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PCL-based Shape Memory Polymers with Variable PDMS Soft Segment Lengths

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Abstract

Thermoresponsive shape memory polymers (SMPs) are stimuli-responsive materials that return to their permanent shape from a temporary shape in response to heating. The design of new SMPs which obtain a broader range of properties including mechanical behavior is critical to realize their potential in biomedical as well as industrial and aerospace applications. To tailor the properties of SMPs, “AB networks” comprised of two distinct polymer components have been investigated but are overwhelmingly limited to those in which both components are organic. In this present work, we prepared inorganic-organic SMPs comprised of inorganic polydimethyl-siloxane (PDMS) segments of varying lengths and organic poly(ϵ -caprolactone) (PCL) segments. PDMS has a particularly low T_g (-125°C) which makes it a particularly effective soft segment to tailor the mechanical properties of PCL-based SMPs. The SMPs were prepared via the rapid photocure of solutions of diacrylated PCL₄₀-*block*-PDMS_{*m*}-*block*-PCL₄₀ macromers ($m = 20, 37, 66$ and 130). The resulting inorganic-organic SMP networks exhibited excellent shape fixity and recovery. By changing the PDMS segment length, the thermal, mechanical, and surface properties were systematically altered.

Keywords

Shape memory polymer; polysiloxanes; poly(ϵ -caprolactone); crosslinking; mechanical properties

INTRODUCTION

Thermoresponsive shape memory polymers (SMPs) are a class of smart materials that change shape upon exposure to heat.^{1–3} Shape memory behavior is the result of netpoints and switching segments. Netpoints are covalent or physical crosslinks which define the permanent shape whereas the switching segments are responsible for holding the temporary shape and recovering the permanent shape when cycled through their transition temperature (T_{trans}). T_{trans} may be either a melting transition temperature (T_m) or a glass transition temperature (T_g). Thus, a temporary shape formed by application of stress at $T > T_{\text{trans}}$ can be fixed by cooling to $T < T_{\text{trans}}$ and the original shape subsequently retrieved by heating to $T > T_{\text{trans}}$.

In contrast to shape memory alloys (SMAs) and shape memory ceramics, SMPs are lightweight, easy to fabricate, are more elastic and may be biodegradable.⁴ However, to reach their potential in devices, new SMPs are needed with a broader range of chemical and physical properties, including sharp T_{trans} , high strain recovery and fixity, high moduli to withstand compressive and tensile forces, and high elasticity. Since first demonstrated as

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potentially useful in biomedical applications,^{5–6} poly(ϵ -caprolactone) (PCL)-based SMPs have received much attention due to the biocompatibility, biodegradability and elasticity of PCL.^{7–8} PCL is useful as a crystalline switching segment for SMPs as its T_{trans} is a well-defined T_m which can be tailored from 45 to 60 °C with increasing M_n .⁹ Such T_{trans} values are useful for *in vivo* deployment as well as other applications which require low heating. Thus, PCL-based SMPs have been widely studied and prepared as both physically^{5,10–14} and chemically^{6,15–20} crosslinked networks.

In order to modify the chemical and physical properties of PCL-based SMPs, AB polymer networks have been prepared through incorporation of organic hard^{5,10–14,17,19–21} or soft segments^{6,15,18} whose T_g 's are higher and lower than that of PCL ($T_g = -60$ °C), respectively. Polydimethylsiloxane (PDMS) exhibits an extremely low T_g (-125 °C) which makes it a particularly effective soft segment candidate. PDMS is comprised of inorganic siloxane backbone and exhibits a unique set of properties including biocompatibility, hydrophobicity, high gas permeability and good thermal and chemical stability.²² Furthermore, hybrid materials comprised of inorganic (e.g. silicon-based) and organic components often achieve properties superior to that of the parent materials.^{23–27} In 2006, Zhu and co-workers reported the first SMPs comprised of PCL and polysiloxane prepared via the radiation crosslinking of physical blends of PCL ($M_w = 50$ k g/mol; 80–95 wt%) with polymethylvinylsiloxane (PMVS; $M_n \approx 60$ k g/mol; 5–20 wt%).¹⁵ This system had significant limitations including blend instability above 20 wt% PMVS, high sol content (i.e. uncrosslinked material; > 50 wt%) and radiation-induced chain scission of PCL. Mather and co-workers formed a shape memory composite by infiltrating and curing silicone within an electrospun PCL fiber mat.²⁸ The composite (~26 wt% PCL) exhibited a low elastic modulus at room temperature (RT) (7.6 MPa) and shape recovery (R_f) that increased after the first thermal cycle (~74% to ~97%).

