Supplementary Information

A simple copolymer with integrated highly impact-stiffening, broadband damping, and active perception for advanced protection

Jianbing Cui[a,b], Pingping Liu[a], Tatsuo Kaneko[a], Weifu Dong[a], Mingqing Chen[a]*, Dongjian Shi[a]*

[a] Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

[b] Puyang Institute of Technology, Henan University, Puyang 457000, China

Corresponding Author: Mingqing Chen, Dongjian Shi

E-mail: mqchen@jiangnan.edu.cn (M.C.); djshi@jiangnan.edu.cn (D.S.)

Supporting information is included as follows:

Figures S1–S18

Tables S1-S5

Section S1. Experimental Section

1.1 Materials

Styrene (St), 2-Ethylhexyl acrylate (EHA) and 2-(2-Ethoxyethoxy) ethyl acrylate (DEEA) was purchased from Tokyo Chemical Industry Co., Ltd. Ethyl acrylate (EA), n-Butyl acrylate (BA), Hexyl Acrylate (HA), Lauryl methacrylate (LMA), Ethylene glycol phenyl ether acrylate (EEA), Benzyl acrylate (BZA), Methyl methacrylate (MMA), Iso-bornyl acrylate (IOBA), and 2-hydroxy-2-methylpropiophenone (HMPP) were supplied by Aladdin Reagent Co., Ltd. Styrene and acrylate monomers were purified with basic alumina before use. Silicone and fluoro rubber were purchased from Jingdong Rubber Co., Ltd. The T_g of silicone rubber and fluorine rubber are -50°C and -25°C respectively, and both are cross-linked polymers.

1.2 Synthesis of PS-PDEEA copolymer

Here we show the synthesis of PS-PDEEA copolymer as an example. The copolymer was prepared by the method of solvent-free bulk polymerization, and the molar ratio of St: DEEA was 1.8:1. Specifically, 1.87 g of styrene (18 mmol), 1.88 g of 2-(2-ethoxyethoxy) ethyl acrylate (10 mmol), and 0.0375 g of photo-initiator HMPP (1 wt%) were mixed evenly. Then, transfer the mixed solution into a Schlenk flask, evacuate the gas from the flask using a vacuum pump, and place it in an ultrasonic cleaner and sonicate for 5 minutes, followed by introducing inert gas of N_2. Repeat this procedure 3 times for deoxygenation. The treated solution mentioned above was injected into a sealed transparent glass mold, and the free radical polymerization reaction was carried out under the irradiation of ultraviolet light with a wavelength of 365 nm for 6 hours to obtain the PS-PDEEA copolymer. In addition, the experimental operation steps for the synthesis of other component copolymers are the same as the above steps.

1.3 Characterizations.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured by Bruker AVANCE III HD 400 using DMSO-d_6 as the solvent. Differential scanning calorimetry (DSC) measurements were conducted on a Netzsch 204 F1 with a heating rate of 10 °C min^{-1} under N_2 atmosphere from -80 to 120 °C. thermogravimetric analysis (TGA) tests were conducted on a Netzsch TG 209 F3 with a heating rate of 10 °C min^{-1} under Ar atmosphere from 40 to 600 °C. Gel permeation chromatography (GPC) was conducted on Waters ACQUITY and using THF as a fluent phase. The sensor performance

was measured at the digital sourcemeter DMM7510. The transparency was measured on a UV-visible spectrophotometer Shimadzu UV-3600i.

Mechanical measurement: Tensile tests were conducted on a universal testing machine (Instron 5967X). The specimens with a rectangular shape (10 mm in width, 2.5 mm in thickness) were prepared and stretched at the different rates. Compression tests were also conducted on a universal testing machine (Instron 5967X), and the specimens with a circular shape (20 mm in diameter, 20 mm in thickness) were prepared.

Wide-angle X-ray scattering measurements: WAXS measurements were conducted on a Xeuss 3.0 SAXS/WAXS devices. The sample-to-detector distance was 60 mm, covering the scattering vector q range from 0.092 to 3.247 A^{-1}.

Drop-ball impact test: The test specimens (300×300×2 mm^3) were positioned on a platform equipped with a force sensor. A 50 g steel ball was dropped freely from a height of 100 cm to impact the platform. Blank represents no sample on the platform.

Rheological measurement: Rheological measurements were performed on TA DHR-3 at the 30 °C. The specimens with a circular shape (20 mm in diameter, 2 mm in thickness) were prepared. Parallel plates with a diameter of 20 mm were used for the rheological experiments. Frequency sweep tests were conducted across a range of 0.1 to 100 Hz at the specified temperatures, applying a strain of 0.1%. The Relative Shear Stiffening effect (RSTe) was used to characterize the magnitude of the stiffening ability of the material and calculated according to the following formula:

$$RSTe = \frac{G'_{100Hz}}{G'_{0.1Hz}}$$

Where G'_{100Hz}和$G'_{0.1Hz}$ are the storage modulus corresponding to 100 Hz and 0.1 Hz, respectively.

