Conjugated microporous polymers for near-infrared photothermal control of shape change

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ABSTRACT Herein, a facile and highly efficient synthetic method to prepare organic photothermal materials with high photo-stability and outstanding photothermal performance is reported. Through direct polymerization of commercial aromatic monomers in the presence of anhydrous aluminium chloride and dichloromethane, four kinds of conjugated microporous polymers (CMPs) were obtained. Detailed structural analysis confirmed that the resultant CMPs possessed abundant micropores with an extended π -conjugated skeleton. Under near-infrared (NIR) light irradiation (808 nm, 1.0 W cm^{-2}), all the CMPs showed fast heating-up behavior with their maximum temperatures higher than 150°C . Moreover, the efficiency of photothermal conversion (η) of the CMPs was found to increase linearly with the increase in the number of conjugated benzene rings within the monomer. Poly-TPE from tetraphenylethylene (TPE) and Poly-TP from *o*-terphenyl (TP) showed high η values of over 47%. Poly-TPE was additionally used as a photothermal filler to remotely and spatially control the shape recovery of thermal-sensitive shape memory polymers (SMPs), while its introduction (1 wt%) had little influence on the thermal and mechanical properties of the polymer matrixes. Owing to their excellent NIR photothermal performance as well as a one-step synthetic preparation, these CMPs may be promising photothermal materials for practical applications.

Keywords: conjugated microporous polymer, photothermal conversion, near-infrared, actuator

INTRODUCTION

In the recent decade, microporous organic polymers (MOPs), which are microporous, covalent and purely organic materials, have attracted great interest in the fields of gas separation, energy storage and catalysis [1–4].

MOPs possess the advantages of having a high surface area with a pore diameter below 2 nm, high chemical and thermal stability, and chemical functionalization, and thus have the prospect to complement typical microporous materials such as activated carbons, zeolites, and the extensively studied metal-organic frameworks [5]. Currently, various MOPs with different structures such as hypercrosslinked polymers, covalent triazine frameworks, conjugated microporous polymers (CMPs) and polymers with intrinsic microporosity have been reported [6–8]. In particular, CMPs with an extended π -conjugated structure are a highly attractive class of MOPs [9,10]. Due to their unique conjugated and porous structure, some CMPs exhibit outstanding luminescence [11] and supercapacitive energy storage properties [12], and thus they have potential applications in optoelectronics and semiconducting fields. Nevertheless, the photothermal conversion behavior of the CMPs has been seldom studied [13]. The extended π -conjugated structure of CMPs may endow them with the ability to convert electromagnetic radiation energy into thermal energy, and thus CMPs may be a new type of photothermal materials.

The research on photothermal materials that can absorb and convert sunlight into heat energy through non-radiative exothermic reaction, is of great importance in terms of environmental protection and energy exploitation [14–16]. Near-infrared (NIR) light can penetrate through materials, and thus NIR photothermal materials are promising candidates for photothermal use in many fields such as medicine, robotics and intelligent systems [17–20]. In comparison with inorganic materials, e.g., carbon or gold-based materials [21–23], organic NIR photothermal materials possess good biocompatibility and functionalization, as well as superior disperse beha-

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vior when blended into polymeric matrixes [24–27]. Therefore, increasing attention has been focused on the development of organic photothermal materials, especially conjugated polymers [28–31]. Besides the common polyaniline [32] and polypyrrole [33], some conjugated polymers have emerged as novel photothermal materials [34]. For example, Cao *et al.* [35] synthesized a narrow-bandgap conjugated polymer containing thiophene and bithiophene which could absorb NIR-II light (1000–1700 nm) that can penetrate tissue deeper than NIR-I light, and convert it into thermal energy. Recently, Chen *et al.* [36] reported a relatively facile synthetic method involving click condensation reaction to prepare conjugated polymers with good NIR photothermal properties. Nevertheless, their monomers were commercially unavailable and the product yield was not high. Generally, conjugated polymers with photothermal effect suffer problems related to several tedious synthetic steps involving low yield, making them hardly considered for practical applications.