Recently, we reported an effective method to prepare SMPs comprised of PDMS and PCL segments.²⁹ These SMPs were prepared by rapid photochemical cure of a series of acrylated triblock copolymers with variable PCL segment lengths: AcO-PCL_n-*block*-PDMS₃₇-*block*-PCL_n-OAc ($n = 30, 40$ or 50). In addition to excellent shape recovery and shape fixity, these SMPs exhibited a systematic and simultaneous increase in modulus, tensile strength and strain at break value with increased PCL segment length. In this present study, we have evaluated the effect of systematically varied PDMS segment length on the thermal, shape memory, mechanical and surface properties of the PCL-based SMP networks. A series of macromers were prepared with variable PDMS segment length having the general formula: AcO-PCL₄₀-*block*-PDMS_m-*block*-PCL₄₀-OAc ($m = 20, 37, 66$, or 130) (Scheme 1). Each macromer was photocured in solution by UV irradiation to produce the corresponding SMP. The properties of the resulting inorganic-organic SMPs were characterized and related to the PDMS soft segment length.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane (D_4) and bis(3-aminopropyl)tetramethyldisiloxane were obtained from Gelest. Potassium hydroxide (KOH), hydrochloric acid (HCl), ϵ -caprolactone, triethylamine (Et_3N), acryloyl chloride, 4-dimethylaminopyridine (DMAP), stannous 2-ethylhexanoate, 2,2-dimethoxy-2-phenylacetophenone (DMP), 1-vinyl-2-pyrrolidinone (NVP), potassium carbonate (K_2CO_3), poly(dimethylsiloxane)-bis(3-aminopropyl) terminated (NH_2 -PDMS_m- NH_2 ; $m = 20$, $M_n = 1,728$ g/mol; $m = 37$, $M_n = 2,986$ g/mol and $m = 66$, $M_n = 5,132$ g/mol), and solvents were obtained from Aldrich. The number average molecular weights (M_n) of the NH_2 -PDMS_m- NH_2 were determined by 1H NMR end-group analysis. Phosphate buffered solution (PBS, pH = 7.4, without calcium and

magnesium) was obtained from Mediatech. Anhydrous magnesium sulfate (MgSO_4) was obtained from Fisher. Reagent-grade CH_2Cl_2 , CHCl_3 , and NMR grade CDCl_3 were dried over $4\text{\AA}$ molecular sieves before use. PCL PCL ($M_w = 70 - 90\text{ k g/mol}$ per manufacturer's specifications) was obtained from Sigma Aldrich.

Materials Synthesis

All reactions were conducted in oven-dried ($100\text{ }^\circ\text{C}$) glassware with Teflon covered magnetic stir bars to agitate reaction mixtures.

Synthesis of $\text{NH}_2\text{-PDMS}_{130}\text{-NH}_2$ — $\text{NH}_2\text{-PDMS}_{130}\text{-NH}_2$ was prepared by base-catalyzed ring-opening polymerization of D_4 in the presence of bis(3-aminopropyltetramethyldisiloxane).³⁰ D_4 (39.96 g, 135 mmol), bis(3-aminopropyltetramethyldisiloxane) (1.68 g, 6.76 mmol) and KOH (0.084 g, 1.50 mmol) were combined in a 150 mL round bottom (rb) flask and stirred for 24 h at $120\text{ }^\circ\text{C}$. After cooling to room temperature (RT), KOH was neutralized by dissolving the crude product in a minimal amount of toluene and sequentially precipitating once into cold methanol ($\sim 10\text{ }^\circ\text{C}$) containing HCl in a molar ratio of 1.1:1 HCl:KOH and twice into neutral cold methanol ($\sim 10\text{ }^\circ\text{C}$). Volatiles were removed from the isolated product under high vacuum at $45\text{ }^\circ\text{C}$ for 20 h. In this way, a clear viscous liquid was obtained (30.77 g, 74 % yield and $M_n = 9,868\text{ g/mol}$ ($n = 130$) by ^1H NMR end group analysis). δ_{H} (300 MHz, CDCl_3): 0.02 – 0.13 (br m, 790H, SiCH_3), 0.52 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 1.25 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 1.45 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 2.66 (m, 4H, NH_2).

Macromer synthesis—The $\text{HO-PCL}_{40}\text{-block-PDMS}_m\text{-block-PCL}_{40}\text{-OH}$ macromers (**a-smp1**: $m = 20$, **a-smp2**: $m = 37$, **a-smp3**: $m = 66$, **a-smp4**: $m = 130$) were synthesized by the ring-opening polymerization of ϵ -caprolactone in the presence of $\text{NH}_2\text{-PDMS}_m\text{-NH}_2$ and a tin catalyst.²⁹ The terminal hydroxyl groups of **a-smps** were subsequently converted to photosensitive acrylate (OAc) groups by reacting with acryloyl chloride to yield $\text{AcO-PCL}_{40}\text{-block-PDMS}_m\text{-block-PCL}_{40}\text{-OAc}$ (**b-smp1**: $m = 20$, **b-smp2**: $m = 37$, **b-smp3**: $m = 66$, **b-smp4**: $m = 130$).