1.4 Molecular dynamics simulations

The molecular dynamics (MD) simulation was calculated by Materials Studio (MS) 2019 software. All-atom MD simulation systems were constructed by randomly distributing the polymer chains in simulation cells using the Amorphous Cell module. The five polymer chains were randomly packed into one cubic simulation box. Then, the Forcite module with the COMPASS Ⅱ force field

was used to optimized the geometry of amorphous cells, and annealed between 300 K and 500 K for 10 circles with 10 heating ramps per circle. The molecular dynamic simulations were carried out for 200 ps NVT at 298 K, 300 ps NPT at 298 K and 1atm, and 200 ps NVT at 298 K, respectively. The Berendsen Barostat and Andersen Thermostat were chosen for controlling the pressure and temperature, respectively. The cohesive energy per chain was calculated by the following formula:

$$E_{cohensive} = \frac{\left(\sum_{i=1}^{5} E_{pot}^{isolated}(i) - E_{pot}^{5}\right)}{5}$$

Where $E_{pot}^{isolated}$ is the average potential energy of an isolated polymer chain in a vacuum, and E_{pot}^{5} is the average potential energy of the condensed system consisting of five polymer chains. The potential energies of the isolated polymer chains were calculated by averaging the potential energy of a single chain in 10 frames. For E_{pot}^{5}, the potential energies were calculated by averaging the potential energy of the condensed system in 10 frames.

Section S2. Supplementary Characterizations

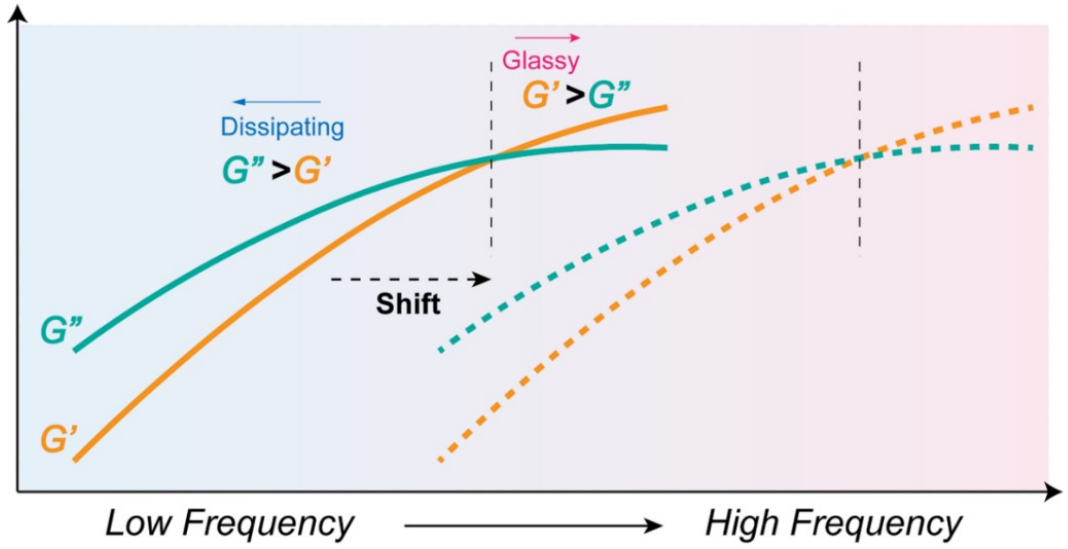

Fig. S1 Shift the frequency range of modulus transition towards the high-frequency direction.

