absorption of these copolymers and their rate of degradation in a phosphate buffer solution (pH 7.0) at 37°C increased significantly with increasing PEG content. The novel photocured ICA/PCL/PEG multiblock copolymers are potentially useful in biomedical applications. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3556–3564, 2011

Key words: multiblock biodegradable copolymers; poly (ε-caprolactone); poly(ethylene glycol); photocurable; shape-memory property

INTRODUCTION

Recently, there has been growing interest in biodegradable shape-memory polymers that have the appropriate thermal and mechanical properties for novel types of medical devices used for minimally invasive surgery such as sutures,[1] stents, and catheters.[2–4] These polymers are usually thermoresponsive; their permanent shape can be recovered at switching temperature (T_{sw}) (or transition temperature) after they have been fixed in a new, temporary shape. T_{sw} is based on either glass transition temperature or melting temperature. For example, when a bulky implant that has been introduced into the body by a minimally invasive surgery is heated above T_{sw}, it returns to an application-relevant shape, and a second operation to remove the implant material is not necessary because it degrades after a given time.[1,5]

Previously reported biodegradable shape-memory polymers include thermoplastic segmented poly

(ester-urethane)s,[1,5–10] photoset AB network copolymers,[11,12] photocured mutiblock copolymers,[13–16] and poly(L-lactide) (PLLA)-based copolyesters.[17,18] These polymers displayed different properties and shape recovery temperatures depending on their chemical structures and copolymer compositions. For medical applications, T_{sw} must be near body temperature. Poly(ε-caprolactone) has been used as a component of such shape-memory polymers because it is biocompatible (biodegradable) and its melting point can be adjusted near the body temperature using low-molecular weight poly(ε-caprolactone) (PCL) oligomer or the copolymerization of another component into a PCL segment. For example, Lendlein et al.[1] prepared linear multiblock copolymers using low-molecular weight PCL diol as a switching segment with a shape-memory effect at 37–40°C. We synthesized photocured PCL/PLLA multiblock copolymers from random PCL/PLLA comacrodiol and they demonstrated a good shape-memory property under a very large deformation of 1000% at 45°C.[15] Another type of biodegradable shape-memory polymer with T_{sw} near body temperature was synthesized from L-lactide-glycolide-trimethylene carbonate terpolymers.[19] Most of biodegradable shape-memory polymers, however, have limited

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applicability in the human body because of their relatively high T_{sw} between 60 and 70°C.

In this study, we prepared biodegradable and photocurable multiblock copolymers with shape-memory properties having a T_{sw} near body temperature from PCL diols with the number average molecular weight (M_n) of 3000, poly(ethylene glycol) (PEG) with an M_n of 3000 and 5-cinnamoyloxyisophthalic acid (ICA) as a photosensitive and less toxic chain extender. The T_{sw} near body temperature could be achieved by using oligomeric PCL and/or PEG as a switching segment which show lower melting points of about 50–58°C. Incorporating these oligomers into polymer backbone would further decrease melting points of them. Irradiation with light of suitable wavelengths (>280 nm) would result in [2 + 2] cycloaddition reaction of the ICA moieties[20] and would form readily the covalently crosslinked polymer networks. The effects of copolymer compositions on the thermal and mechanical properties of the networks and the network's shape-memory ability near body temperature were examined. Shape-memory properties such as strain fixity ratio and strain recovery ratio were quantified by cyclic thermomechanical tensile testing.[1,16] Considering their potential applications in biodegradable medical devices, hydrolytic degradation studies were also performed. PCL-based biodegradable shape-memory polymers were previously as having the limitation of low biodegradation rate for some practical applications. PEG is the most widely used polyether block because of its outstanding properties including hydrophilicity, water solubility, and nontoxicity. Thus, PCL/PEG copolymers can exhibit an outstanding combination of properties such as hydrophlicity and degradability.[21,22]

EXPERIMENTAL

Materials

5-Cinnamoyloxyisophthalic acid (ICA) was synthesized from 5-hydroxyisophthalic acid and cinnamoyl chloride, and the diacyl chloride of ICA was prepared by refluxing the ICA with thionyl chloride. The procedures involved in their synthesis were described in detail in our previous paper.[23] Poly(ε-caprolactone) diol (PCL-diol) (M_n = 3000) [α,ω-dihydroxy poly(ε-caprolactone)] was supplied by Aldrich, and it had the following formula: H[—O(CH$_2$)$_5$CO—]$_n$O(CH$_2$CH$_2$O)$_2$ [—CO(CH$_2$)$_5$O—]$_m$H. Poly(ethylene glycol) (M_n = 3000) (PEG) was donated by the Sanyo-Chemical Company. These macrodiols were dried over P$_2$O$_5$ at ambient temperature *in vacuo*.