Synthesis of a-smp1— $\text{NH}_2\text{-PDMS}_{20}\text{-NH}_2$ (3.77 g, 2.20 mmol), ϵ -caprolactone (20.0 g, 175.49 mmol), and stannous 2-ethylhexanoate (0.048 g, 0.123 mmol) were reacted to prepare **a-smp1**. The obtained product (19.85 g, 84% yield; $M_n = 10,848\text{ g/mol}$) was a yellow, waxy solid. M_n and PDMS: PCL ratio was determined by ^1H NMR spectroscopy. δ_{H} (300 MHz, CDCl_3): 0.04 – 0.11 (br m, 130H, SiCH_3), 0.51 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 1.37 (m, 160H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 1.64 (m, 320H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2.16 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 2.30 (m, 160H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.22 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 3.64 (m, 2H, NH), 4.05 (m, 160H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$).

Synthesis of a-smp2—**a-smp2** was prepared as previously reported.²⁹

Synthesis of a-smp3— $\text{NH}_2\text{-PDMS}_{66}\text{-NH}_2$ (15.0 g, 2.92 mmol), ϵ -caprolactone (25.2 g, 220.4 mmol), and stannous 2-ethylhexanoate (0.1 g, 0.26 mmol) were reacted as above. The obtained product (29.96 g, 75% yield; $M_n = 14,252\text{ g/mol}$) was a yellow, waxy solid. δ_{H} (300 MHz, CDCl_3): 0.01 – 0.13 (br m, 410H, SiCH_3), 0.53 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 1.39 (m, 160H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 1.65 (m, 320H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2.16 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 2.31 (m, 160H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 3.20 (m, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 3.65 (m, 2H, NH), 4.07 (m, 160H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$).

Synthesis of a-smp4— $\text{NH}_2\text{-PDMS}_{130}\text{-NH}_2$ (10.0 g, 1.01 mmol), ϵ -caprolactone (9.23 g, 80.8 mmol), and stannous 2-ethylhexanoate (0.048 g, 0.123 mmol) were reacted as above.

The obtained product (13.53 g, 70% yield; $M_n = 18,988$ g/mol) was a yellow, viscous liquid. δ_H (300 MHz, $CDCl_3$): 0.02 – 0.13 (br m, 790H, $SiCH_3$), 0.52 (m, 4H, $-SiCH_2CH_2CH_2-$), 1.38 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2OH$), 1.63 (m, 320H, $-CH_2CH_2CH_2CH_2CH_2OH$), 2.18 (m, 4H, $-SiCH_2CH_2CH_2-$), 2.30 (m, 160H, $-CH_2CH_2CH_2-CH_2CH_2OH$), 3.22 (m, 4H, $-SiCH_2CH_2CH_2-$), 3.64 (m, 2H, NH), 4.06 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2OH$).

Synthesis of b-smp1—a-smp1 (19.85 g, 1.83 mmol), DMP (0.0023 g, 0.02 mmol), Et_3N (0.366 g, 3.62 mmol), acryloyl chloride (0.652 g, 7.24 mmol) were reacted as previously described.²⁹ The obtained product (12.54 g, 63% yield, $M_n = 10,956$ g/mol) was a waxy, yellow solid. 1H NMR spectroscopy confirmed the acrylation of -OH groups and maintenance of PDMS:PCL ratio and M_n . δ_H (300 MHz, $CDCl_3$): 0.04 – 0.12 (br m, 130H, $SiCH_3$), 0.52 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 1.37 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2O-$), 1.64 (m, 320H, $-CH_2CH_2CH_2CH_2CH_2O-$), 2.16 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 2.30 (m, 160H, $-CH_2CH_2CH_2-CH_2CH_2O-$), 3.22 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 3.64 (m, 2H, NH), 4.05 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2O-$), 5.81 (dd, 2H, $J = 10.2$ and 1.5 Hz, $-CH=CH_2$), 6.11 (dd, 2H, $J = 17.1$ and 11.1 Hz, $-CH=CH_2$), 6.39 (dd, 2H, $J = 17.1$ and 1.2 Hz, $-CH=CH_2$).