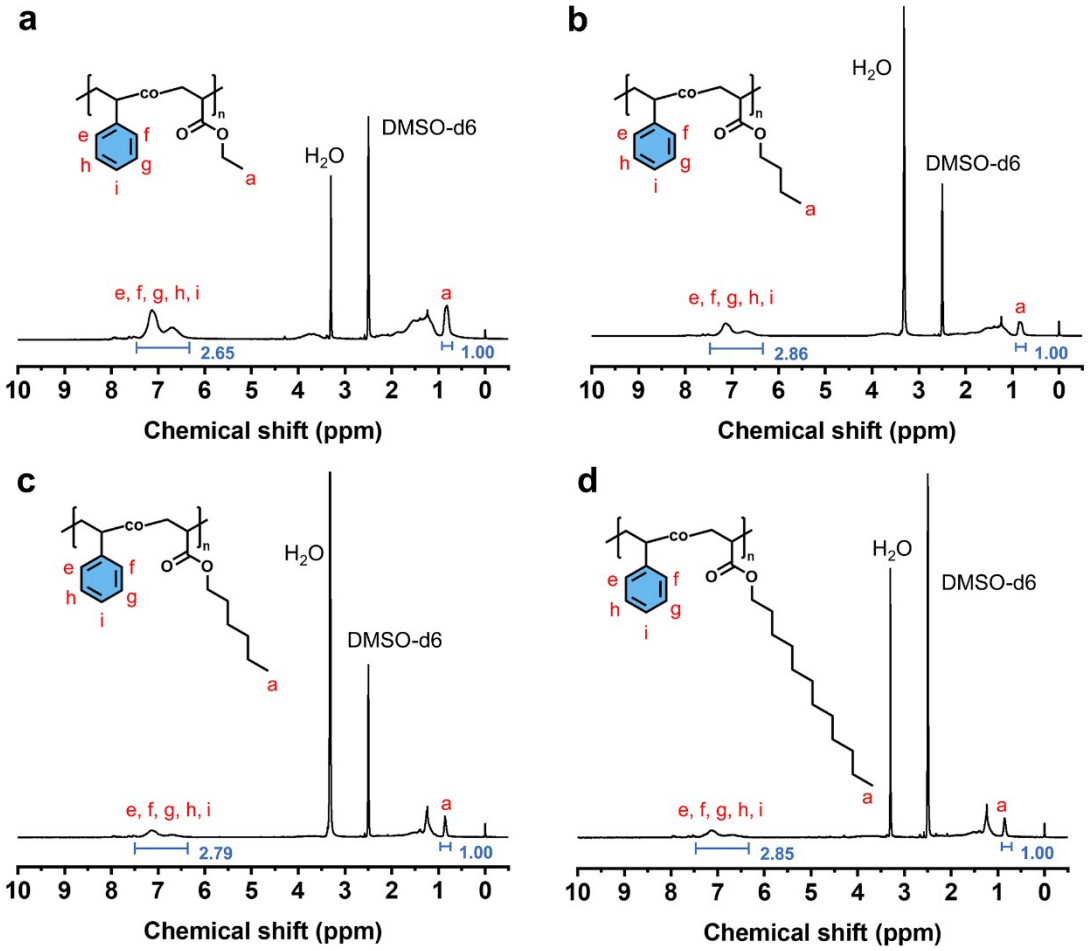

Fig. S2 ^{1}H NMR spectra of the (a) PS-PEA, (b) PS-PBA, (c) PS-PHA and (d) PS-PLMA copolymers.

Notes to Fig. S2: As ^{1}H NMR spectrum shown in Figure. S2, the chemical shift peaks (ppm) are attributed as follows: 0.86 (3H, -CH_3), 7.13 (25H, -Ph-H). Meanwhile, by comparing the peak area ratios of the proton peaks of styrene (7.13 ppm, 25H) and acrylic ester (0.86 ppm, 3H), the molar ratios of styrene to acrylic ester in the copolymers PS-PEA, PS-PBA, PS-PHA, and PS-PLMA were calculated to be 1.59:1, 1.72:1, 1.67:1, and 1.71:1, respectively. Additionally, combining these molar ratios with number-average molecular weights (M_n), the results demonstrate that the monomer units of styrene and acrylate in the molecular chains of the four kinds of copolymers were essentially equivalent. Detailed data are provided in Table S2.

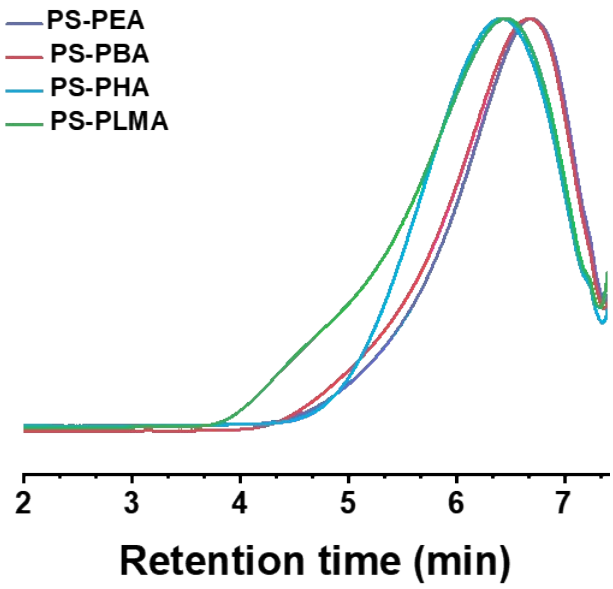

Fig. S3 GPC curves of the PS-PEA, PS-PBA, PS-PHA and PLMA copolymers.

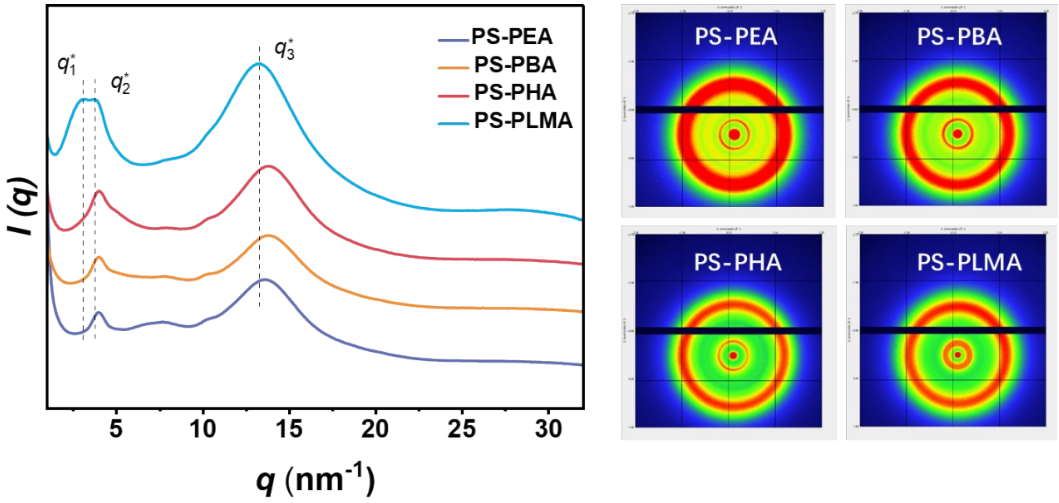

Fig. S4 1D WAXS profiles and 2D WAXS patterns of the PS-PEA, PS-PBA, PS-PHA and PS-PLMA copolymers.