Herein, we report a one-step, high-yielding synthetic method to obtain organic photothermal materials with good NIR photothermal properties using commercially available aromatic monomers. As shown in Scheme 1, four kinds of aromatic monomers including benzene (B), biphenyl (BP), *o*-terphenyl (TP) and tetraphenylethylene (TPE) were polymerized in the presence of anhydrous aluminium chloride (AlCl_3) and dichloromethane (CH_2Cl_2) to obtain the corresponding polymers named Poly-B, Poly-BP, Poly-TP and Poly-TPE, respectively. Recently, the syntheses of Poly-B and Poly-BP using the same method, and their porous structure and gas storage were reported [37,38]. However, their photothermal performance was not studied. We focus on investigating the relation between the efficiency of photothermal conversion and molecular structure of the CMPs. Also, the CMPs will be used as NIR photothermal actuators to control the shape recovery of shape memory polymers (SMPs).

EXPERIMENTAL SECTION

Materials

Anhydrous AlCl_3 , B, BP, TP and TPE were purchased from Shanghai Macklin Biochemical Corporation Ltd. ϵ -caprolactone (CL, 99%), diphenyl phosphate (DPP, 99%) were purchased from Aladdin. Ethylene glycol (EG, AR) was from Guangzhou Chemical Reagent Factory. Dibutyltin dilaurate (DBTL, 95%) and hexamethylene diisocyanate (HDI, 99%) were offered by Sigma. Ethanol was purchased from the National Medicines Corporation Ltd.

Scheme 1 Schematic illustration of the synthesis of CMPs by using commercial aromatic monomers in the presence of AlCl_3 and CH_2Cl_2 .

Anhydrous CH_2Cl_2 and toluene were dried with CaH_2 and distilled under an N_2 atmosphere. CL was dried with CaH_2 and collected through reduced pressure distillation.

Syntheses

Preparation of CMPs

To a solution of B, BP, TP or TPE monomer (5 mmol) in anhydrous CH_2Cl_2 (100 mL), anhydrous AlCl_3 (50 mmol, 6.67 g) was added. The mixture was stirred at 80°C under an N_2 atmosphere for 24 h. The reaction was terminated with ethanol and then the resulting precipitate was filtered and washed with $\text{HCl-H}_2\text{O}$ (20 mL, $v/v = 1:1$), deionized water and ethanol in succession. Further purification was applied by a Soxhlet extractor with CH_2Cl_2 for 24 h to remove any residual monomer. The final product was dried in a vacuum oven at 60°C for 12 h and a dark powder was obtained. Yields: Poly-B, 0.51 g (130%), ^{13}C cross-polarization/magic-angle spinning nuclear magnetic resonance (CP/MAS NMR) δ (ppm): 136.0, 129.8, 66.0, 40.4, 20.3; Poly-BP, 0.96 g (125%), ^{13}C CP/MAS NMR δ (ppm): 140.9, 131.9, 67.4, 35.5, 20.3; Poly-TP, 1.57 g (136%), ^{13}C CP/MAS NMR δ (ppm): 140.2, 131.2, 66.0, 36.9, 18.2; Poly-TPE, 2.22 g (134%), ^{13}C CP/MAS NMR δ (ppm): 139.5, 130.5, 68.1, 39.7, 19.6.

Synthesis of poly(ϵ -caprolactone) diols (PCL)

CL (20.0 g, 175.2 mmol), 0.2722 g of EG (4.4 mmol) and 2.1942 g of DPP (8.8 mmol) were added into 175 mL of dry toluene and stirred at room temperature (r.t.) in a glove box of N_2 atmosphere for 16 h. The polymerization was terminated by adding benzoic acid and the crude powder was precipitated in methanol three times. The

product was dried under vacuum for 12 h. Yield: 98%. M_n of PCL calculated by ^1H NMR: 4600 g mol^{-1} .