Synthesis of b-smp2—b-smp2 was prepared as previously reported.²⁹

Synthesis of b-smp3—a-smp3 (29.96 g, 2.08 mmol), DMP (0.0063 g, 0.055 mmol), Et_3N (0.425 g, 4.2 mmol), acryloyl chloride (0.757 g, 8.4 mmol) were reacted as above. The obtained product (22.26 g, 74% yield, $M_n = 14,360$ g/mol) was a waxy, yellow solid. δ_H (300 MHz, $CDCl_3$): 0.003 – 0.11 (br m, 410H, $SiCH_3$), 0.53 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 1.38 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2O-$), 1.65 (m, 320H, $-CH_2CH_2CH_2CH_2CH_2O-$), 2.17 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 2.31 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2O-$), 3.23 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 3.65 (m, 2H, NH), 4.06 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2O-$), 5.82 (dd, 2H, $J = 10.4$ and 1.5 Hz, $-CH=CH_2$), 6.12 (dd, 2H, $J = 17.3$ and 10.5 Hz, $-CH=CH_2$), 6.40 (dd, 2H, $J = 17.6$ and 1.5 Hz, $-CH=CH_2$).

Synthesis of b-smp4—a-smp4 (13.53 g, 0.737 mmol), DMP (0.0023 g, 0.02 mmol), Et_3N (0.149 g, 1.47 mmol), acryloyl chloride (0.266 g, 2.95 mmol) were reacted as above. The obtained product (11.15 g, 81% yield, $M_n = 19,096$ g/mol) was a tacky, yellow solid. δ_H (300 MHz, $CDCl_3$): 0.01 – 0.11 (br m, 790H, $SiCH_3$), 0.52 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 1.37 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2O-$), 1.64 (m, 320H, $-CH_2CH_2CH_2CH_2CH_2O-$), 2.16 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 2.30 (m, 160H, $-CH_2CH_2CH_2-CH_2CH_2O-$), 3.22 (m, 4H, $-SiCH_2CH_2CH_2NH-$), 3.64 (m, 2H, NH), 4.06 (m, 160H, $-CH_2CH_2CH_2CH_2CH_2O-$), 5.82 (dd, 2H, $J = 10.4$ and 1.5 Hz, $-CH=CH_2$), 6.12 (dd, 2H, $J = 17.7$ and 10.8 Hz, $-CH=CH_2$), 6.39 (dd, 2H, $J = 18.3$ and 1.2 Hz, $-CH=CH_2$).

Photocrosslinking

To obtain crosslinked networks [SMP1-4], 25 wt% CH_2Cl_2 solutions of b-smp1-4 were each photochemically crosslinked. Per 1 mL of precursor solution was added 150 μ L of photocatalyst solution (10 wt% solution of DMAP in NVP). The solution was pipette into a circular silicone mold (45 mm $\times$ 22 mm; McMaster-Carr), sandwiched between glass slides and exposed to UV light (UV-Transilluminator, 6 mW/cm², 365 nm) for 3 min. The solvent-swollen disc was removed from the mold, air dried (RT, 12 h) and dried *in vacuo* (36 in. Hg, 80 °C, 4 h). Uncrosslinked material (i.e. sol) was removed by soaking the disc in ethanol (3 h), air drying overnight and drying *in vacuo* (36 in. Hg, 80 °C, 4 h).

A PCL film for contact angle studies was prepared by dissolving PCL pellets in DCM at 2.5 % w/v. Then, 16 mL of the solution was cast on a glass Petri dish (60 mm diam.), air dried (24 h) and dried *in vacuo* (36 in. Hg, 80 °C, 12 h).

CHARACTERIZATION

NMR

^1H spectra of polymers were obtained on a Mercury 300-MHz spectrometer operating in the Fourier transform mode. Five percent (w/v) CDCl_3 solutions were used to obtain spectra. Residual CHCl_3 served as an internal standard.

Thermal Properties

Differential scanning calorimetry (DSC) measurements was performed on a TA Instruments Q100. Network specimens were sealed in hermetic pans and heated from -140 to 95°C at $5^\circ\text{C}/\text{min}$ for two cycles. T_m and enthalpy change (ΔH_m) of PCL was measured from the endothermic melting peak of the second cycle. The percent crystallinity ($\% \chi_c$) was calculated from the equation:

$$\% \chi_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

where ΔH_m^0 is 139.5 J/g for 100% crystalline PCL.³¹ The reported results are based on the average of three measurements.

Shape Memory Properties

Shape memory properties of networks were quantitatively measured by strain-controlled cyclic-thermal mechanical tensile tests over four cycles (N) using a TA Instrument Q800 dynamic mechanical analyzer (DMA). Rectangular strips ($\sim 6.5 \text{ mm} \times \sim 3.0 \text{ mm} \times \sim 1.0 \text{ mm}$) were sequentially subjected to the following sequence: (1) after equilibrating at 80°C (T_{high}) for 5 min, elongate to a maximum strain ($\epsilon_m = 75\%$) at a rate of 50% strain/min (or 3.1 mm/min), (2) hold at ϵ_m for 5 min and then cool to 25°C (T_{low}) to fix the temporary shape, (3) remove the load and immediately measure ϵ_u , and (4) reheat the sample to 80°C (T_{high}) to recover the permanent shape, measure ϵ_p and then begin the second cycle. For each network composition, the analysis was done in triplicate. The shape memory effect was quantified by strain fixity (R_f), strain recovery (R_r) and total strain recovery ($R_{r,\text{tot}}$).⁴ Strain fixity (R_f) quantifies the ability of the material to maintain a mechanical deformation (ϵ_m) after cooling resulting in a temporary deformation (ϵ_u):