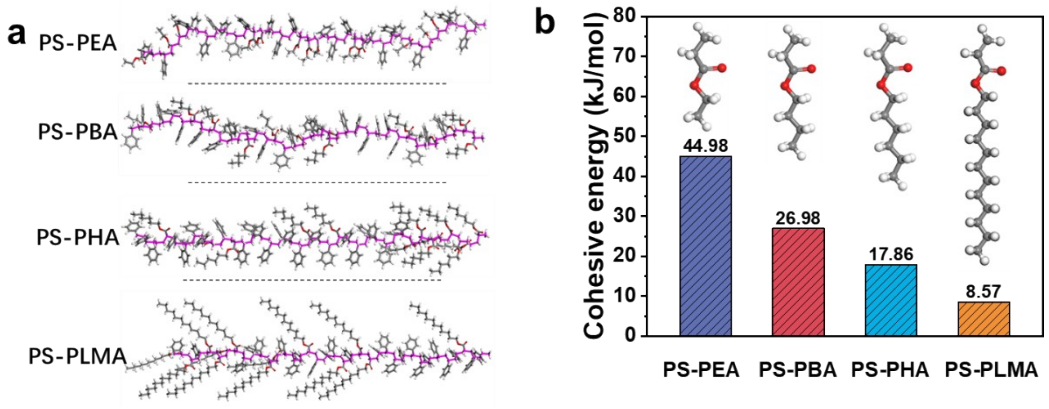

Fig. S5 Amorphous polymer chain model and corresponding cohesive energy of the PS-PEA, PS-PBA, PS-PHA and PS-PLMA copolymers.

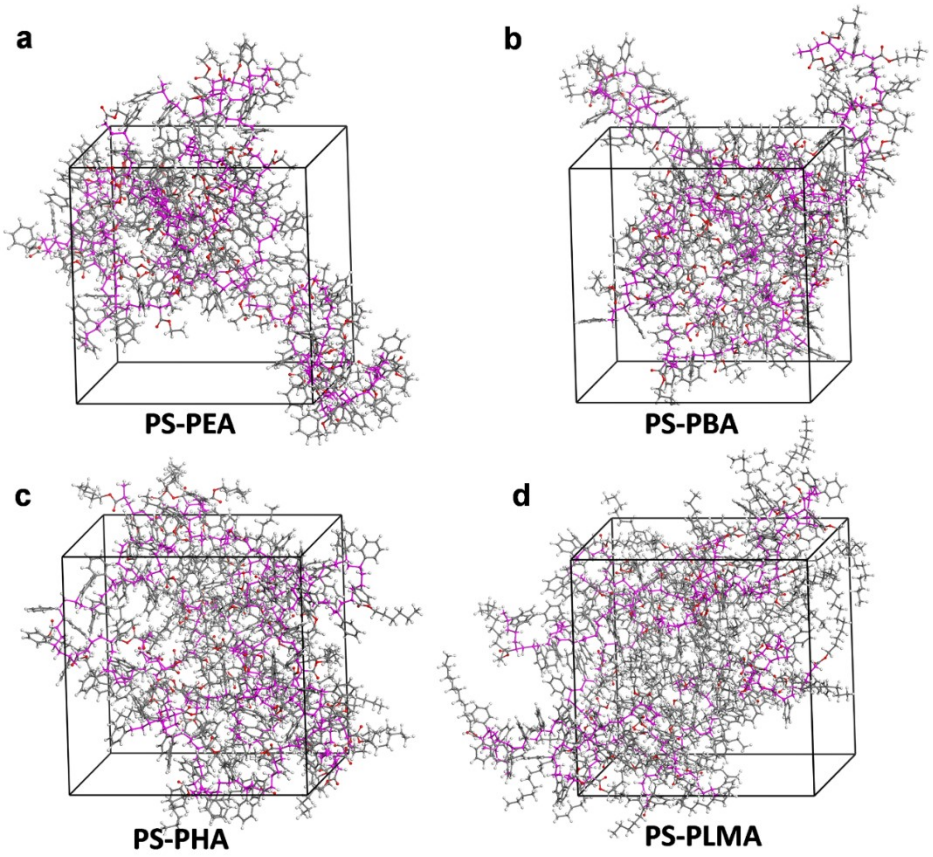

Fig. S6 Amorphous cell of the (a) PS-PEA, (b) PS-PBA, (c) PS-PHA and (d) PS-PLMA copolymers.

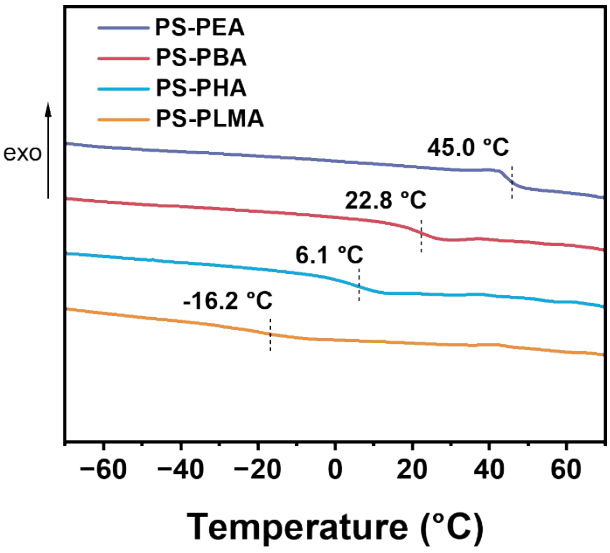

Fig. S7 DSC curves and glass transition temperatures of the PS-PEA, PS-PBA, PS-PHA and PS-PLMA copolymers.

