Soft Bacterial Polyester-Based Shape Memory Nanocomposites Featuring Reconfigurable Nanostructure

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ABSTRACT: In this work, a novel soft shape memory polymer nanocomposite derived from a bacterial medium-chain-length polyhydroxyalkanoate, poly(3-hydroxyoctanoate-co-3-hydroxyundecenoate) (PHOU), used to form a covalent network grafted with polyhedral oligomeric silsesquioxane (POSS), a crystallizable inorganic–organic hybrid nanofiller, was prepared. The PHOU–POSS nanocomposite, PHOU–POSSw-net [w (POSS content, wt %) = 0, 20, 25, 30, and 38], is a completely amorphous elastomer (w ≤ 20) or contains POSS nanocrystals embedded in the amorphous PHOU matrix (w ≥ 25). The hybrid nanostructure of PHOU–POSSw-net (w ≥ 25) is featured by its reconfigurability, based on aggregation and disaggregation of POSS covalently connected to the PHOU network, which enables excellent shape fixing and recovery. Furthermore, it exhibits soft and elastomeric mechanical properties even in the fixed state. Taking advantage of the shape memory ability as well as the softness in the fixed state, we demonstrate microscale dynamic surface topography of PHOU–POSSw-net. © 2011 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 50: 387–393, 2012

KEYWORDS: elastomers; polyesters; polyhedral oligomeric silsesquioxane; polyhydroxyalkanoates; reconfigurable nanostructures; shape memory polymers; soft nanocomposites; stimuli-sensitive polymers; X-ray

INTRODUCTION Shape memory polymers (SMPs), which are a class of responsive polymers that can be "fixed" into a deformed temporary shape and later recover to a permanent shape "memorized" by a crosslinked network structure upon a stimulus, most commonly heat,1–3 have gained much attention in recent years owing to the intrinsic versatility in a wide range of applications such as actuators,4 sensors,5 deployable medical devices,6 drug-delivery systems,7 and "active" cell culture substrates.8 For most existing SMPs, network vitrification or crystallization, the two primary mechanisms for shape fixing, leads to material rigidity [typically, elastic modulus (E) = 10¹ to 10¹⁵ MPa] in the fixed state below the transition temperature.1–11 However, recently, soft and elastomeric SMPs with low stiffness (E = 10⁻² to 10¹ MPa) in the fixed state have emerged adopting different mechanisms or structures for shape fixing instead of network chain phase transitions; these include: (1) thermoreversible interchain associations in covalently or physically crosslinked amorphous networks,12–15 and (2) physical blending of semicrystalline polymers and amorphous elastomers.16,17 The former approach, which offers homogeneity to small length-scales, has potential for those applications involving microscale surface patterning, such as dry adhesion, microfluidics, biosensors, tissue engineering, and cell mechanics research, by introducing soft and active surface topology onto the material. However, the reported soft SMPs of approach (1) require substantial improvements in shape fixing and recovery completeness, topographical fidelity during the shape memory cycles, biocompatibility, and tailored tunability of surface properties for specific target applications.

Here, we report the preparation of a novel soft SMP nanocomposite with excellent bulk and surface shape memory properties, derived from a bacterial medium-chain-length polyhydroxyalkanoate (mcl-PHA), poly(3-hydroxyoctanoate-co-3-hydroxyundecenoate) (PHOU), used to form a covalent network grafted with polyhedral oligomeric silsesquioxane (POSS), a biocompatible18 and crystallizable inorganic–organic hybrid nanofiller. The biological polyesters PHAs, including PHOU, feature a variety of advantages such as biocompatibility19 and biological degradability19 over many synthetic polymers. PHOU is an attractive starting material in this study because of its high molecular weight, low-glass transition temperature (Tg), low crystallinity, the random sequence structure of saturated and unsaturated alkyl side chains along the main chain, and the facile controllability of copolymer composition.20–22 The dangling vinyl groups provide reactive sites for crosslinking,23 conversion to other

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functional groups,24 and binding to functional molecules.25 In our case, a portion of the vinyl groups along the chain is utilized for both covalent crosslinking and grafting of POSS [Fig. 1(a)]. Unreacted vinyl groups should be distributed throughout the material including the material surface, and is potentially useful to tune the surface properties by further chemical modification at the surface. Unlike traditional polymer nanocomposites in which the nanostructure (once formed) never changes, it is shown in this study that the aggregation and disaggregation of dangling POSS in the PHOU network at moderate temperatures provide a unique mechanism to “reconfigure” the nanostructure under externally imposed thermomechanical conditions, resulting in excellent shape memory behavior.

