Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.
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Supporting information:

Facile Fabrication of Ternary Nanocomposites with Selective Dispersion of Multi-walled Carbon Nanotubes to Access Multi-stimuli-responsive Shape-memory Effect

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Experimental Part:

1. Evaluation of thermally-induced SME for PBSPCL copolymer

The cyclic thermal-mechanical analysis of PBSPCL copolymer was conducted by DMA, the T_m of the copolymers are served as T_{trans} to trigger the recovery of materials. In the program, the deformation temperature is ~ $T_{m,PCL}$ + (5 ~ 15 °C). The shape memory cycle is detected by the following program: firstly, the temperature is kept at ~ $T_{m,PCL}$ + (5 ~ 15 °C) for 10 min to make sure the sample is completely melt down, and then the sample is elongated from the initial strain ($\varepsilon_{p(N-1)}$), cooled to $T_{c,PCL}$ — 20 °C at 10 °C/min under constant stress leading to $\varepsilon_{m(N)}$. Then the external stress is removed at $T_{c,PCL}$ — 20 °C for additional 1 min, resulting in the temporary shape ($\varepsilon_{u(N)}$). The recovery process is implemented by a heating procedure under stress free conditions. In the recovery process, the unconstrained strain recovery was triggered by heating to ~ $T_{m,PCL}$ + (5 ~ 15 °C) at 10 °C/min, and thermally equilibrated for 20 min to reach a plateau. Then, the temporary shape which is controlled by T_m is recovered, and is denoted as $\varepsilon_{p(N)}$.

2. Evaluation of electro-induced SME *of PBSPCL/MWCNTs nanocomposites*

The electro-induced SME of PBSPCL/MWCNTs were determined by bending test. The films were cut into a "∏" shape , and the most important parameters of shape memory properties, *i.e.*, the shape fixity ratio (R_f) and the shape recovery ratio (R_r), were determined as follows: firstly, the samples were bended at a given angle θ_i after equilibrating at T_{high} ($T_{m,PCL}$ + 5 ~ 15 °C) for 10 minutes to erase the thermal history; then the temporary shape was quenched to T_{low} ($T_{\mathrm{c,PCL}}-$ 20 °C) and was frozen for 10 minutes, and a fixed angle θ_{f} was recorded when the external stress was removed; and the recovery angle θ_{r} was obtained from the recovery of permanent shape after the film was reheated by the Joule heat in circuit; finally, the values of R_{f} and R_{r} were calculated by the following equations:

$$R_{\mathrm{f}} = \frac{\theta_{\mathrm{f}}}{\theta_{\mathrm{i}}} \times 100\% \qquad \text{(S1)}$$

$$R_{\mathrm{r}} = \frac{180° - \theta_{\mathrm{r}}}{180°} - 100\% \qquad \text{(S2)}$$

Shape memory recovery process was shot by the digital camera..

3. *Evaluation of NIR-induced* SME *of PBSPCL/MWCNTs nanocomposites*

The NIR-induced SME of PBSPCL/CNTs were also determined by bending test. The films were cut into a strip , and then, the sample was rolled into a spiral shape after equilibrating at T_{high} ($T_{\mathrm{m,PCL}}$ + 5 ~ 15 °C) for 10 minutes to erase the thermal history; then the temporary shape was quenched to T_{low} ($T_{\mathrm{c,PCL}}$ − 20 °C) and was frozen for 10 minutes, and a fixed spiral shape was obtained when the external stress was removed, using its corresponding pristine copolymer as the reference. Subsequently, we used NIR laser as the light source perpendicularly positioned 25 cm from both of the samples to irradiate them until the entire recovery process is complete. And the power density delivered to the sample was about 3.2 mW/mm^2 (Lasever Inc. Ningbo, China, Model NO. LSR808H-FC-7.5 W).

Theoretically analysis of the affinity between MWCNTs with the two segments:

In order to calculate the interfacial energy between MWCNTs with the two segments according to equation (5) and (6), the surface energy need to obtain firstly, which can be calculated in accordance with the geometric mean method:[1]

$$\gamma_{LV}(1 + \cos\theta) = 2\left(\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{d}}\gamma_{\mathrm{LV}}^{\mathrm{d}}} + \sqrt{\gamma_{\mathrm{SV}}^{\mathrm{p}}\gamma_{\mathrm{LV}}^{\mathrm{p}}}\right) \qquad \text{(S3)}$$

$$\gamma_{SV} = \gamma_{\mathrm{SV}}^{\mathrm{d}} + \gamma_{\mathrm{SV}}^{\mathrm{p}} \qquad \text{(S4)}$$

where θ is the contact angle, subscripts 'LV' and 'SV' denote the interfacial liquid-vapor and surface-vapor tensions, respectively, while the superscripts 'd' and 'p' denote the disperse and polar components of total surface tension (γ^{SV}), respectively.