Polymerization

Multiblock copolymers were prepared by a high-temperature solution polycondensation in diphenyl ether.[13] The preparation process cal procedure was typically as follows. A mixture of 1.0 mmol (0.476 g) of ICA dichloride, 0.6 mmol (1.80 g) of PCL diol (M_n = 3000), 0.4 mmol (1.20 g) of PEG (M_n = 3000), and 15 mL of diphenyl ether was introduced into three-necked round-bottomed flask equipped with a thermometer, magnetic stirrer, and drying tube, under a continuous dry nitrogen flow. The temperature was raised to 170–180°C for 30 min and heated at 180°C for 2 h, and then hot viscous solution was poured into a large excess amount of cold *n*-hexane. The precipitated block copolymer was filtered off, precipitated from chloroform into *n*-cold hexane again and vacuum dried at room temperature. The copolymer sample is designated as ICA/PCL/PEG (60/40).

Characterization

Gel permeation chromatography (GPC) was carried out on a Waters system. Three styragel columns (300 mm × 7.8 mm) were placed in a series and operated at a flow rate of 1 mL/min in chloroform at 35°C. PEG and poly(ethylene oxide) standards with low polydispersities were used for calibration. ^{1}H-NMR spectra were obtained at 25°C in CDCl$_3$ using a JEOL GX-270W NMR spectrometer with TMS as the internal standard. The thermal analysis was performed at a heating rate of 10°C/min in a nitrogen atmosphere using a Shimadzu DSC-50 differential scanning analyzer controlled by a TA-50 work station. The UV/Vis spectra were recorded on a Shimadzu UV/Vis-2100 spectrophotometer. The mass density of the film was measured by using a sink-and-float method in a sodium chloride aqueous solution at 25°C.

Film preparation

Multiblock copolymer films of about 180–200 μm were prepared by the melt-pressed method at 60–70°C, followed by quenching in an ice-cooled bath, and then dried for 24 h *in vacuo*.

Photocuring, gel contents, and degree of swelling

Photocuring was performed using a 400 W high-pressure mercury lamp (Sen Light Company, Osaka, Japan) through a cooling jacket, and with a Pyrex filter to cut off wavelengths below 280 nm. The UV light intensity was measured on a spectrophotometer (Spectronics DRC100X, New York). The melt-pressed films were irradiated for various times. After irradiation was completed, the film was weighed (w_{dry}) and washed extensively with fresh chloroform to remove the unreacted soluble part of the polymer, and the gels were dried *in vacuo* and weighed (w_g). The gel content G (%) was calculated as $100 \times w_g/w_{dry}$.

The equilibrium swelling properties in chloroform were measured according to procedures described elsewhere.[15] The dried gels were weighed (w_{dry}) and soaked in chloroform for 30 min. The swollen gel was removed from the solution, dried of any excess fluid with a tissue, and then weighed (w_g). The degree of swelling S of the photocured films in chloroform was calculated by the following equation[10,16]: $S = 1 + 100 \times \rho_2/\rho_1 (w_g/w_{sw} - 1)$, where w_{sw} is the weight of the sample in the swollen state, w_g is the weight of the dry sample, and ρ_1 and ρ_2 are the specific densities of the measured medium and polymer film, respectively.

Mechanical and shape-memory properties

Tensile tests and thermomechanical experiments on film specimens (length, 10 mm; width, 5 mm; thickness, ca. 200 μm) were performed at several temperatures (22, 37, 45, and 60 ± 2°C) using a Shimadzu AG-1 autograph equipped with a temperature-controlled thermochamber. The strain rate was 20 mm/min. The samples were annealed at the testing temperature for 10 min before each experiment. The averaged values for 5–10 specimens were used.

Shape-memory tests were carried out using thermocyclic mechanical test procedure described in the literature.[1,16] The sample was stretched uniaxially to a maximum strain ε_m (100–500%) of the original length ε_0 at a strain rate of 20 mm/min at 60°C. After this, strain was maintained for approximately 5 min, the film was cooled to room temperature (22°C) to cause it to crystallize. After 10 min, the stress was removed completely resulting in a temporary shape characterized by ε_u. The sample was then heated again to 60°C to cause the crystallites to melt so that the permanent shape was fixed, and the shrinkage ε_s was measured after a 10 min residence time. This cycle was repeated three times. The strain fixity ratio R_f and the strain recovery ratio R_r were calculated by the following equation:

$$R_f\ (\%) = 100 \times (\varepsilon_u - \varepsilon_0)/(\varepsilon_m - \varepsilon_0),$$
$$R_r\ (\%) = 100 \times (\varepsilon_m - \varepsilon_s)/(\varepsilon_m - \varepsilon_0)$$

where ε_0 is the length of the film at the beginning of the cycle, ε_m is the length of the extended film at 60°C, ε_u is the length of the film after unloading at room temperature, and ε_s is the length of the film after shrinkage at 60°C. The above thermocyclic test was also performed using a similar procedure at 37 and 45°C.