PHOU–POSS nanocomposites were prepared by one-step UV-initiated thiol-ene reaction of PHOU [the unsaturated “U”-unit content = 55 mol % (1H NMR, Supporting Information Figure S1), the number-average molecular weight, $M_n = 149,200$ and polydispersity index, PDI = 1.9 (gel permeation chromatography, GPC)] with “tetra-thiol” crosslinking agent with four thiol groups and thiol-functionalized POSS (“POSS thiol,” the feed weight contents $w = 0, 20, 35, 30,$ and 40 wt %) in tetrahydrofuran (THF) solutions in the presence of photo-initiator DMPA, which simultaneously crosslinks the linear PHOU and grafts POSS molecules to the side chains at random locations but in a controlled fashion [Fig. 1(a)]. It is noted that the free radical condition can also induce the reaction between vinyl groups, which forms another type of

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**FIGURE 1** (a) Synthetic scheme of soft SMP nanocomposites, PHOU–POSSw-net. (b) 1D WAXS profiles of POSS thiol, PHOU, and PHOU–POSSw-net ($w = 0, 20,$ and 38). Peaks and $d$-spacing values for PHOU and PHOU–POSSw-net obtained by curve deconvolution are shown using colors of pink (PHOU crystalline), blue (PHOU amorphous), red (POSS crystalline), and green (POSS amorphous). (c) POSS content-dependence of $T_m$, $\Delta H_m$, and $T_g$ values of PHOU–POSSw-net determined based on DSC. (d) DMA curves ($3 \degree C \ min^{-1}$, 1 Hz) for storage modulus ($E'$) and loss tangent ($\tan \delta$).
covalent crosslinking. Based on thermogravimetric analysis (TGA, Supporting Information Figure S2) after the extraction of soluble components, the actual content of POSS (w) covalently connected to PHOU network was determined to be 0, 20, 25, 30, and 38 wt %. In this study the nomenclature of “PHOU–POSS-w-net” (w = 0, 20, 25, 30, and 38) is used for the nanocomposites.

Wide-angle X-ray scattering (WAXS) was utilized to characterize the structure of PHOU–POSS-w-net. One-dimensional (1D) WAXS profiles for POSS thiol, PHOU (uncrosslinked), and PHOU–POSS-w-net are shown in Figure 1(b) and Supporting Information Figure S3. POSS thiol showed strong diffraction peaks at 20 = 8.2°, 11.1°, and 19.2°, derived from {10\(\overline{1}\)1}, {11\(\overline{2}\)0}, and {11\(\overline{2}\)3}/[30\(\overline{3}\)0] planes of hexagonal POSS crystal, respectively. As for neat, uncrosslinked PHOU, it is known that PHOU and other mcl-PHAs crystallize as a 2\(\overline{1}\) helix in an orthorhombic lattice with two molecules per unit cell, and the polyester chains form ordered sheets with extended planar zigzag conformation of the alkyl side chains. Curve deconvolution for the WAXS profiles of PHOU and PHOU–POSS-w-net was performed to separate diffraction peaks and amorphous halos [Fig. 1(b)]. PHOU showed several diffraction peaks, and the d-spacing values of 19.3 Å and 4.6 Å are attributed to the distance between two main chain helices in the same sheet and that between two sheets, respectively. PHOU also showed large and broad amorphous halos at two positions (d = 14.7 Å and 4.6 Å), attributed to two different average interchain distances in the amorphous phase, similar to that seen in poly(ethylene terephthalate). Similar broad halos from the amorphous phase were observed for all of PHOU–POSS-w-net. However, PHOU crystallization was completely suppressed by the covalent crosslinking: PHOU–POSS-w-net lost the diffraction peaks from PHOU phase entirely.