Synthesis of shape memory polyurethanes (SMPUs)

PCL (5.0 g), HDI (0.4029 g) and DBTL (5 drops) were stirred at 80°C in a glove box of N_2 atmosphere for 15 min. Then EG (0.1029 g) and dry N,N -dimethylformamide (DMF, 10 mL) were added into the reaction mixture. The reaction was completed after 5 h. The product was dried at 80°C under vacuum.

Preparation of SMPU/CMP composite films

The films were created by using an evaporation method with DMF as the solvent. CMP powder was dispersed in 2 mL of DMF and the SMPU was dissolved in 3 mL of DMF, respectively. Then they were mixed together and poured into a Teflon mold. The mixture was dried at 60°C in an oven for 12 h, and then further dried at 80°C in a vacuum oven. Finally, a SMPU/CMP film was obtained.

Characterizations

Chemical structure

Solid-state ^{13}C CP/MAS NMR spectra were measured on a 400 MHz Bruker superconducting Fourier transform nuclear magnetic spectrometer with a spinning frequency of 20 kHz and a 2.5-mm MAS probe. ^1H NMR spectra of PCL and SMPUs were performed on a Bruker AVANCE III 400 MHz instrument at r.t. with CDCl_3 as the solvent. Fourier-transform infrared (FT-IR) spectra were measured by using a Nicolet/Nexus 670 FI-IR spectrophotometer. The samples were firstly mixed with KBr and then pressed into transparent wafers. Raman spectra were collected on a laser micro-Raman spectrometer (Thermo Fisher DXR2xi) with a laser source of 532 nm. X-ray photoelectron spectroscopy (XPS) spectra of the CMPs were recorded on an ESCALAB 250 surface analysis system. Wide-angle X-ray diffraction (WAXRD) patterns were tested by using the XRD diffractometer (D-MAX 2200 VPC) with Ni-filtered $\text{Cu K}\alpha$ radiation. The diffractometer was scanned in the 2θ range from 2° to 80° at a rate of $1.5^\circ\text{ min}^{-1}$. A field-emission scanning electron microscope (SEM, Hitachi) was used to observe the morphologies of CMPs and SMPU/CMP composite films. Before observation, the composite films were fractured in liquid nitrogen.

Thermal property

Thermogravimetric analysis (TGA) was performed using a Perkinelmer PE Pyris1 TGA in a temperature range

from 50 to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ under an N_2 atmosphere. Samples were degassed at 100°C under an N_2 flow for 5 min before testing. The melting temperature (T_m) and crystalline properties of SMPU and its composites were measured using a PerkinElmer DSC-4000, under an N_2 atmosphere with a $10^\circ\text{C min}^{-1}$ heating (or cooling) rate from -60 to 100°C (or reverse). The storage modulus was tested on DMA (TA, Q800). The testing temperature was from -80 to 100°C with a 5°C min^{-1} heating rate and a frequency of 1 Hz.

Microporous structure

The surface area and pore size parameters were characterized by using a Micromeritics ASAP2460 surface area and porosity analyzer. Before analysis, the samples were degassed at 110°C under 10^{-5} bar vacuum for 5 h.

Light absorption and emission

The data of UV-Vis spectroscopy was collected by using a Hitachi U3500 instrument at r.t. NIR emission spectrum was recorded by using an Edinburgh FLS980 fluorescence spectrometer.

Photothermal effect

The photothermal effect characterization was performed under a LASERWAVE 808 nm laser resource, and a FLUKE thermal imager was utilized as a recorder. Each polymeric powder was spread on a quartz slide to form a thin round layer of about 8 mg cm^{-2} , and the measurement was performed at a distance of 8 cm from the light guide.