$$R_f(N) = \frac{\epsilon_u(N)}{\epsilon_m}$$

For each cycle (N), strain recovery rate (R_r) quantifies the ability of a material to return to its permanent shape (ϵ_p) after application of mechanical deformation (ϵ_m):

$$R_r(N) = \frac{\epsilon_m - \epsilon_p(N)}{\epsilon_m - \epsilon_p(N-1)}$$

where $\epsilon_p(N-1)$ and $\epsilon_p(N)$ are strains of the sample in two successively passed cycles in the stress-free state. Total strain recovery rate ($R_{r,\text{tot}}$) is defined as the total recovered strain for each independent cycle ($\epsilon_p(N)$) as compared to the original strain deformation (ϵ_m):

$$R_{r,tot}(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m}$$

Tensile Properties

Tensile tests of networks were performed at RT on a tensile tester (Instron 3345). Rectangular strips ($\sim 10 \text{ mm} \times \sim 3.2 \text{ mm} \times \sim 1.0 \text{ mm}$) were subjected to a constant strain rate (50 mm/min) in tension until broken.³² From the stress-strain curves, tensile modulus (E), tensile strength (TS) and percent elongation at break ($\% \varepsilon$) were determined. The reported values are an average of three measurements.

Toughness

Toughness (MJ/m^3) of networks was calculated as the area under their stress-strain curve produced via tensile tests above. The reported results are based on the average of three measurements.

Stress Relaxation Behavior

Rectangular samples ($\sim 8.5 \text{ mm} \times \sim 3.0 \text{ mm} \times \sim 1.0 \text{ mm}$) were subjected to a 1% instantaneous strain at 37 °C using the DMA operating in the tension mode. The ratio of instantaneous stress to the initial stress (i.e. reduced stress) was determined by tracking the change in stress for 10 h while maintaining a constant strain (1%).³³ The reported results are an average of three measurements.

Surface Properties

Static (θ_{static}), advancing (θ_{adv}), and receding (θ_{rec}) contact angles of distilled/deionized (DI) water droplets at the solid-air interface of networks were measured at RT with a CAM 200 (KSV Instrument) contact angle measurement system equipped with an autodispenser, video camera and drop-shape analysis software. θ_{static} measurements were acquired from a 5 μL sessile water droplet at 15 s and 120 s following deposition. The θ_{adv} was measured by addition of a 3 μL (0.25 $\mu\text{L/s}$) to a 5 $\mu\text{L/s}$ water droplet to advance the contact line. The θ_{rec} was measured by subsequent removal of 4 μL (0.25 $\mu\text{L/s}$) from the same droplet to recede the contact line. The θ_{static} , θ_{adv} , and θ_{rec} values reported are an average of three from measurements taken on different areas of the same specimen.

Swelling Behavior

For each composition, three rectangular strips ($\sim 20 \text{ mm} \times \sim 3.2 \text{ mm} \times \sim 1.0 \text{ mm}$) were sealed inside a centrifuge tube containing 30 mL of PBS, immersed in a temperature-controlled water bath at 37 °C for 24 and 72 h, removed, gently blotted with a Kim Wipe and weighed. The swelling ratio was calculated according to the equation³⁴:

$$q = W_s / W_i$$

where W_s is the mass measured immediately after soaking and W_i is the initial mass before soaking. The reported results are the average of three specimens.

RESULTS AND DISCUSSION

Photocrosslinking

PCL-based SMPs with PDMS soft segments of varying lengths were formed by the convenient photochemical cure of AcO-PCL₄₀-*block*-PDMS_{*m*}-*block*-PCL₄₀-OAc (*m* = 20, 37, 66, or 130) (**b-smp1-4**) (Scheme 1, Table 1). A constant, sufficiently long PCL segment length (*n* = 40) was selected to permit sufficient PCL crystallization capable of producing shape memory behavior. By systematic control of the PDMS segment length, PDMS:PCL ratio, *M_n* and crosslink density of the resulting SMP networks were altered. The sol content of **SMP1-4** were determined to all be less than 10 wt% and did not significantly increase with longer soaking times. We observed that photocrosslinking of macromers in the melt state, rather than DCM-based solutions of macromer, produced fragile and brittle networks.