Water absorption

The water absorption of the copolymers was quantified by measurement of the amount of water that
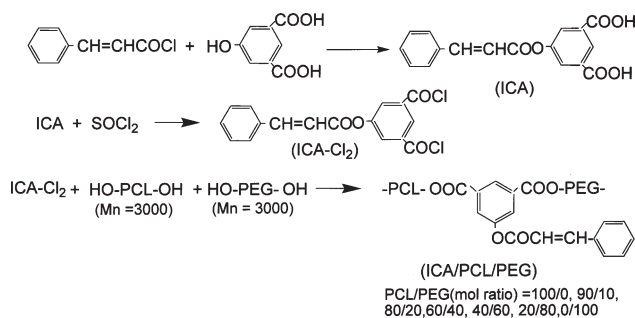
Scheme 1 Synthetic route of photosensitive PCL/PEG multiblock copolymers with a pendent cinnamate group.

each polymer absorbed at 37°C. The films were immersed in the distilled water and kept at 37°C for 1 h. The films were removed from the water, wiped gently with a tissue and weighed immediately. The water absorption was calculated according to the following equation: Water absorption = $100 \times (w_{sw} - w_{dry})/w_{dry}$, where w_{sw} and w_{dry} represent the weight of the dry sample and of the wet sample, respectively.

Hydrolytic degradation

The film specimen (10 mm × 10 mm, ca. 200 μm thickness) was placed in a small bottle containing 10 mL of 1/15 mol phosphate buffer solution (pH 7.0), which was replaced with freshly prepared solution every 2 days. The bottle was incubated at 37°C for various periods of time. After incubation, the film was washed with distilled water and dried at room temperature for 24 h *in vacuo*. The degree of degradation was estimated from the weight loss according to the following equation: weight loss (%) = $100 \times (w_0 - w_t)/w_0$, where w_0 and w_t are the dry sample weight before and after degradation, respectively. The weight loss averaged for two specimens was used.

RESULTS AND DISCUSSION

Synthesis of ICA/PCL/PEG multiblock copolymers

A novel series of photosensitive multiblock copolymers containing a cinnamate moiety in the side chain were prepared by a conventional high-temperature solution polycondensation in diphenyl ether from a mixture of PCL diol and PEG with a ICA dichloride. The synthetic route is given in Scheme 1. The results of polycondensation are summarized in Table I. High-molecular weight copolymers were obtained in good yields. Their GPC curves showed a narrow and monomodal MW distribution, which indicated that the copolymers did not contain unreacted PCL-diols and PEGs.

TABLE I
Synthesis and Thermal Properties of ICA/PCL/PEG Multiblock Copolymers

Copolymer code	Yield (%)	PCL/PEG[a] ratio (mol %)	M_n[b]	M_w/M_n[b]	T_g[c] (°C)	T_{cc}[c] (°C)	T_m[c] (°C)	ΔH_m[c] (J/g)
ICA/PCL	89	100/0	45,100	1.34	−61	−23	47	54
ICA/PCL/PEG(90/10)	86	88/12	34,000	1.78	−61	−35	44	36
ICA/PCL/PEG(80/20)	85	78/22	31,300	1.86	−60	−35	43	45
ICA/PCL/PEG(60/40)	84	58/42	44,900	1.68	−61	−46	35, 41[d]	38
ICA/PCL/PEG(40/60)	75	40/60	42,200	1.50	−60	−49	39	54
ICA/PCL/PEG(20/80)	64	19/81	40,500	2.00	−60	−50	42	59
ICA/PEG	80	0/100	45,000	1.32	−61	−50	42	84

[a] Determined by ^{1}H-NMR.
[b] Determined by GPC with poly(ethylene glycol) and poly(ethylene oxide) standards.
[c] Determined by DSC for melt-quenched samples.
[d] Double peaks were appeared.

The chemical structure of the copolymers was confirmed by their ^{1}H-NMR spectrum, as shown in Figure 1. Detailed assignments of each peak are given in Figure 1, which showed two doublet signals at 6.39 ppm and 7.66 ppm with a coupling constant of 16 Hz, which is characteristic for a *trans*-cinnamoyl moiety. The copolymer compositions were determined by an integral peak ratio of 4.05 ppm (—CH_2OCO— of PCL) and 3.60 ppm (—CH_2OCH_2— of PEG) in the ^{1}H-NMR spectrum. The observed compositions are listed in Table I. The copolymer compositions were in substantial agreement with the feeding monomer ratio.

Photocuring of multiblock copolymers

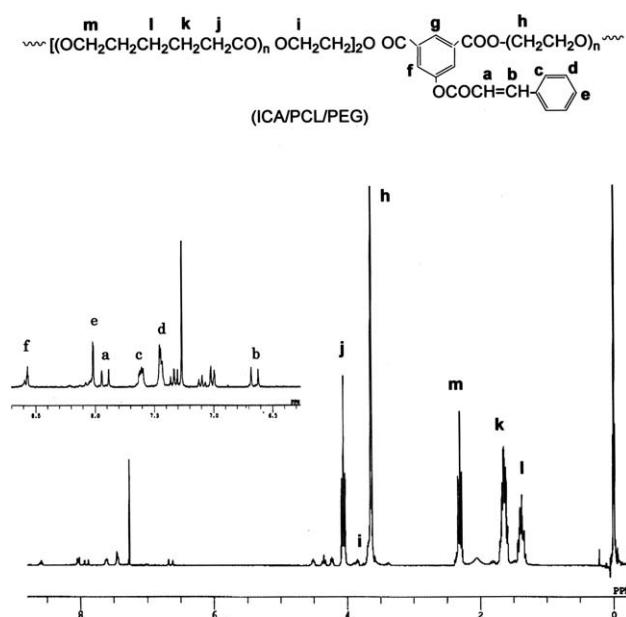The photocuring of multiblock copolymers was performed in a dry thin film that was cast from chloroform solution onto a quartz plate at ambient temperature, by irradiation of a 400-W high-pressure mercury lamp at λ > 280 nm. The reaction was monitored by the UV absorption changes of the cast copolymer film. Figure 2 shows typical UV absorption spectrum changes for ICA/PCL/PEG(40/60). The cinnamate absorption maximum at 286 nm decreased with irradiation time, indicating that the cinnamate group could undergo a photochemical reaction in a film state. Cinnamoyl group is well known to (2 + 2) photocycloaddition, resulting in the formation of a cyclobutane ring as shown in Figure 3.[20]