NIR sensitive SME

A rectangular shape was cut from the SMPU/CMP (5 wt%) film to perform the local recovery. The sample was deformed to a "U" shape in an oven at 60°C . Then the temporary shape was fixed in an ice/water mixture. Next, part of the "U" shape was put under the 808 nm NIR light of 0.6 W cm^{-2} light intensity.

RESULTS AND DISCUSSION

Synthesis and characterization of CMPs

In order to study the influence of the conjugated structures of CMPs on the efficiency of NIR photothermal conversion, four aromatic monomers were chosen to prepare the corresponding polymers as shown in Scheme 1. The polymerization was performed using AlCl_3 as the catalyst and CH_2Cl_2 as the solvent at 80°C . After polymerization for 24 h, polymeric powders of dark color and micro-size particles (Fig. S1a) were obtained with

extremely high yields of over 120%. The polymers were insoluble in common organic solvents such as CH_2Cl_2 , tetrahydrofuran, DMF and toluene. In addition, through TGA (Fig. S2), it was found that the polymers have high thermal stability with a decomposition temperature of over 350°C under an N_2 atmosphere. The chemical structures of the resultant CMPs were characterized by using FT-IR and ^{13}C CP/MAS NMR. Fig. 1a presents the FT-IR spectra of the four polymers. The absorbance bands ascribed to the C–H stretching vibration of the alkyl chain are observed in the region of $2750\text{--}3000\text{ cm}^{-1}$ for all the polymers, indicating that the Friedel-Crafts alkylation reaction occurred during the polymerization process. In the ^{13}C CP/MAS NMR spectra of the polymers (Fig. 1b), the resonance peaks around 130 and 140 ppm are ascribed to non-substituted aromatic carbons and substituted aromatic carbons, respectively. The resonance peaks around 67 and 20 ppm belong to the CH_2 and CH_3 of $\text{ArCH}_2\text{OCH}_2\text{CH}_3$ units, respectively. The units were introduced when Friedel-Crafts alkylation reaction was quenched by ethanol. The resonances of the CH_2 next to two benzene rings were detected in the upfield region of $25\text{--}45\text{ ppm}$, further confirming the existence of the methylene units between the aromatic rings, which is derived from CH_2Cl_2 serving as an external cross-linker as previously reported [39,40]. Thus, it is reasonable that the yields of the products were discovered to be higher than 120% when only the amount of monomer was taken into account for the calculation. In addition, it should be noted that the AlCl_3 catalyst residue did not exist in the products, which is confirmed by the XPS spectra of the polymers (Fig. S3). Any peak around 70 eV relating to Al element was not detected.

The structures of the polymers were further studied by

Raman spectrometry and WXR measurement. As shown in Fig. 2a, besides the appearance of a broad peak at $5^\circ\text{--}30^\circ$ signifying their amorphous nature, a small diffraction peak at 42.5° is observable in all the WXR patterns, indicating the existence of an in-plane sp^2 domain within the polymers [41.] In the Raman spectra of Fig. 2b, the G and D bands belonging to the in-plane sp^2 domains also appeared at 1590 and 1371 cm^{-1} , respectively [42]. These results mean that apart from the Friedel-Crafts alkylation reaction, a Scholl coupling reaction to form the aryl-aryl bonds also occurred during the polymerization, which led to the formation of the extended π -conjugated skeleton among the polymers. Moreover, through calculating the ratios of the peak intensities of the D and G bands, the I_D/I_G ratios can be obtained, which are related to the regularity of the conjugated structure [43]. It was found that the I_D/I_G ratio of Poly-TPE (0.70) was the smallest among the synthesized polymers. This indicates that in comparison with the other three polymers, Poly-TPE has a more regular conjugated structure and a larger in-plane sp^2 domain, attributed to the TPE monomer possessing four conjugated benzene rings.