According to the research of Chen *et al*,[2] we can measure the contact angles of some representative liquids on the surface of polymer. Generally, the selected representative liquids are double distilled water (H_2O) and methylene iodide (CH_2I_2). The surface energy data of H_2O and CH_2I_2 are $\gamma^p = 51.0$ dyn cm^{-1} and $\gamma^d = 21.8$ dyn cm^{-1} for H_2O, and $\gamma^p = 2.3$ dyn cm^{-1} and $\gamma^d = 48.5$ dyn cm^{-1} for CH_2I_2,[3] and the contact angles of H_2O and CH_2I_2 on the surfaces of PBS and PCL are 82.32° and 95.83° for H_2O, and 26.97° and 38.51° for CH_2I_2. According to eqn (S3) and (S4), the surface energy data can be counted and the results are shown in Table S1. For MWCNTs, there are two different parameters for their degree of modification which can be cited from the literature. For example, when MWCNTs have high numbers of functional groups on their surface, the total surface energy (γ) of MWCNTs is 45.3 mJ m^{-2}, and the γ^d and γ^p are 18.4 and 26.9 mJ m^{-2}, respectively.[4] These figures are similar to those for MWCNTs which have been modified by strong acid. When few functional groups are present on the surface of MWCNTs, the corresponding surface energy data are suggested to be 27.8 mJ m^{-2} for γ, 17.6 mJ m^{-2} for γ^d and 10.2 mJ m^{-2} for γ^p.[5] In this work, MWCNTs were only heated at 800 °C for 1 h in argon atmosphere and therefore the lower surface energy data were used. The interfacial tensions between components were then calculated according to eqn (5) and (6), and the results are shown in Table S2.

Table S1 The surface energy data of components.

Components	γ (mJ m^{-2})	γ^d (mJ m^{-2})	γ^p (mJ m^{-2})
PBS	45.43	43.25	2.18
PCL	41.32	41.18	0.14
MWCNTs	27.80	17.60	10.20

Table S2 Interfacial tensions as calculated using harmonic and geometric mean equations.

	Interfacial tension	
	Based on harmonic-mean	Based on geometric-mean

Component couple	equation (mJ m^{-2})	equation (mJ m^{-2})
PBS/PCL	1.87	1.25
PBS/ MWCNTs	15.99	8.61
PCL/ MWCNTs	19.24	12.90

TEM images of composites:

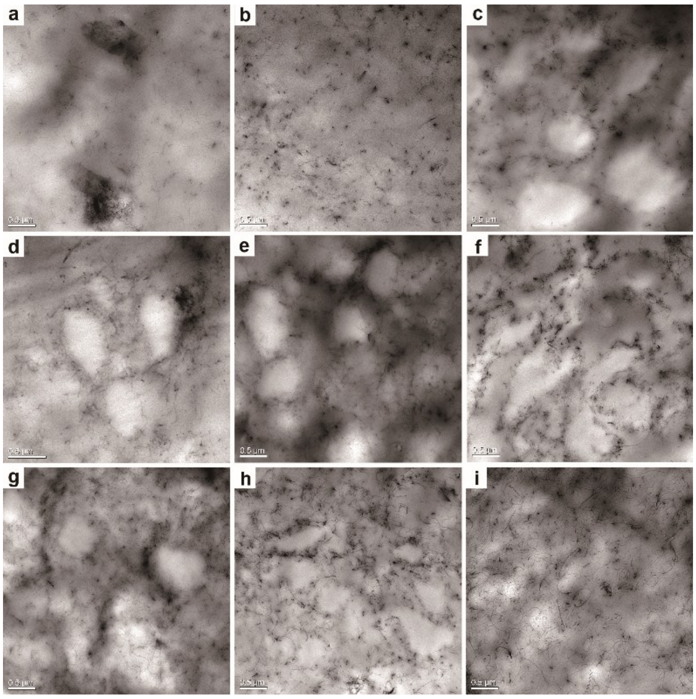

Figure S1 TEM images of (a) PCL$_{6.3}$/MWCNTs$_{1.0}$, (b) PBS$_{4.2}$/MWCNTs$_{1.0}$, (c)PBS$_{4.2}^{2}$/PCL$_{6.3}^{8}$/MWCNTs$_{1.0}$, (d)PBS$_{4.2}^{2}$PCL$_{6.3}^{8}$/MWCNTs$_{1.0}$, (e) PBS$_{4.2}^{3}$PCL$_{6.3}^{7}$/MWCNTs$_{1.0}$, (f) PBS$_{4.2}^{4}$PCL$_{6.3}^{6}$/MWCNTs$_{1.0}$, (g) PBS$_{4.2}^{2}$PCL$_{6.3}^{8}$/MWCNTs$_{3.0}$, (h) PBS$_{4.2}^{3}$PCL$_{6.3}^{7}$/MWCNTs$_{3.0}$, (i) PBS$_{4.2}^{4}$PCL$_{6.3}^{6}$/MWCNTs$_{3.0}$

Programmed cyclic thermomechanical curves of PBSPCL copolymers:

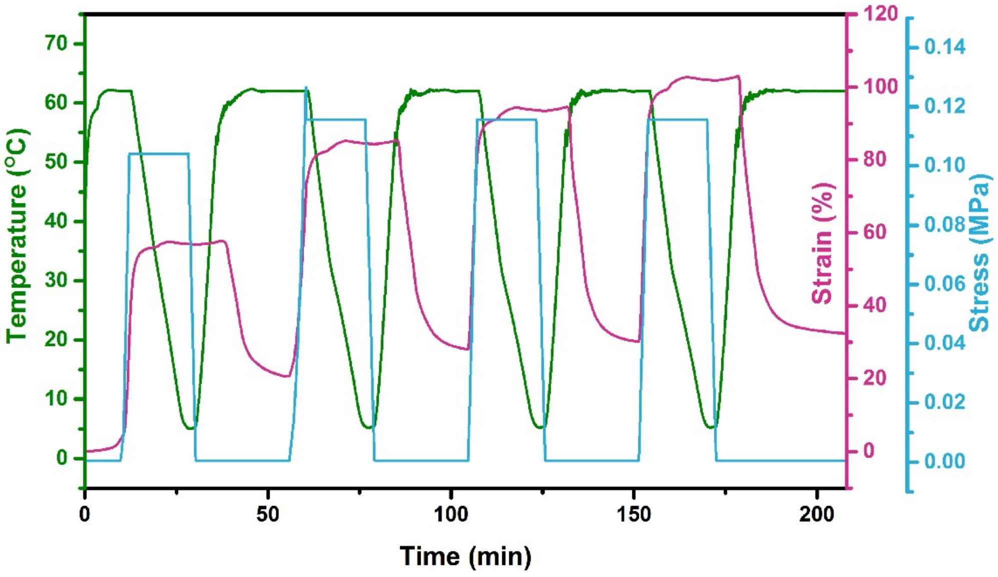

Figure S2 The DMA curves of the $PBS_{4.2}{}^{3}PCL_{6.3}{}^{7}$ copolymer

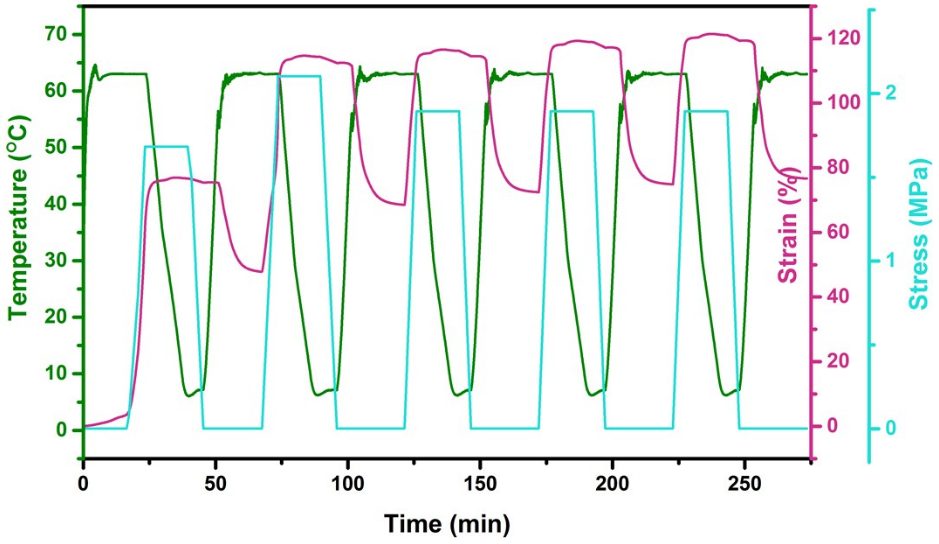

Figure S3 The DMA curves of the $PBS_{4.2}{}^{4}PCL_{6.3}{}^{6}$ copolymer

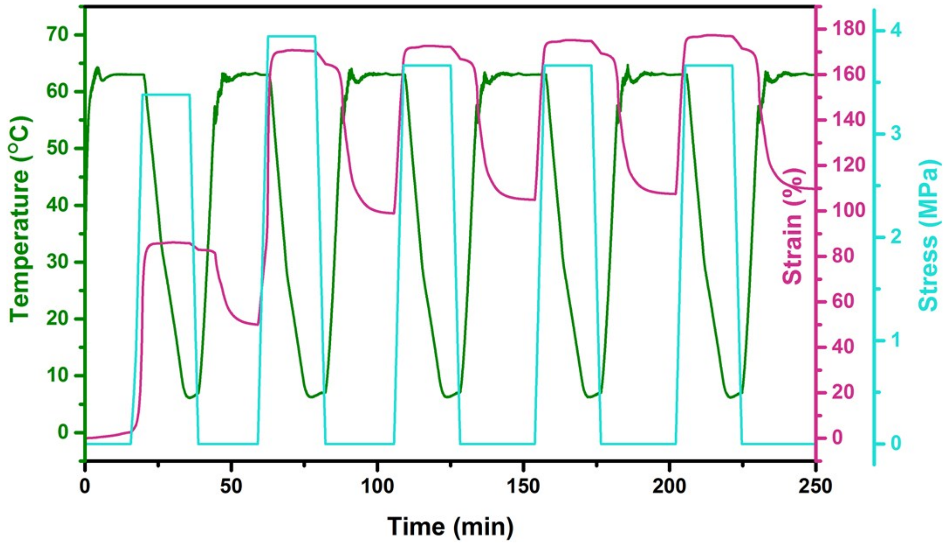

Figure S4 The DMA curves of the $PBS_{4.2}{}^{5}PCL_{6.3}{}^{5}$ copolymer

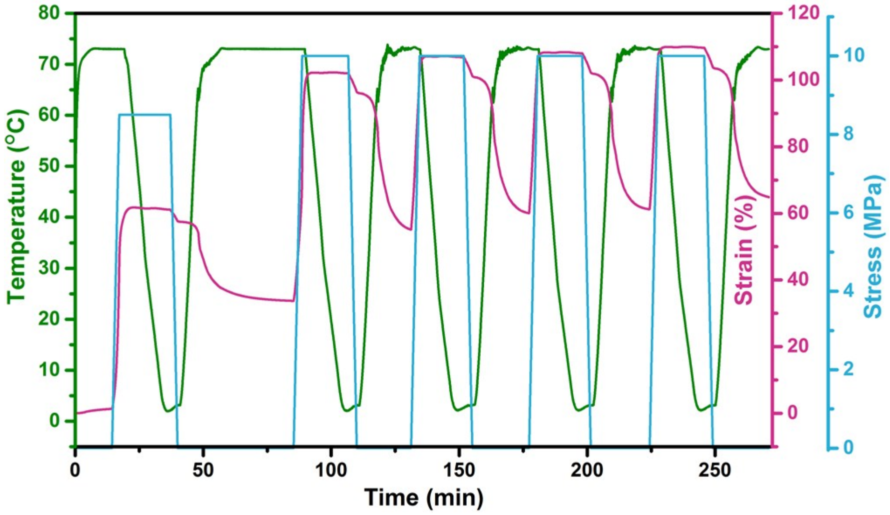

Figure S5 The DMA curves of the $PBS_{4.2}{}^{6}PCL_{6.3}{}^{4}$ copolymer

References

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