Figure 4 shows gel yields G and degree of swelling S in chloroform for ICA/PCL/PEG(60/40) melt-pressed film against irradiation time at ambient temperature. S is a measure for comparing the crosslinking densities of different photocured copolymers, considering that chloroform is a good solvent for both PCL and PEG. The G of the block copolymers increased rapidly with time and reached nearly 100% after 10 min, while the S decreased and
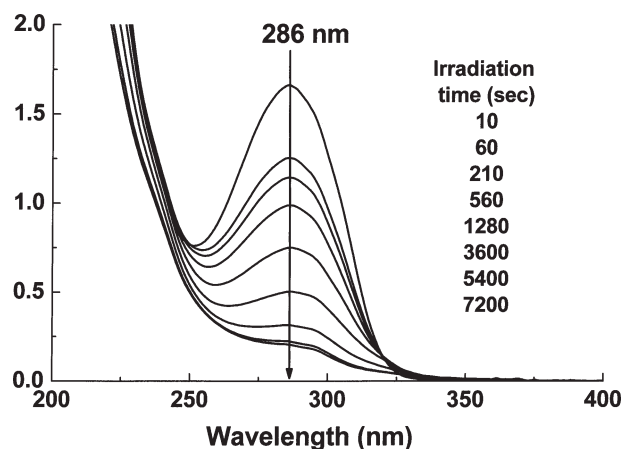

Figure 1 ^{1}H-NMR spectrum of ICA/PCL/PEG(60/40) in chloroform-*d*.

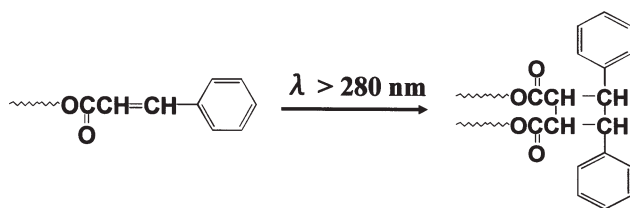Figure 2 Photodimerization reaction of cinnamate.

Figure 3 Changes of the UV/Vis spectra absorbance of ICA/PCL/PEG(60/40) thin film, upon irradiation with a 400-mW high-pressure Hg lamp at ambient temperature. UV intensity: 1.0 mW/cm^2.

leveled off after 40 min. The values for G and S after 40 min are summarized in Table II. The values for S, which ranged from 350 to 1550%, were hardly affected by the compositions of the copolymer.

DSC of multiblock copolymers

The thermal properties of the multiblock copolymers before and after photocuring were determined by DSC for the melt-quenched samples. Figure 5 shows typical DSC profiles for the copolymers, the ICA/PCL and the ICA/PEG before and after photocuring. The phase transition temperatures such as glass transition (T_g), cold crystallization (T_{cc}), and melting (T_m) along with heat of fusion (ΔH_m) are summarized in Tables I (before photocuring) and II (after photocuring), respectively. Only one T_g was detected around $-60°C$ for all copolymers. We attribute this to the fact that the T_g of the PCL segment ($-64°C$) is very close to that of the PEG segment ($-62°C$). All the copolymers showed a single melting peak probably due to the overlapping of each melting endotherm, except for CAC/PCL/PEG(60/40), for which a double melting transition was observed, demonstrating the presence of the two crystalline domains. The T_{cc} for the copolymers gradually decreasedwith increasing PEG content. Considering that the heat of fusion values for pure PCL and PEG are 135[24] and 205[25] J/g, respectively, the crystallinity of the ICA/PCL and ICA/PEG homopolymers was calculated to be 40 and 41%, respectively, showing that the crystallinity is nearly the same for both homopolymers. The ΔH_m and T_m of the copolymers were smaller than they were for the ICA/PCL or ICA/PEG homopolymers, which suggests that the copolymerization hinders the crystal formation of pure polymer.

The photocuring of copolymers slightly decreased the T_m and ΔH_m, as shown in Table II. This suggests that the crosslinking reactions disturb the mobility of the chain, that is, disturb the crystallization of polymer.