Unlike PHOU–POSS-w-net (w ≤ 20) in which POSS is well-dispersed in the amorphous PHOU matrix, PHOU–POSS-w-net (w ≥ 25) showed sharp diffraction peaks derived from POSS crystals [Fig. 1(b) and Supporting Information Figure S3]. Based on the peak positions [Fig. 1(b)], d-spacing values for {10\(\overline{1}\)1} and {11\(\overline{2}\)0} planes of hexagonal POSS crystallite were calculated (Supporting Information Figure S4a). The d-spacing values of PHOU–POSS-w-net (d_{10\(\overline{1}\)1} = 10.6 Å and d_{11\(\overline{2}\)0} = 7.9 Å) were not affected by the POSS content and almost identical with those of POSS thiol, indicating that the molecular packing of POSS in the hexagonal crystallites was not disturbed by PHOU chains. Apparent POSS crystallite sizes along the {10\(\overline{1}\)1} direction were estimated from the width of diffraction peaks at 20 = 8.4° for PHOU–POSS-w-net (w = 25, 30, and 38) using the Scherrer equation \(D_{10\(\overline{1}\)1} = \lambda/(\beta \cos(\theta))\), where \(D_{10\(\overline{1}\)1}\) is the apparent crystallite size perpendicular to the {10\(\overline{1}\)1} planes, \(\lambda\) is the X-ray wavelength, \(\beta\) is the full width at half maximum of diffraction peak). The calculated values were 20 ± 1 nm and, quite surprisingly, were not affected by the POSS content (Supporting Information Figure S4b). On the other hand, areas of the diffraction peaks increased with an increase in POSS content, indicating the degree of crystallinity of those nanocomposites increased (Supporting Information Figure S3).

Phase behavior of PHOU–POSS-w-net was investigated using differential scanning calorimetry (DSC). The glass transition temperature \(T_g\), melting temperature \(T_m\), and heat of melting \(\Delta H_m\) are plotted against POSS content in Figure 1(c). The \(T_g\) value linearly increased from −43 °C to −26 °C with an increase in POSS content from 0 to 38 wt %, indicating the chain mobility was restricted by the bulky POSS molecules. PHOU–POSS-w-net (w ≥ 25) exhibited well-defined melting associated with the POSS crystals. The \(T_m\) and \(\Delta H_m\) values increased in the range of 24–49 °C (bracketing physiological temperature) and that of 0.8–3.1 J g\(^{-1}\), respectively, with an increase in POSS content. The higher \(\Delta H_m\) value for higher POSS content was directly related to the higher degree of crystallinity. The \(T_m\) data implies that the crystal size increases with an increase in POSS content. Combined with WAXS data, we conclude that this crystal thickening must happen in a growth direction other than \{10\(\overline{1}\)1\}.

Figure 1(d) shows the storage modulus \(E’\) and the loss tangent (\(\tan \delta\)) of PHOU–POSS-w-net obtained with dynamic mechanical analysis (DMA). PHOU–POSS-w-net (w ≤ 20) exhibited only one step decrease of \(E’\) and one peak of \(\tan \delta\) due to the glass to rubber transition; the materials are ordinary elastomers. In contrast, PHOU–POSS-w-net (w ≥ 25) showed two step decreases of \(E’\), derived from the glass-rubber transition at a lower temperature and the melting of POSS crystallites at a higher temperature, the two desirably bracketing room temperature so that the materials are soft under ordinary conditions. Both transition temperatures increased with an increase in POSS content, in good agreement with the DSC data. The \(E’\) values of PHOU–POSS-w-net (w = 25, 30, and 38) at 25 °C (and at 37 °C) were 1.49 MPa (0.58 MPa), 15.1 MPa (9.36 MPa), and 26.1 MPa (18.7 MPa), respectively, and \(\tan \delta\) values at both temperatures were ≤0.14 [Fig. 1(d) and Table 1], and thus those nanocomposites are proven to be relatively soft and elastic materials. Furthermore, above the \(T_g\) (w ≤ 20) and the \(T_m\) of POSS (w ≥ 25) of PHOU–POSS-w-net, all the samples did not flow and showed a stable plateau region at low \(E’\) values of 0.3–0.4 MPa owing to covalent crosslinkage. The molecular weights between crosslinking points \(M_c\) were calculated using the \(E’\) values at 90 °C (Table 1). The calculated \(M_c\) values were 21,000–30,000 g mol\(^{-1}\), which are unexpectedly large considering the feed molar ratio of PHOU and tetrathiol (10/1 double bond of PHOU/thiol group of tetrathiol, \(M_c\) in feed is ~3000). The reactivity between vinyl groups should further reduce the \(M_c\) value. The deviation between the “theoretical” and “actual” \(M_c\) values should be partially derived from imperfect thiolen reaction, but can also be attributed to the plasticizing effect of side chains which lowers the modulus of the material, as observed for crosslinked densely grafted polymers.