In addition, the polymers possess a microporous structure with a narrow pore width less than 2 nm, as measured by the N_2 sorption isotherm experiment (Figs S4 and S5). The BET surface area and the pore volume of Poly-TPE are the highest among the synthesized polymers reaching up to $1156\text{ m}^2\text{ g}^{-1}$ and $0.59\text{ cm}^3\text{ g}^{-1}$, respectively (Table S1).

According to the above structural analyses, the resulting polymers have two kinds of crosslinking networks: one is obtained *via* the Friedel-Crafts alkylation reaction and the other is *via* the Scholl coupling reaction to form

Figure 1 (a) FT-IR spectra and (b) ^{13}C CP/MAS NMR spectra of the CMPs.

the extended π -conjugated structure as shown in Scheme 1. Because of the large π -conjugated structure, the largest UV absorption peaks for all the polymers appear at 450–600 nm (Fig. 3a), which is red-shifted by around 200 nm compared with the peaks of their corresponding monomers (Fig. 3b). All the polymers show a very broad UV absorbance band from 200 to 1200 nm with their absorbance values being fairly high at around 800 nm (about 0.8). This indicates that the CMPs have the feature of NIR absorbance.

Additionally, the CMPs showed negligible light emission upon irradiation at 808 nm (Fig. S6), demonstrating the dominant non-radiative transition reactions of the CMPs. Therefore, the NIR photothermal conversion performances of these CMPs were studied by using NIR light of 808 nm.

Photothermal conversion property of CMPs

Under irradiation by NIR light of 808 nm (1.0 W cm^{-2}),

all the polymers showed a remarkable temperature raise and reached their temperature plateaus within 1 min as shown in Fig. 4a, indicating their fast heating-up ability. Also, it was found that the maximum temperature of the CMPs presented a closely linear increasing trend with the increase in the number of aromatic rings within the monomers (Fig. S7). The maximum photothermal temperature of 160°C for Poly-TPE is obviously higher than that of 152°C for Poly-B. This suggests that an increase in the number of conjugated aromatic rings of the monomers favors the formation of large in-plane sp^2 domains among the polymers. Moreover, the results of the heat-to-cool cyclic tests demonstrate the high photo-stability of the CMPs at high temperatures (Fig. 4b), which is attributed to the high thermal-stability and effective NIR absorbance of materials. Fig. 4c exhibits that there is a linear relation between the photothermal effect of the CMPs and the NIR light intensity from 0.5 to 1.0 W cm^{-2} , suggesting the thermal control performance of materials.

Figure 2 (a) WAXRD patterns and (b) Raman spectra of the polymer networks.

Figure 3 UV-vis spectra of (a) the polymer networks and (b) the monomers.

Figure 4 (a) Time-dependent photothermal conversion curves (808 nm, 1.0 W cm^{-2}) of the polymers. (b) Photothermal cyclic curves of Poly-TPE (808 nm, 1.0 W cm^{-2}). (c) Temperature rises of Poly-TPE at different NIR laser powers. Inset shows the average maximum temperature (T_{max}) as a function of light intensity. (d) IR camera images of Poly-TPE patterned letters SYSU (808 nm, 1.0 W cm^{-2}).

In addition, the letter patterns “SYSU” were fabricated with Poly-TPE powders and rapidly became imageable (Fig. 4d), under irradiation by NIR light of 808 nm (1.0 W cm^{-2}). It means that the CMPs are of potential use in photothermal imaging and therapy fields. It should also be noted that the monomers did not show NIR photothermal effect (Fig. S8), indicating that the NIR photothermal conversion behavior of the polymers is fully ascribed to their extended π -conjugated structures.