Mechanical and shape-memory properties of multiblock copolymers

We investigated the mechanical and shape-memory properties of photocured ICA/PCL/PEG copolymer

films above and below the T_m of copolymers. Figure 6 shows the representative stress–strain plots for ICA/PCL/PEG(60/40) before and after photocuring. The results of tensile tests at 22°C are summarized in Table III. All films exhibited a yield point that was less distinct for photocured films, probably because of the decreased crystallinity caused by photocuring. As expected, the photocuring significantly decreased the ultimate elongation. The stress–strain plots above T_m of the copolymer films did not show a yield point, but rather a steady linear increase of stress with strain, as is expected for amorphous elastic materials. The tensile properties above T_m of the photocured films (45°C or 60°C) are given in Table IV. The tensile strength at break, elongation, and Young's modulus showed much lower values compared to those at 22°C; this might be mainly caused by the melting of the crystalline region of the copolymer films. The tensile strength at break and elongation decreased rapidly with increasing PEG content.

The cyclic tensile behaviors above T_m of copolymers were examined fat different maximum tensile strains. Figure 7 shows exemplary hysteresis cycles of ICA/PCL/PEG(60/40) and (20/80) films at 37°C for a maximum tensile strain of 100%. Both films resulted in a residual strain of ca. 13 and 3% for ICA/PCL/PEG(60/40) and (20/80), respectively, after the first cycle ($N = 1$). This result could be due to the alignment of the cylinders induced by the applied strain, from which the aligned polymer could not fully recover.[26] Once this alignment was achieved, subsequent cycles displayed identical stress–strain curves (uniform cyclic deformation properties). This lack of complete recovery can also be explained by the slippage of trapped entanglements in the PCL segments during deformation because it is not reversible instantaneously.[27,28] The residual strain decreased with increasing PEG content.
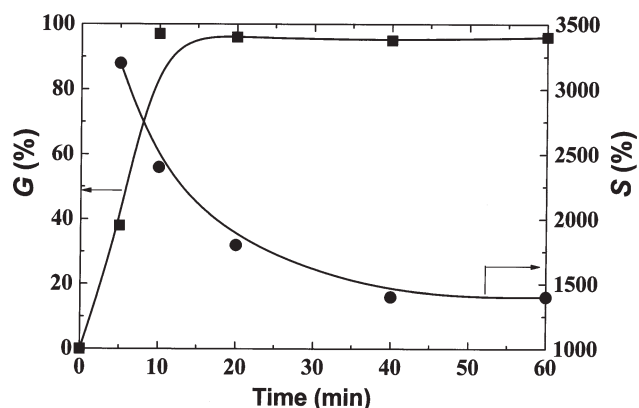

Figure 4 Gel content G and degree of swelling S of CA/PCL/PEG(60/40) film against irradiation time. UV intensity: 1.0 mW/cm^2, filled symbols: G, open symbols: S.

Gel Content, Degree of Swelling, and Thermal Properties of Photocured ICA/PCL/PEG Multiblock Copolymers

Copolymer code	G^a (%)	S^b (%)	T_g^c (°C)	T_{cc}^c (°C)	T_m^c (°C)	ΔH_m^c (J/g)
ICA/PCL	98	1550	−57	−18	46	48
ICA/PCL/PEG(90/10)	99	1510	−61	−36	41	33
ICA/PCL/PEG(80/20)	91	1420	−60	−34	40	33
ICA/PCL/PEG(60/40)	96	1360	−61	−45	29, 39^d	31
ICA/PCL/PEG(40/60)	94	1350	−60	−48	35	50
ICA/PCL/PEG(20/80)	96	1380	−61	−49	37	51
ICA/PEG	94	1530	−57	−50	41	70

[a] Gel content.
[b] Degree of swelling.
[c] Estimated by DSC for melt-quenched samples.
[d] Two peaks were observed.

Shape-memory properties were determined by following a thermocyclic mechanical test procedure described in a previous paper.[1,16] Table V shows the shape fixity ratio (R_f) and shape recovery ratio (R_r) of photocured copolymer films at 37, 45, and 60°C. ICA/PCL exhibited good shape-memory ability with an R_f of 96–100% and an R_r of 94–99% at a maximum tensile strain (ε_m) of 100–500% at 60°C, which would be ascribed to their relatively higher crystallinity, as shown in Table II. With increasing maximum tensile strain, R_f and R_r decreased slightly, probably due to the chain scission. The relatively high T_{sw} (60°C) for ICA/PCL and ICA/PCL/PEG (90/10), however, would limit the applicability in the human body. For the copolymer films with a PEG content greater than 20 mol %, the shape-memory test was performed at 37–45°C for ε_m of 100% because the elongation of these copolymers ranged from 100 to 200%. The R_f and R_r at 45°C wereslightly higherthanthey wereat 37°C probably due to the complete melting of the films at 45°C. R_f and R_r increased slightly as the number of test cycles increased, and their values after the third cycle exceeded 98% for all films, except for the R_f of ICA/PCL/PEG(80/20) at 37°C. This relatively lower R_f value was likely due to the fact that it did not melt completely because of the high T_m of 40°C.