A well-established four-step cyclic thermomechanical method (one-way shape memory cycle)\(^{1–3}\) was utilized to quantitatively characterize the shape memory properties. The results for PHOU–POSS-w-net (w = 0 and 30) are shown in Figure 2(a). Those for the other samples are shown in Supporting Information Figure S5. For PHOU–POSS30-net, a rectangular film was first heated to 75 °C to melt the POSS crystallites...
and stretched by gradually ramping the tensile force (I). Then, the stretched material was cooled to 0 °C while maintaining the external force constant, and kept at the temperature for 10 min to allow POSS crystallization (II). After that, the force was gradually removed to evaluate shape fixing (III). PHOU–POSS30-net showed little change in strain after unloading, and that, significantly, the plate-like nanocrystals form layered structure reversible; we refer to this as reconfigurability. Azimuthal profiles of 2D SAXS patterns of fixed and unstretched PHOU–POSS38-net [Fig. 2(c), right] indicate that, unlike unstretched sample, the fixed sample has well-oriented layered structure of plate-like nanocrystals along to the stretching direction over the material. The POSS crystals retain the deformed covalent network and macroscopically, the deformed shape is fixed.

In contrast to PHOU–POSSsw-net (w ≥ 30), PHOU–POSSsw-net (w ≤ 20) did not show any usable shape fixing due to the lack of POSS crystallization (therefore insufficient nanoscale reconfigurability), and the stretched film recovered to its original dimensions as the external force was released. Continuing the shape memory cycle, PHOU–POSS30-net was finally reheated to 75 °C to melt the POSS crystals and trigger shape recovery. The same cycle was repeated two more times to examine repeatability. The fixing and recovery ratios (Rf and Rr, respectively) were calculated according to the literature and listed in Table 1. PHOU–POSSsw-net (w ≥ 30) showed very high Rf and Rr values with minimal changes over three cycles (Rf ≥ 96% and Rr ≥ 98%), indicating nearly perfect fixing and recovery, and good cycle repeatability. Another composition, PHOU–POSS25-net, showed shape memory behavior but with moderate shape fixing (average

<table>
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<tr>
<th>Sample</th>
<th>E 25 °C (MPa)b</th>
<th>E 37 °C (MPa)c</th>
<th>E 90 °C (MPa)d</th>
<th>Mw (kg mol⁻¹)e</th>
<th>Cyclef</th>
<th>Rf (%)g</th>
<th>Rr (%)h</th>
<th>T5% (°C)i</th>
<th>T50% (°C)j</th>
<th>T95% (°C)k</th>
<th>ΔT95%–5% (K)l</th>
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<td>0.30</td>
<td>0.32</td>
<td>28</td>
<td>1</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>–</td>
<td>–</td>
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<tr>
<td>w = 20²</td>
<td>0.29</td>
<td>0.28</td>
<td>0.30</td>
<td>30</td>
<td>1</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>w = 25³</td>
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<td>0.44</td>
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<td>97.7</td>
<td>100</td>
<td>59</td>
<td>66</td>
<td>76</td>
<td>17</td>
</tr>
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</table>

- PHOU–POSSsw-net.
- Storage moduli at 25 °C (b), 37 °C (c), and 90 °C (d).
- The number-average molecular weight between the crosslinking points (Mw) calculated from
- ³ The cycle number of shape memory cycle shown in Figure 2(a) and Supporting Information Figure S5.
- ⁵ Shape fixing ratio calculated from Rf(N) = w0(N)/w∞(N) × 100, where w∞, w0, and N represent the strain before unloading, the strain after unloading, and the cycle number, respectively.
- Shape recovery ratio calculated from Rs(N) = \( r_d(N) / (r_d(N) - r_p(N - 1)) \) × 100, where \( r_p \) represents the residual strain after heat-induced recovery.
- Temperatures at which samples showed the shape recovery of 5% (i), 50% (j), and 95% (k).
- Shape fixing temperatures were –10 °C (i), –20 °C (m), 0 °C (n), and 10 °C (o).