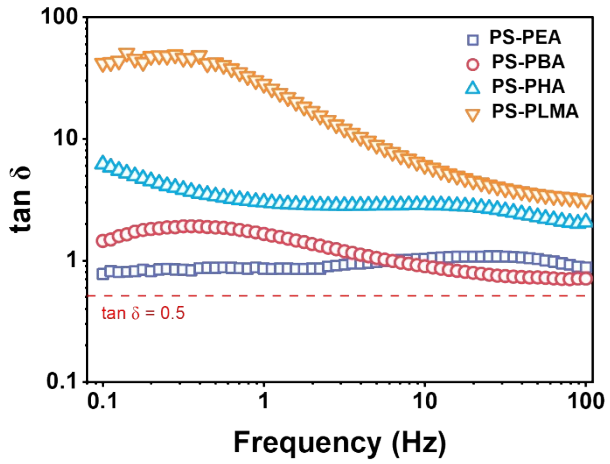

Fig. S8 Loss factor (tan δ) of the PS-PEA, PS-PBA PS-PHA and PS-PLMA copolymers.

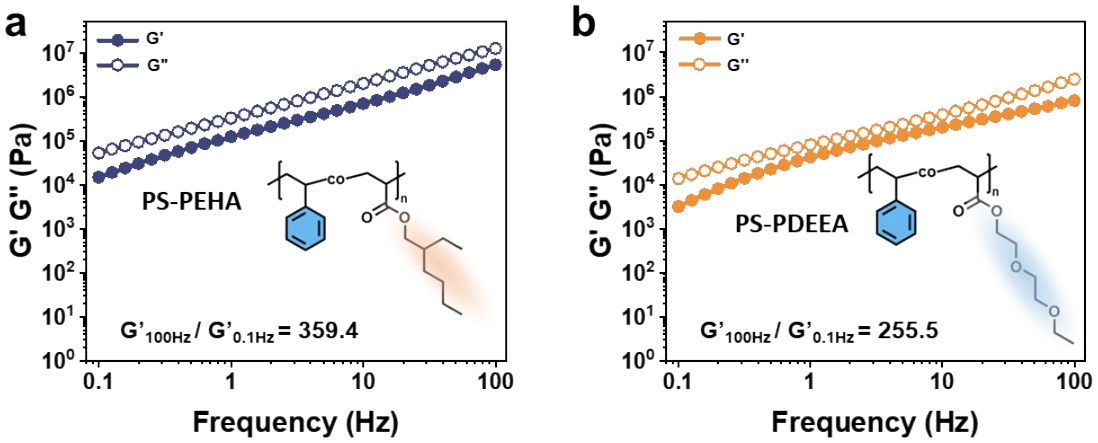

Fig. S9 Dynamic rheological frequency scans of the (a) PS-PEHA and (b) PS-PDEEA copolymers. The molar ratio of styrene to acrylate is 1.8:1.

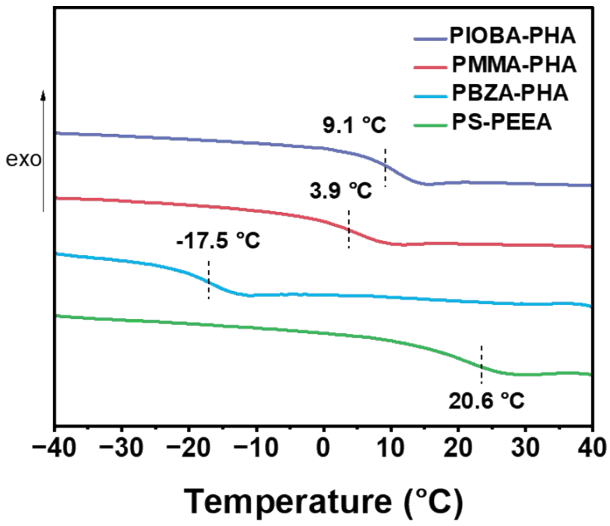

Fig. S10 DSC curves and glass transition temperatures of the PIOBA-PHA, PMMA-PHA, PBZA-PHA and PS-PEEA copolymers.