During the shape-memory transitions, the recovery stress values for all the copolymers were 0.5–0.8 MPa at 45–60°C at a tensile strain of 100%. The major limitation of biodegradable shape-memory polymers is that their mechanical properties are inadequate for certain practical applications.[29] By contrast, ICA/PCL/PEG (80/20) and (60/40) at a maximum tensile strain of 100% produced about 2.0 MPa of maximum recovery stress at 37°C (body temperature), which resembles the mechanical stress in soft tissue.[1] This suggests that these shape-memory copolymers can be useful in tissue engineering. This recovery stress decreased, however, with a further increase in PEG content.

Finally, a demonstration of the macroscopic shape-memory effect of the photocured ICA/PCL/PEG(100/0) is presented in Figure 8. The film was first stretched up to 300% of its original length,
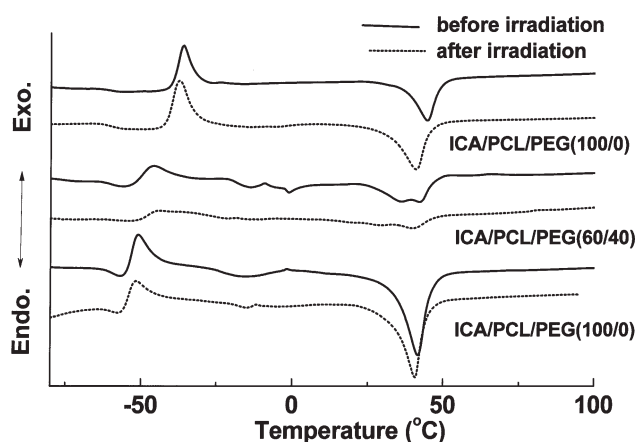
Figure 5 DSC curves of some melt-quenched films before and after photocuring.
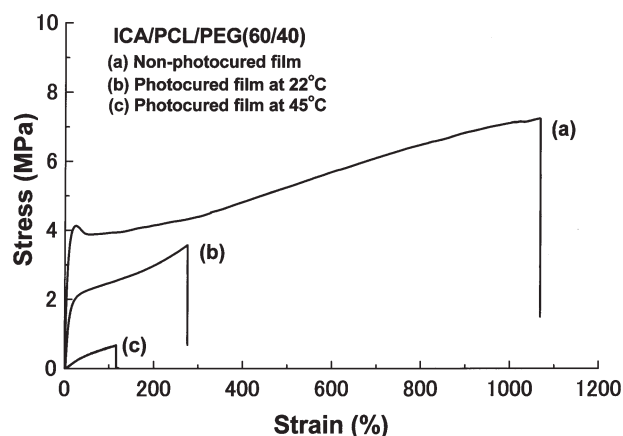
Figure 6 Representative stress–strain curves of ICA/PCL/PEG(60/40) films before and after photocuring at different temperatures.

TABLE III
Tensile Properties of Copolymer Films Before and After Photocuring at 22°C

Copolymer code	Tensile strength at break (MPa)	Elongation (%)	Young's modulus (MPa)
ICA/PCL	14 ± 3.0	1800 ± 60	150 ± 20
Photocured	11 ± 1.7	710 ± 40	105 ± 23
ICA/PCL/ PEG(90/10)	13 ±.0.4	1600 ± 40	120 ± 7
Photocured	12 ± 0.4	770 ± 10	80 ± 10
ICA/PCL/ PEG(80/20)	8.1 ± 1.1	1580 ± 20	62 ± 2.3
Photocured	8.0 ± 0.2	500 ± 30	42 ± 4.7
ICA/PCL/ PEG(60/40)	10 ± 1.0	1600 ± 150	68 ± 0.4
Photocured	6.7 ± 1.5	320 ± 15	37 ± 3.7
ICA/PCL/ PEG(40/60)	7.0 ± 0.2	1030 ± 40	63 ± 7.0
Photocured	3.3 ±.0.4	230 ± 25	25 ± 4.4
ICA/PCL/ PEG(20/80)	7.2 ± 0.1	810 ± 40	82 ± 4.5
Photocured	5.1 ± 0.1	270 ± 10	67 ± 11
ICA/PEG	8.7 ± 3.0	830 ± 140	114 ± 15
Photocured	5.3 ± 0.2	330 ± 110	73 ± 7.0

shaped into a spiral form at 60°C, and then quenched to room temperature. When the spiral sample was placed in an oven at 60°C, it recovered its shape within 30 s.