*Not determined.*
Rf = 81.3%) due to the low degree of POSS crystallinity. It is noted that the temperature range where the samples showed the shape recovery (ΔT 55–5%, Table 1) became significantly narrower with an increase in POSS content, which is probably related to the difference in size distribution of POSS nanocrystals and/or that in homogeneity of heat conductivity.

Finally, we visually demonstrate the shape memory of the soft PHOU–POSS nanocomposite (Fig. 3). As shown in Figure 3(a), a flat and rectangle PHOU–POSS38-net film was deformed and fixed in a twisted shape. The twisted and fixed sample exhibited soft and elastic properties as shown in the picture, which corresponds with the thermomechanical analysis mentioned above. The fixed material recovered its original permanent shape quickly (≤5 s) upon heating above the POSS melting temperature. The PHOU–POSS nanocomposites are also suitable for a variety of surface shape memory applications. For example, they can be used to generate controlled surface patterns in a facile fashion. To demonstrate this, a rectangular film of PHOU–POSS38-net was first fixed into a bent shape and the convex surface was spatter coated with gold (thickness, ~30 nm). Heating was then applied to trigger shape recovery, resulting in formation of periodical wrinkles perpendicular to the stretching direction [Fig. 3(b)] owing to the difference in modulus between the soft substrate and the harder metal coating. Two-dimensional fast Fourier transform (2D-FFT) of the SEM image [inset of Fig. 3(b)] indicates the wrinkles are uniaxially well-oriented with coexistence of two wavelengths of ~2.5 and ~5 μm. To further demonstrate the benefit of softness, we show an example of "reversible embossing". A PHOU–POSS38-net film was compressed onto two embossing masters with different surface patterns at 90 °C and then cooled to 10 °C. Since the material is elastomeric even at the fixed state, it could be easily peeled off the master while preserving the negatively replicated surface topology [Fig. 3(c)]. Heating the embossed material removes the surface features completely [Fig. 3(c)], allowing the use of the material reversibly and repeatedly as a medium for surface replication or as a pumping mechanism for microfluidic devices.

To conclude, we have prepared a novel soft SMP nanocomposite by molecularly functionalizing bacterial biopolyester PHOU with POSS. The soft mechanical properties and excellent shape memory ability are attributed to the capability of POSS embedded in the PHOU matrix to reconfigure the nanocrystal structure of the material under external thermomechanical conditions. Further chemical modification for the PHOU–POSS nanocomposites for the control of hydrophilicity/hydrophobicity balance, cell adhesion, and degradability will enable "tailored" SMP preparation for various biomedical and biotechnological applications.

**EXPERIMENTAL**

**Synthesis**

PHOU ("U"-unit content = 55 mol %, Mn = 149,200, PDI = 1.9) was biosynthesized using *Pseudomonas putida* GPO1 (ATCC 29347) and carefully purified according to the previous literature. The PHOU comprised five comonomer units; 3 mol % of 3-hydroxyhexanoate, 42 mol % of 3-hydroxyoctanoate, 5 mol % of 3-hydroxyheptenoate, 35 mol % of 3-hydroxynonenoate, and 15 mol % of 3-hydroxyundecenoate. PHOU–POSS nanocomposites were synthesized by photo-cure (k = 365 nm, 2.5 mW cm⁻², 1 h) for THF solutions of PHOU (0.25 g mL⁻¹), 1-(3-mercapto)propyl-3,5,7,9,11,13,15-isobutylpentacyclo[9.5.1.13,9.15,15.17,13]octasiloxyan (POSS thiol, 0, 20, 30, 35, and 40 wt %), and 1-(3-mercaptopropyl)-3,5,7,9,11,13,15-isobutylpentacyclo[9.5.1.13,9.15,15.17,13]octasiloxyan (POSS thiol, 0, 20, 30, 35, and 40 wt %).
having repeated peaks with a height of 50
recovered PHOU–POSS38-net films. Two kinds of microscale
3D images obtained from surface profilometry for fixed and
is shown in the upper right corner. (c) "Reversible embossing":
POSS38-net film. The scale bar represents 20
mm. (b) SEM image of wrinkled surface of gold-coated PHOU–
ent shape at 90
elastic behavior at room temperature and can recover its perma-
FIGURE 3 (a) Shape memory behavior of PHOU–POSS38-net
film: a straight permanent shape can be easily fixed to a twisted
temporary shape. The fixed nanocomposite exhibits a soft and
elastic behavior at room temperature and can recover its perma-
ate at 90 °C overnight to measure the gel fractions (= 89–91 wt %
for all the samples), and the remaining insoluble materials
were dried again under vacuum at room temperature for 2
days prior to all the analyses.
Analytical Procedures
Chemical composition of PHOU was determined using 1H
NMR (300 MHz, CDCl3, Supporting Information Figure S1)
and 13C NMR (75 MHz, CDCl3). The $M_w$, weight-average mo-
lecular weight ($M_w$), and PDI values were determined using
GPC (THF, 40 °C) equipped with Waters 2414 refractive index (RI)
detector and a multi-angle laser light scattering apparatus (Wyatt mini-DAWN TREOS). TGA was performed from 40 to 600 °C at 10 °C min⁻¹ in a nitrogen atmosphere.
WAXS/SAXS measurements were carried out at room tem-
perature using Rigaku S-MAX3000 operated at 45 kV and
and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 5 mg mL⁻¹)
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days prior to all the analyses.