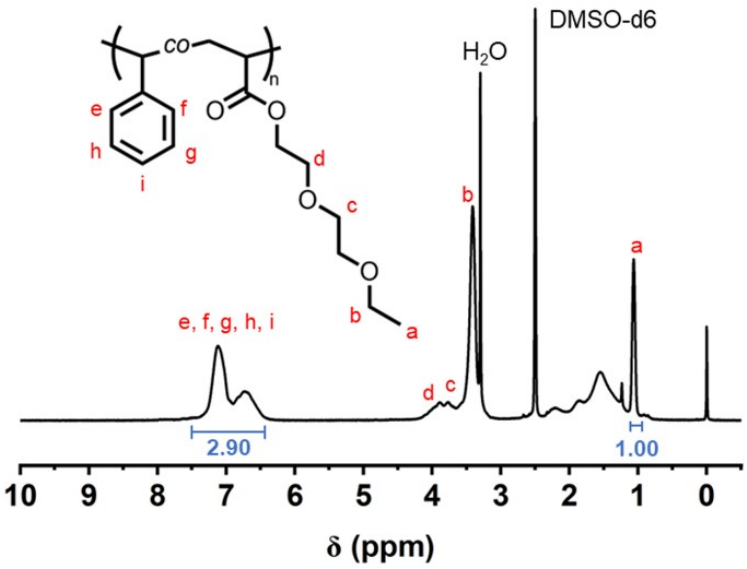

Fig. S11 ^{1}H NMR spectrum of the PS-PDEEA copolymer.

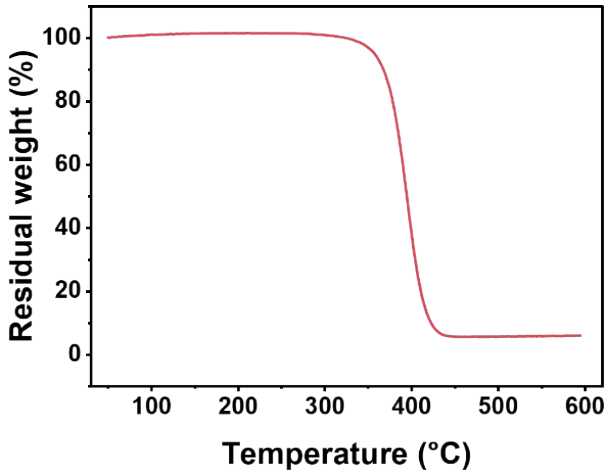

Fig. S12 TGA curves of the PS-PDEEA copolymers with the initiator of 1wt%.

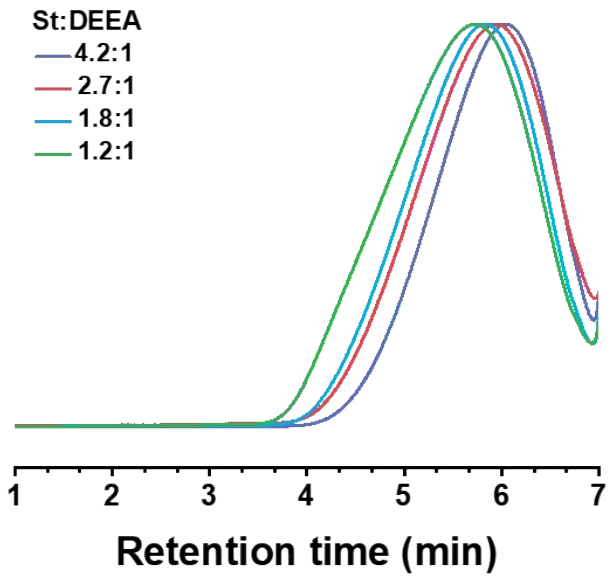

Fig. S13 GPC curves of the PS-PDEEA copolymers with different molar ratio of St/DEEA.

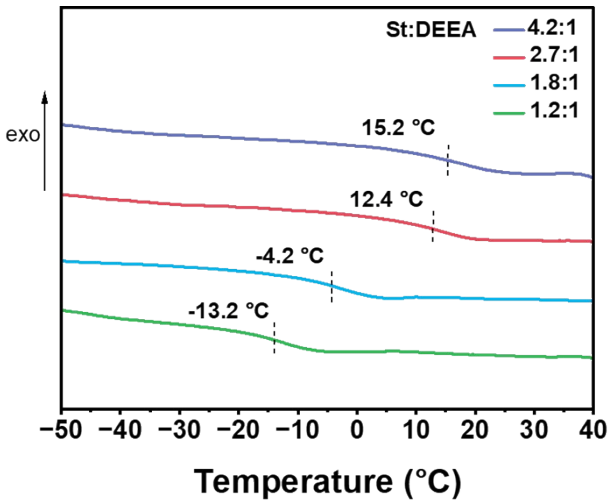

Fig. S14 DSC curves and glass transition temperatures of the PS-PDEEA copolymers with different molar ratio of St/DEEA.

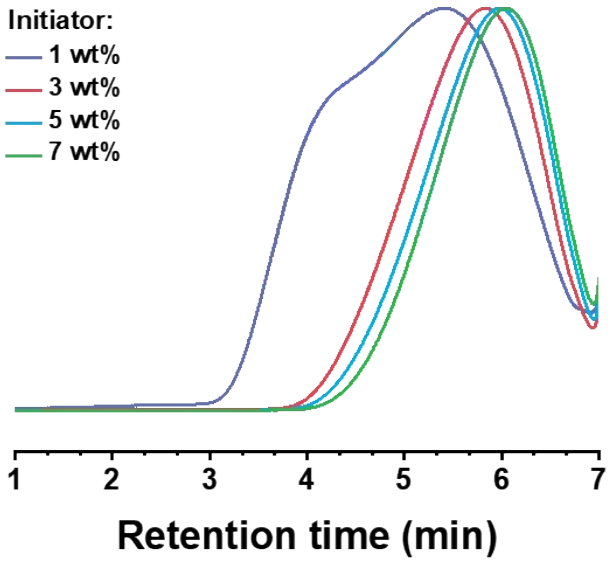

Fig. S15 GPC curves of the PS-PDEEA copolymer with different contents of initiator.