Thermal Properties

The thermal properties of **SMP1-4** networks were determined by DSC (Table 1). With increasing PDMS segment length, the *T_m* of PCL segments did not vary substantially. However, crystallinity decreased from 32 % (**SMP1**, *m* = 20) to 19% (**SMP4**, *m* = 130) and ΔH_m similarly decreased. This indicates that increasing the length of PDMS segments somewhat interferes with PCL segment crystallization. However, **SMP1-4** all exhibited shape memory behavior, indicating that 19% PCL crystallinity is sufficient.

Shape Memory Properties

Shape memory properties of **SMP1-4** were quantified in terms of *R_f*, *R_r* and *R_{r,tot}* strain-controlled cyclic thermal mechanical tensile tests over four cycles (*N*) (Table 2). Ideally, *R_f*, *R_r* and *R_{r,tot}* should be 100% reflecting perfect shape fixity and shape recovery. Despite the lower PCL crystallinity and lower crosslink density produced by increasing PDMS segment length from **SMP1** to **SMP4**, all SMPs exhibited very high shape fixity and recovery due to sufficient crystallinity (> 19%) and also the high regularity imparted by chemically crosslinked systems.¹⁶ For all networks, *R_f* was ~99% after each cycle. *R_r* and *R_{r,tot}* of **SMP1-4** were not significantly different from each other and were approximately 97–98% (*R_r*) or 91–96% (*R_{r,tot}*). *R_{r,tot}* decreased with each cycle (*N*) and most significantly from *N* = 1 to *N* = 2 due to the extensive chain realignment of original cast film chains when first deformed.^{10–11} Previously reported SMP networks formed from diacrylated PCL_{*n*}-*block*-PDMS₃₇-*block*-PCL_{*n*} (*n* = 30 or 50) exhibited similarly high values of *R_f* (~98 or ~99%, respectively), *R_r* (~98%) and *R_{r,tot}* (~93 or ~96%, respectively).

Tensile Properties and Toughness

Tensile tests were used to characterize the effect PDMS soft segment length on SMP network mechanical properties (Table 3) and compared to thermoplastic PCL.³⁵ An increase in PDMS segment length (**SMP1** < **SMP2** < **SMP3** < **SMP4**) produced a decrease in crosslink density, an increase in low *T_g* PDMS segment content and a decrease in PCL % crystallinity. Thus, as expected, *E* decreased from 75 MPa (**SMP1**) to 15.3 MPa (**SMP4**) and *TS* decreased from 10.2 MPa (**SMP1**) to 3.4 MPa (**SMP4**). Although %*ε* was expected to decrease with lower crosslink density, %*ε* decreased in the order: **SMP1** ≈ **SMP2** > **SMP3** > **SMP4**. This trend and relatively low %*ε* observed for **SMP4** may be explained by examining the corresponding stress-strain curves generated by from the tensile tests (Figure 1). For **SMP1-4**, there was observed an initial sharp linear increase in stress due to elongation of tie chains followed by a relative plateau in stress due to separation of PCL lamellae.³⁶ The plateau continued over the largest %*ε* for **SMP1** which had the highest % crystallinity of PCL. For **SMP1-3**, stress began to subsequently increase and failed at very high %*ε*. In contrast, **SMP4** exhibited a minor increase in stress and failed relatively lower

% ϵ . Following rupture of PCL crystalline lamellae, the high amount of stress transferred to amorphous tie chains which were increasingly comprised of rubbery PDMS segments were apparently unable to withstand the stress.³⁷ Thus, relatively higher PCL content and corresponding greater % crystallinity produced SMP networks with higher E and TS as well as % ϵ .

Notably distinct from other PCL-based SMPs were the high E and TS values coupled with high % ϵ achieved by these SMP networks, particularly by **SMP1**. Photochemical cure of oligo(ϵ -caprolactone)dimethacrylates (M_n 1.5k to 10k g/mol) produced SMPs whose % ϵ increased (16 to 296 %) but E (71 to 2.4 MPa) and TS (16.2 to 0.4 MPa) simultaneously decreased.¹⁶ PCL-based SMPs containing poly(n -butyl acrylate) soft segments ($T_g = -55$ °C) were prepared by crosslinking of n -butyl acrylate with oligo(ϵ -caprolactone)dimethacrylates ($M_n = 10k$ g/mol).⁶ As the amount of n -butyl acrylate was increased (from 20 to 71 wt%), crosslink density decreased and % ϵ typically increased (290 to 555 %) but with a simultaneous decrease in E (58 MPa to ~7.8 MPa) and TS (14.6 to 4.3 MPa). SMP networks formed from diacrylated PCL_{*n*}-*block*-PDMS₃₇-*block*-PCL_{*n*} ($n = 30$ or 50) also exhibited high values of E , TS and % ϵ . For $n = 30$, $E = 49.0$ MPa, $TS = 7.0$ MPa, % $\epsilon = 459$ and for $n = 50$, $E = 60.5$ MPa, $TS = 15.9$ MPa, % $\epsilon = 1197$.²⁹ Thus, PCL-based SMPs with tunable and exceptional tensile properties may be achieved by varying both the PCL and PDMS segment lengths.