Water absorption and hydrolytic degradation of multiblock copolymers

Water absorption at 37°C was determined for photocured copolymer films, as shown in Figure 9, because this was expected to have substantial impact on hydrolytic degradation. The degree of water absorption increased with increasing PEG content,

TABLE IV
Tensile Properties of Photocured Copolymer Films at 45 and 60°C

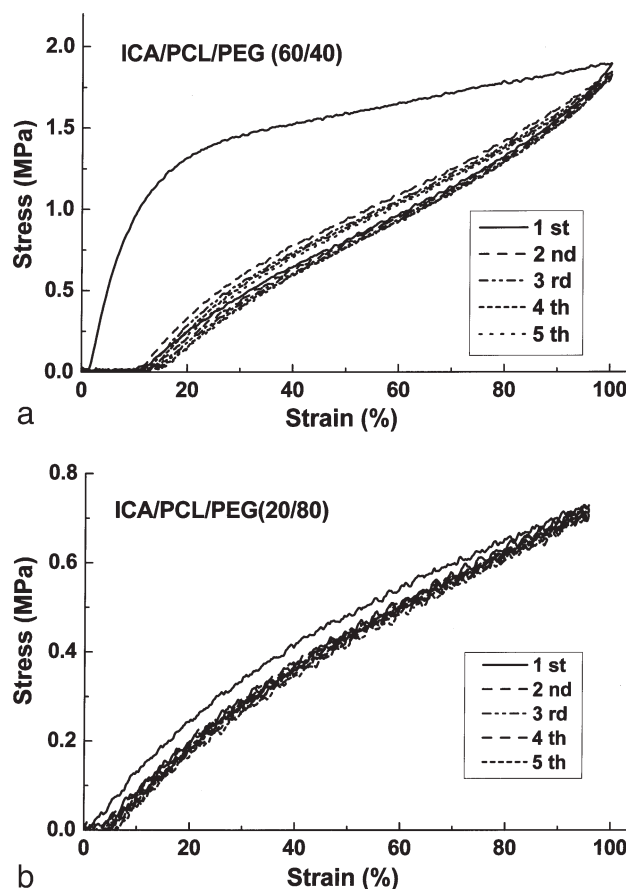| Copolymer code	Test temp. (°C)	Tensile strength at break (MPa)	Elongation (%)	Young's modulus (MPa)
ICA/PCL	45	5.6 ± 0.6	1160 ± 30	1.6 ± .0.1
	60	1.2 ± 0.2	620 ± 20	1.5 ± .0.3
ICA/PCL/ PEG(90/10)	45	2.7 ± 0.3	450 ± 200	1.3 ± 0.2
	60	1.1 ± 0.1	320 ± 10	1.2 ± 0.1
ICA/PCL/ PEG(80/20)	45	1.3 ± 0.0	260 ± 10	0.9 ± 0.0
ICA/PCL/ PEG(60/40)	45	1.0 ± 0.5	120 ± 15	0.6 ± 0.2
ICA/PCL/ PEG(40/60)	45	0.7 ± 0.4	110 ± 0.4	1.0 ± 0.2
ICA/PCL/ PEG(20/80)	45	0.8 ± 0.1	130 ± 10	1.2 ± 0.3
ICA/PEG	45	0.6 ± 0.1	140 ± 30	0.9 ± 0.1

Figure 7 Exemplary hysteresis cycles up to 100% strain of ICA/PCL/PEG(60/40) and ICA/PCL/PEG(20/80) films at 37°C.

but it increased dramatically above ca. 60 mol % PEG, which suggests that PEG becomes continuous phase above 60 mol % PEG.[20,21]

Hydrolytic degradation of photocured copolymer films was investigated in a phosphate buffer solution at pH 7.0 and 37°C. The weight loss of the copolymers was plotted against the incubation time, as shown in Figure 10. The weight loss of the copolymers increased significantly with increasing PEG content, which could be ascribed to the increased water absorption of the copolymers, as shown in Figure 9. This implies that the hydrolytic degradation of the copolymers results mainly from the hydrolysis of ester bonds between ICA and PEG in the main chain. ICA/PEG(0/100) lost more than 50% of its weight after 8 days. By contrast, the ester linkage in the PCL segment appears resistant to be reluctant to hydrolytic degradation under these degradation conditions because ICA/PCL retained approximately 100% of its original weight after 30 days. The rapid weight loss at an early stage of incubation (within a few days) observed for most copolymers would be due to the degradation of loosely crosslinked low-

TABLE V
Shape-Memory Properties of Photocured Copolymer Films

Copolymer code	$\varepsilon_m{}^a$ (%)	$T_{sw}{}^b$ (%)	$R_f{}^c$ (%)			$R_r{}^d$ (%)		
			N(1)[e]	N(2)	N(3)	N(1)	N(2)	N(3)
ICA/PCL	100	60	100	100	100	98	98	98
	300	60	100	98	98	96	98	99
	500	60	98	96	96	94	98	99
ICA/PCL/PEG(90/10)	100	60	100	100	100	98	100	100
	300	60	99	95	96	85	98	98
ICA/PCL/PEG(80/20)	100	37	82	75	78	80	91	92
	100	45	99	98	99	96	98	98
ICA/PCL/PEG(60/40)	100	37	95	96	92	82	95	100
	100	45	95	94	94	90	95	100
ICA/PCL/PEG(40/60)	100	37	95	95	96	88	92	94
	100	45	96	94	94	90	92	96
ICA/PCL/PEG(20/80)	100	37	96	95	95	92	95	95
	100	45	100	100	97	92	98	98
ICA/PEG	100	37	92	94	95	55	92	94
	100	45	100	100	99	87	97	100