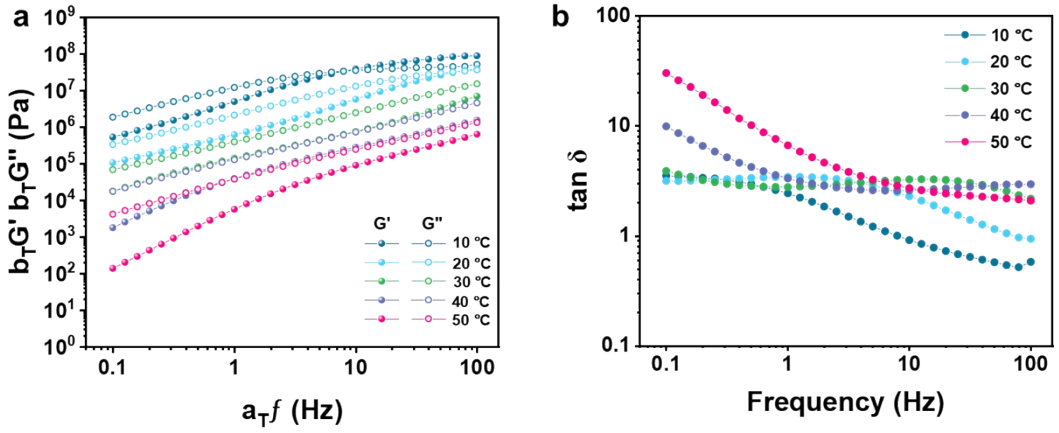

Fig. S16 Dynamic rheological frequency scans and loss factor of the PS-PDEEA copolymer prepared with 1 wt% of initiator.

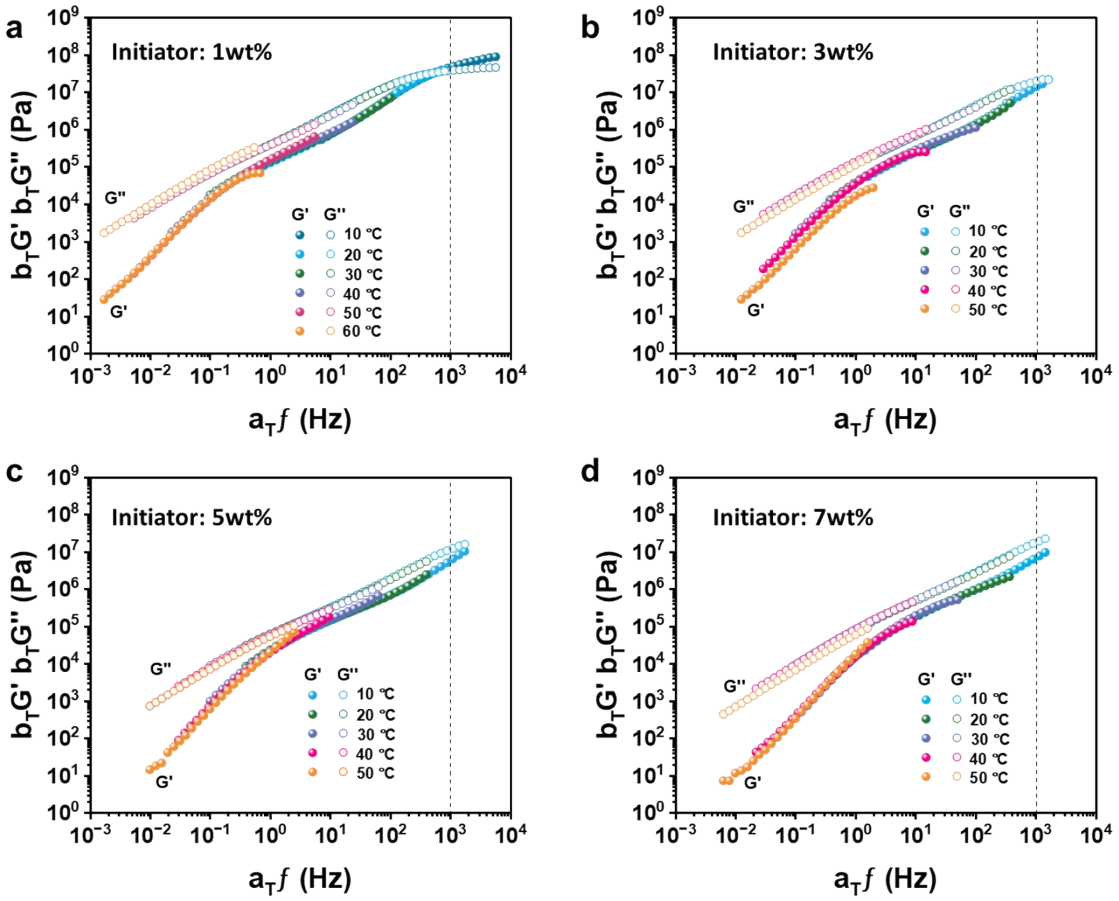

Fig. S17 Time-temperature superposition rheological master curves of the PS-PDEEA copolymer with different contents of initiator.