To calculate the efficiency of the photothermal conversion (η), the rate in the temperature decrease of the polymers after removing the light source was measured (Fig. S9). The η values of all the polymers were calculated according to Ref. [44] and the details were offered in the Supplementary information. As listed in Table 1, the η values of these CMPs follow this order: Poly-TPE > Poly-TP > Poly-BP > Poly-B, which is in accordance with the maximum photothermal temperature result of the CMPs. Moreover, the η values of Poly-TPE and Poly-TP are as high as 48.1% and 47.5%, respectively. These data are comparable to the high η values of the reported photothermal polymers, such as selenophene-derived polymer films (40%), and thiophene-fused benzodifurandione-based oligo(*p*-phenylenevinylene) films (50.5%) [17,35].

Table 1 Photothermal conversion parameters of the CMPs

Samples	T_{max}^a (°C)	τ_s^b (s)	Abs. ^c	η^d (%)
Poly-B	152±1	8.19	0.81	33.1
Poly-BP	155±1	7.56	0.85	36.3
Poly-TP	157±1	6.10	0.75	47.5
Poly-TPE	160±1	5.92	0.84	48.1

a) Equilibrium temperature under 1.0 W cm^{-2} irradiation; b) system constant time; c) UV absorbance at 808 nm; d) NIR photothermal conversion efficiency.

As mentioned above, there are methylene bridges between the aromatic rings within these CMPs except for the conjugated structure. Nevertheless, Poly-TPE and Poly-TP still showed such high photothermal conversion performance, perhaps ascribed to their microporous structure. It is reported that light trapping of porous polymers could be enhanced and their η values could be improved due to the porous structure [45]. These results indicate that our synthesized CMPs have excellent thermal/photo-stability and high photothermal conversion efficiencies, as well as the feasibility of synthesis from commercially available monomers using a scalable and efficient method, thus enabling them to be considered a

highly attractive class of photothermal materials for many application fields.

NIR-responsive SMP/CMP composites

To investigate the potential NIR photothermal application of the CMPs for the control of phase change, CMP powders were introduced into conventional thermoresponsive SMP matrixes to prepare NIR-responsive SMPs. Currently, NIR-responsive SMPs have attracted great interest in application fields (e.g., biomedicine, aerospace and flexible electronics) due to their remote, spatial and real-time control of temporary shapes of SMP materials [46]. However, only a few organic NIR photothermal fillers such as polydopamine and polyaniline have been used to control shape recovery of SMPs [47–49].

Herein, Poly-TPE powder was used as an example to blend into the typical SMPU matrixes, to form SMPU/CMP composite films. The morphology of the composites was firstly studied by SEM. The SEM micrograph (Fig. S1b) shows the flat-like and no distinct “ball-and-socket” surface topography of cold fractured SMPU/CMP-1 film (1 wt%) edges. It indicates that the composite has good compatibility, which is important for the photothermal performance, thermal and mechanical properties of the composite. Under irradiation by NIR light of

808 nm (1.0 W cm^{-2}), it is clearly observed that the temperature of the SMPU/CMP-3 film (3 wt%) remarkably increased while the one of the blank film changed little, through using an infrared thermal imager (Fig. 5a). Similar to pure Poly-TPE powder, the composite films showed rapid heating-up behavior and reached the maximum temperature within 1 min (Fig. 5b). Obviously, along with an increase in the content of Poly-TPE powder or the NIR intensity, the composite films showed superior photothermal effect (Fig. 5c). Under 0.6 W cm^{-2} irradiation, the temperature of the SMPU/CMP-1 film (1 wt%) reached 48.5°C within 1 min, and that of the SMPU/CMP-5 (5 wt%) was over 60°C in only 10 s, which are sufficient for the phase transition of SMPU ($T_m = 45.4^\circ\text{C}$). A SMPU/CMP-5 strip was firstly programmed into a U shape upon heating. Then as the NIR light was focused on the designated places (indicated by purple rings), the U shape unfolded step by step into the original shape as shown in Fig. 5d (Movie S1). However, the temporary L shape of pure SMPU strip still kept the shape and cannot recover to the original straight one under NIR light (Movie S2). These results indicate that the shape recovery of SMPU/CMP films can be remotely and spatially controlled through NIR irradiation.