Wrinkle Formation and Reversible Embossing
For wrinkle formation on the surface of PHOU–POSS38-net,
a flat rectangle film (15 × 2 × 0.5 mm²) was bent around a
glass bar (diameter = 5 mm) at 90 °C and cooled down at 4 °C for 10 min to fix the bent temporary shape. The fixed
film was coated with gold (thickness, ~30 nm) using a sputter coater at room temperature. The shape recovery from the bent fixed shape to the straight shape of the gold-
coated film was performed at 90 °C. The wrinkled film sur-
face was observed using SEM JEOL 5600. The 2D-FFT for a
square SEM image was carried out using the Gwyddion
pentaeerythritol tetrakis(3-mercaptopyronionate) (tetrathiol,
2.5 mol % of "U"-units of PHOU, target $M_w$ ~ 3000 g mol⁻¹),
and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 5 mg mL⁻¹)
using a mold consisting of two glass slides and a Teflon
spacer (0.8-mm thickness). The cured materials were dried
under vacuum at room temperature for 2 days. Soluble com-
ponents were extracted from the cured materials using THF at
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NMR (300 MHz, CDCl3, Supporting Information Figure S1)
and 13C NMR (75 MHz, CDCl3). The $M_w$, weight-average mo-
lecular weight ($M_w$), and PDI values were determined using
GPC (THF, 40 °C) equipped with Waters 2414 refractive index (RI)
detector and a multi-angle laser light scattering apparatus (Wyatt mini-DAWN TREOS). TGA was performed from 40 to 600 °C at 10 °C min⁻¹ in a nitrogen atmosphere.
WAXS/SAXS measurements were carried out at room tem-
temperature using Rigaku S-MAX3000 operated at 45 kV and
and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 5 mg mL⁻¹)
were dried again under vacuum at room temperature for 2
days prior to all the analyses.

Wrinkle Formation and Reversible Embossing
For wrinkle formation on the surface of PHOU–POSS38-net,
a flat rectangle film (15 × 2 × 0.5 mm²) was bent around a
glass bar (diameter = 5 mm) at 90 °C and cooled down at 4 °C for 10 min to fix the bent temporary shape. The fixed
film was coated with gold (thickness, ~30 nm) using a sputter coater at room temperature. The shape recovery from the bent fixed shape to the straight shape of the gold-
coated film was performed at 90 °C. The wrinkled film sur-
face was observed using SEM JEOL 5600. The 2D-FFT for a
square SEM image was carried out using the Gwyddion
software (version 2.23). Fixed microscale surface embossed patterns were prepared for PHOU-POSS38-net film (5 × 2 × 0.5 mm³) using TA Instruments AR-G2 Rheometer and a patterned epoxy resin with repeated peaks of 150 µm in interval and 50 µm in height (master 1) and a patterned silicon wafer with square wells of 30 µm in size at the surface and 12 µm in depth (master 2) employing a similar procedure in the previous literature (b) except for the deformation temperature (90 °C) and shape fixing temperature (10 °C). The embossed patterns recovered to the original flat shape at 90 °C for 10 min. The surface profilometry for the fixed and recovered films was conducted using KLA Tencor P-16+ with 1000 × 1000 µm² and 300 × 300 µm² scan area, 20 µm and 10 µm scan speed, 100 µm and 5 µm line spacing for the experiments using masters 1 and 2, respectively.

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REFERENCES AND NOTES