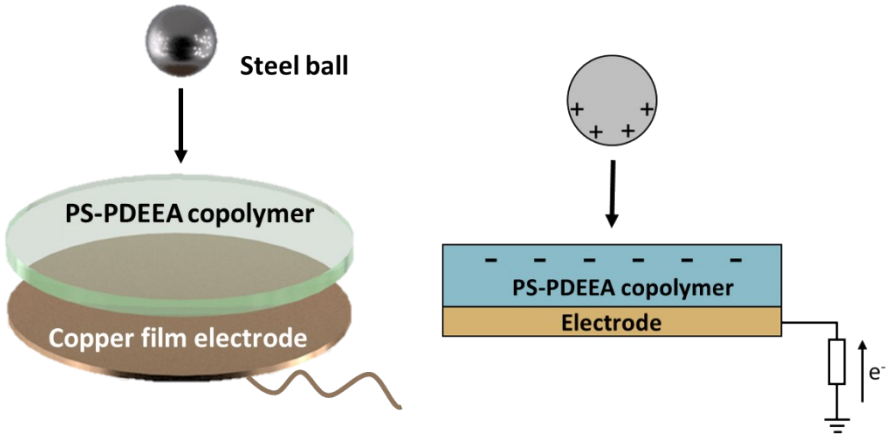

Fig. S18 Structure design of self-sensing intelligent protective material.

Table S1. Comparison of the impact-stiffening response and loss factor among impact-stiffening materials.

Materials	G′ at 0.1 Hz (kPa)	G′ at 100 Hz (kPa)	Impact-stiffening response (times)	Tan δ (at 100 Hz)	References
Silica suspension	~0.0001	~0.02	200	~0.5	S1
PBS	~0.7	~300	429	~0.03	S2
PDBS	~4	~300	75	~0.05	S3
PolyTA/arginine	21	45276	2156	~0.3	S4
APFG	~150	~2000	13	~1.9	S5
PTS SSG	~0.025	70	2800	~0.1	S6
NPU-20HFG	~70	~1500	21	~1.1	S7
PS-PDEEA	0.30	553	1843	1.74	This work

Table S2. Number of units for different copolymers (Calculated by ^{1}H NMR and GPC)

Sample	Initiator content (wt%)	M_n (kg/mol)	Polymer unit ratio (Calculated by ^{1}H NMR)	Number of units
PS-PEA	3	4.1	PS: PEA=1.59:1	$PS_{25.0}$-*co*-$PEA_{16.0}$
PS-PBA	3	4.2	PS: PBA=1.72:1	$PS_{24.0}$-*co*-$PBA_{14.0}$
PS-PHA	3	5.0	PS: PHA=1.67:1	$PS_{25.0}$-*co*-$PHA_{15.0}$
PS-PLMA	2	5.6	PS: PLMA=1.71:1	$PS_{23.0}$-*co*-$PLMA_{14.0}$

Table S3. Molecular weight of the PS-PDEEA copolymers with different molar ratio of St/DEEA

Initiator content	M_n (kg/mol)	M_w (kg/mol)	PDI
4.2:1	5.7	8.5	1.51
2.7:1	6.0	9.2	1.54
1.8:1	6.7	10.3	1.60
1.2:1	7.8	13.5	1.74

Table S4. Molecular weight of the PS-PDEEA copolymers prepared by different contents of initiator

Initiator content	M_n (kg/mol)	M_w (kg/mol)	PDI
1 wt%	12.0	39.0	3.30
3wt%	6.7	10.3	1.60
5 wt%	5.8	8.7	1.50
7 wt%	5.4	7.8	1.45

Table S5. Summary of impact-stiffening response and storage modulus

Initiator content	G' at 0.1 Hz (Pa)	Impact-stiffening response (times)
1 wt%	15419.7	86.1
3wt%	3181.5	255.5
5 wt%	591.8	1122.3
7 wt%	302.0	1843.0

References

1. A. K. Gurnon and N. J. Wagner, J. Fluid Mech., 2015, 769, 242-276.

2. S. Liu, S. Wang, M. Sang, J. Zhou, T. Xuan, J. Zhang, S. Xuan and X. Gong, Chem. Eng. J., 2023, 473, 145214.

3. Q. Wu, Y. Peng, H. Xiong, Y. Hou, M. Cai, Y. Wang, L. Zhao and J. Wu, Sci. China Mater., 2023, 66, 4489-4498.

4. H. Qiao, B. Wu, S. Sun and P. Wu, J. Am. Chem. Soc., 2024, 146, 7533-7542.

5. G. Chen, J. Wu, Z. Wang, H. Zhu, S. Zhu and Q. Zhang, Sci. Adv., 2025, 11, eadv5292.

6. Z. Chen, H. Chen, Y. Li, B. Wang, S. Chen, Z.-Y. Chen, Q. Huang, X.-F. Yu and R. He, Nat. Commun., 2025, 16, 8949.

7. J. Cheng, S. Fu, S. Ma, Z. Zhang, C. Ma and G. Zhang, Adv. Mater., 2024, 36, 2411700.