Toughness, a measure of a material's ability to absorb energy prior to fracture, is an important property of an implanted device.³⁸ Toughness of common polymers varies significantly [e.g. poly(L-lactide) (PLA; 1.6 MJ/m³)³⁹ polymethylmethacrylate (PMMA; ~2 MJ/m³)⁴⁰, polycarbonate (PC; 8.9 MJ/m³)⁴¹ and UHMWPE (~60 MJ/m³)⁴²]. While tensile toughness of SMPs have not been widely reported, that of a series of SMPs based on methacrylate networks were shown to vary from approximately 1 to 25 MJ/m³ depending on their composition.³⁴ Toughness of **SMP1-4** are reported in Table 3. **SMP1** and **SMP2** exhibited very high toughness values of 53.3 and 56.0 MJ/m³, respectively. With higher PDMS soft segment lengths, the toughness of **SMP3-4** decreased significantly (30.4 and 6.5 MJ/m³, respectively). Again, this is attributed to their lower PCL content and resulting diminished PCL % crystallinity which led to lower E and % ϵ values, particularly for **SMP4**.

Stress Relaxation Behavior

Stress relaxation of SMPs at body temperature (37 °C) is of interest when considering their use as implanted medical devices. The effect of PDMS soft segment length on PCL-based SMP stress relaxation behavior was assessed by subjecting specimens to a small, constant strain (1%) and measuring the reduced stress, defined as the ratio of instantaneous stress to initial stress (Figure 2).³³ As a result of decreasing crosslink density and PCL % crystallinity, reduced stress decreased from **SMP1** to **SMP4** (Figure 2). The reduced stress values of **SMP1-3** were substantially higher than that of **SMP4**. **SMP4** ($m = 130$) is comprised of PDMS soft segments nearly twice the length of **SMP3** ($m = 66$) which led to a significant enhancement in molecular relaxation and hence stress relaxation. A small increase in reduced stress was noted for **SMP1** and **SMP2** before reaching a steady state which may have resulted from strain induced crystallization of amorphous PCL segments.

Surface Properties and Swelling Behavior

Minimizing adsorption of water by SMPs is useful as this can lead to diminished shape memory and mechanical properties because of plasticization.^{34,43} Surface properties and swelling behavior was used to characterize the interaction of SMP networks with water (Table 4) and compared to silicone⁴⁴ and PCL controls. Although cured between glass slides, **SMP1-4** produced θ_{static} values expected on the basis of their composition relative to

silicone and PCL controls which were cured in air. Possible restructuring effects at the glass interface was eliminated since a solvent-swollen network (i.e. not a neat film) was produced in the mold, removed and then dried in air. As expected, **SMP1-4** are hydrophobic as indicated by θ_{static} values above 90° ⁴⁵ and also higher than that of pure PCL due to the presence of hydrophobic PDMS segments. θ_{static} of **SMP4**, perhaps due to the increased crosslink density and PCL crystallinity, was slightly higher than that of the silicone control. Hysteresis ($\theta_{\Delta} = \theta_{adv} - \theta_{rec}$) was similarly observed to be quite small indicating minimal surface reconstruction with water contact over a short period of time (~15 sec).⁴⁶ In addition, θ_{static} (at 2 min) was only slightly lower than that of θ_{static} (at 15 sec) which suggests the surface reconstruction was still minor even with longer exposure time to water (105 sec). As a result of their hydrophobicity, **SMP1-4** adsorbed very little water (~ < 3%) when exposed to PBS at 37 °C (Table 3). Increasing exposure time from 24 to 72 hr did not increase the swelling ratio. These swelling ratios are quite low among SMP networks including methacrylate-based SMPs and should favor minimal plasticization when exposed to water.^{34,43}

CONCLUSIONS

PCL-based SMP networks containing PDMS soft segments (**SMP1-4**) were prepared by the photochemical cure of AcO-PCL₄₀-*block*-PDMS_m-*block*-PCL₄₀-OAc (m = 20, 37, 66 and 130) in CH₂Cl₂ (25 wt%). The length of PCL segments was maintained at sufficient level (n = 40) to permit adequate crystallization of PCL switching segments needed to produce shape memory behavior. All SMPs exhibited excellent shape recovery and shape fixity. As the length of PDMS soft segments were tuned, the tensile properties were systematically altered. With relatively shorter PDMS soft segments (n = 20 and n = 37), particularly high values of *E*, *TS*, %*e* as well as toughness were achieved. Because of their hydrophobicity, these SMPs absorb little water which could otherwise lead to plasticization effects.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Figure 2.

Scheme 1.