[a] Maximum strain.
[b] Switching temperature.
[c] Strain fixity ratio, margin of error: ±5%.
[d] Strain recovery ratio, margin of error: about ±5%.
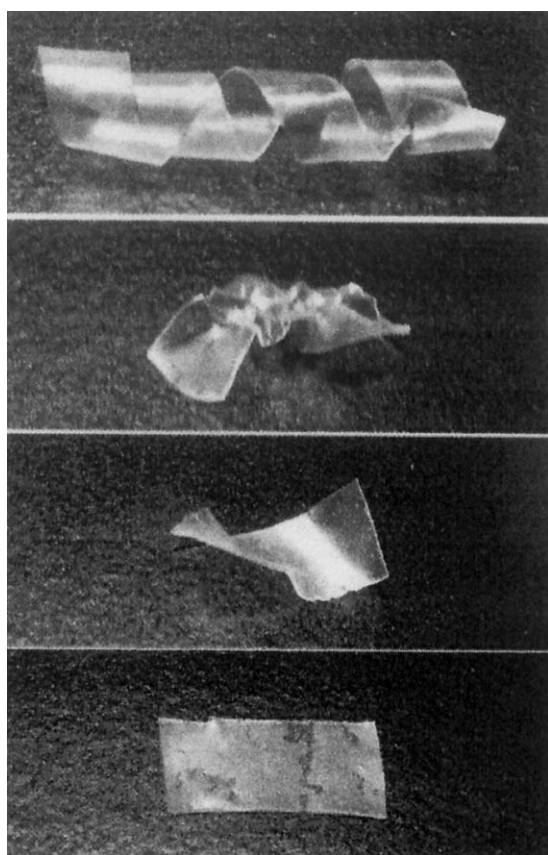[e] Cycle number.

Figure 8 Photograph of the shape-memory effect of ICA/PCL/PEG(100/0). The pictures show the transition from a temporary shape to a permanent shape in 30 s at 60°C. The permanent shape is a flat film and the temporary shape is a spiral form.

molecular weight polymer chains in the photocured films.

CONCLUSIONS

Biodegradable photosensitive multiblock copolymers were synthesized by the high-temperature solution polycondensation of poly(ε-caprolactone) (PCL) diols of molecular weight (M_n) = 3000 and PEG of M_n = 3000 with a dichloride of ICA as a chain extender. These copolymers could be photocured easily without a photoinitiator by means of UV irradiation, forming a cyclobutane ring. The photocured ICA/PCL/PEG copolymer films displayed the good
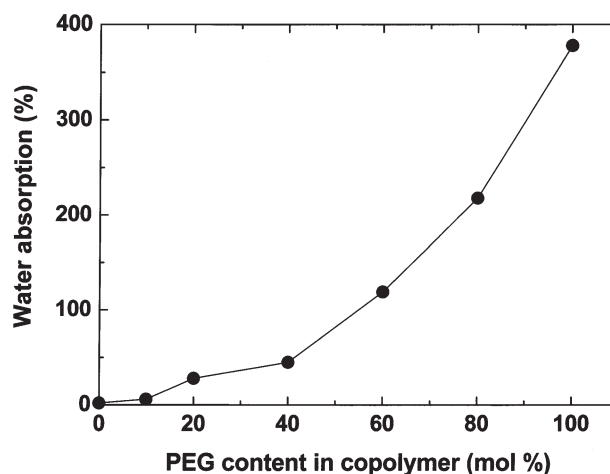

Figure 9 Water uptake of photocured copolymer films versus copolymer compositions.
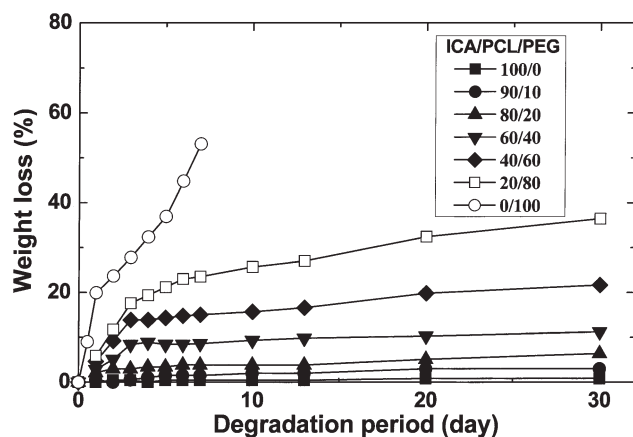
Figure 10 Weight loss of photocured copolymer films as a function of time in a phosphate buffer solution (pH 7.0) at 37°C.

shape-memory property with strain fixity ratio and strain recovery ratios of up to approximately100% at maximum tensile strain of 100–300% at 37–60°C. The water absorption of the copolymers and the rate of degradation in a phosphate buffer solution (pH 7.0) at 37°C increased with increasing PEG content. The photocured ICA/PCL/PEG copolymer films have the potential for applications in numerous areas, particularly in medical applications, because of their lower switching temperature (37–45°C), hydrophilicity, and biocompatibility of their components.

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