Table 1

Thermal properties of networks

Network	PDMS (m)	M_n (g/mol)	T_m (°C)	ΔH_m (J/g)	Cryst. (%)
SMP1	m = 20	10,956	48 ± 0.4	44 ± 4.1	32 ± 2.9
SMP2 *	m = 37	12,214	50 ± 0.1	37 ± 2.0	26 ± 1.4
SMP3	m = 66	14,360	50 ± 0.1	36 ± 1.5	26 ± 1.1
SMP4	m = 130	19,096	53 ± 0.3	27 ± 1.9	19 ± 2.3

*The data was reported in reference 29.

Table 2

Shape memory properties of networks

Network	Cycle (N)	R_r (N), %	$R_{r,tot}$ (N), %	R_f (N), %
SMP1	1	97.0 ± 0.9	97.0 ± 0.9	99.9 ± 0.1
	2	98.9 ± 0.3	96.0 ± 0.7	99.9 ± 0.1
	3	99.1 ± 0.1	95.1 ± 0.8	99.9 ± 0.1
	4	99.2 ± 0.1	94.3 ± 0.8	99.9 ± 0.1
	Ave (1–4)	98.6 ± 0.2	95.6 ± 0.8	99.9 ± 0.1
SMP2 *	1	94.3 ± 0.5	94.3 ± 0.5	99.0 ± 0.2
	2	97.3 ± 1.0	91.7 ± 1.0	99.1 ± 0.2
	3	98.6 ± 0.3	90.4 ± 0.3	99.1 ± 0.2
	4	98.8 ± 0.3	89.3 ± 0.3	99.1 ± 0.2
	Ave (1–4)	97.3 ± 0.5	91.4 ± 0.5	99.1 ± 0.2
SMP3	1	95.8 ± 1.0	95.8 ± 1.0	99.9 ± 0.1
	2	96.6 ± 0.8	92.6 ± 1.6	99.9 ± 0.1
	3	97.9 ± 0.7	90.7 ± 2.2	99.9 ± 0.1
	4	98.3 ± 0.6	89.1 ± 2.6	99.9 ± 0.1
	Ave (1–4)	97.2 ± 0.8	92.1 ± 1.9	99.9 ± 0.1
SMP4	1	97.0 ± 0.4	97.0 ± 0.4	99.4 ± 0.1
	2	98.6 ± 0.2	95.7 ± 0.2	99.5 ± 0.1
	3	99.2 ± 0.3	94.9 ± 0.1	99.5 ± 0.1
	4	98.8 ± 0.7	93.8 ± 0.7	99.5 ± 0.1
	Ave (1–4)	98.4 ± 0.4	95.4 ± 0.4	99.5 ± 0.1

* The data was reported in reference 29.

Table 3

Tensile properties of networks

Network	PDMS (m)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain at break (%)	Toughness (MJ/m ³)
SMP1	m = 20	75.0 ± 1.7	10.2 ± 0.7	719 ± 21	53.3 ± 7.5
SMP2 [*]	m = 37	47.4 ± 2.8	10.4 ± 0.3	814 ± 36	56.0 ± 5.5
SMP3	m = 66	37.2 ± 1.9	6.9 ± 0.5	543 ± 77	30.4 ± 4.8
SMP4	m = 130	15.3 ± 1.0	3.4 ± 0.4	233 ± 23	6.5 ± 0.5

PCL (thermoplastic, $M_n = 50,400$ g/mol); E (68 MPa), TS (14 MPa), e % (830%),³⁵^{*} Data was reported in reference 29.

Table 4

Surface properties of networks

Network	Static Contact Angle		Dynamic Contact Angle		Swelling ratio	
	$\theta_{\text{static}} (^{\circ})$ @ 15 s	$\theta_{\text{static}} (^{\circ})$ @ 120 s	$\theta_{\text{adv}} (^{\circ})$	$\theta_{\text{rec}} (^{\circ})$	(After soaking in PBS for 24 h)	(After soaking in PBS for 72 h)
SMP1	96 ± 1	94 ± 1	86 ± 1	83 ± 1	1.014 ± 0.003	1.014 ± 0.002
SMP2	101 ± 1	97 ± 1	106 ± 2	100 ± 2	1.020 ± 0.002	1.019 ± 0.002
SMP3	99 ± 1	96 ± 2	103 ± 2	99 ± 2	1.027 ± 0.003	1.029 ± 0.002
SMP4	121 ± 2	119 ± 1	126 ± 1	120 ± 2	1.021 ± 0.003	1.022 ± 0.002
PCL *	81 ± 1	78 ± 1	79 ± 2	79 ± 1	-	-
Silicone*	116 ± 1	115 ± 1	121 ± 1	115 ± 1	-	-

PCL: solvent cast film

Silicone: Dow corning Silastic T-2 film cured on a glass microscope slide⁴⁴