Additionally, the introduction of Poly-TPE has negli-

Figure 5 (a) Optical and IR thermal images of SMPU and SMPU/CMP-3 films under 808 nm laser irradiation. (b) Local temperature as a function of irradiation time for SMPU/CMP-3 film (laser irradiation: 808 nm). (c) The temperature as a function of light intensity for SMPU and composite films with different CMP contents. (d) Spatial control of the shape recovery of a SMPU/CMP-5 strip.

Table 2 Thermal properties of SMPU film and SMPU/CMP composite films

Samples	T_m^a (°C)	ΔH_m^a (J g ⁻¹)	X_c^b (%)
SMPU	44.6	45.1	44.7
SMPU/CMP-1	45.4	46.8	46.9
SMPU/CMP-3	45.2	43.8	44.8
SMPU/CMP-5	45.5	40.6	42.2

a) Melting point and melting enthalpy of PCL segment; b) crystallinity of PCL segment was obtained by dividing the measured heat of fusion by the theoretical data (135 J g⁻¹) for pure PCL.

gible influence on the thermal properties of SMPUs even if the particle content was as high as 5 wt%, confirmed by DSC, TGA and dynamic thermomechanical analysis tests (Figs S10–S12). As shown in Table 2, the melting temperatures (T_m) of the composites are almost the same as that of the blank SMPU, and the composites still possess high crystalline ability of PCL segment. In addition, the SMPU/CMP-1 (1 wt%) film had comparable mechanical properties including tensile strength and tensile modulus to the blank SMPU film (Fig. S13).

CONCLUSIONS

In conclusion, a kind of organic photothermal materials including Poly-TP and Poly-TPE with high efficiency of photothermal conversion is reported. To the best of our knowledge, research into the photothermal properties of CMPs remains scarce. We found that the resulting CMPs not only possess microporous structure but also have large in-plane sp^2 domains within the polymers. Owing to the extended π -conjugated structure, all the resulting CMPs can efficiently absorb NIR light and convert it to heat energy. More importantly, comparative studies reveal the significance of the conjugated structure of the monomers on the photothermal performance of the polymers. Poly-TP and Poly-TPE whose monomers have more than two conjugated benzene rings, show superior photothermal conversion efficiencies of over 47%. Also, the high thermal-/photo-stability ensure the repeated use of these CMPs for sustainable energy conversion. Poly-TPE was demonstrated to act as a photothermal filler to remotely and spatially control the shape recovery of thermal-sensitive SMP materials under NIR irradiation at 808 nm. Therefore, the excellent NIR photothermal performance of Poly-TPE and Poly-TP, in combination with their facile one-step synthetic preparation, makes them highly promising polymeric materials for photothermal use in practical applications such as medicine, robotics and intelligent systems.

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Author contributions Huang H and Liang G designed the project. Wu J, Wu Y and He Z performed the experiments. Huang H and Wu J co-wrote the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper, including TGA, nitrogen sorption isotherm and pore size distribution curves, and NIR emission spectra of CMPs, calculation process of photothermal conversion efficiency, and DSC, TGA, DMA and strain-stress curves of SMPU/CMP composite films.

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共轭多孔聚合物应用于近红外光热转换材料

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摘要 近红外光热转换材料在光热治疗、光驱动智能器件等医学和能源领域受到广泛重视. 本文以商业化芳香小分子为单体, 通过一步简单的交联聚合方法制得了四种共轭多孔聚合物, 并首次系统研究了它们的光热转换性能. 结果表明, 它们均具有灵敏的近红外光热响应性, 且材料的光热转换效率与单体结构中共轭苯环数有很大关系, 其中两种聚合物的光热转换效率可高达47%以上. 同时, 该类共轭多孔聚合物可作为光热转换填料, 将其少量填充于热敏型形状记忆材料基体中, 可实现远程、快速、定点调控材料形状的回复, 且其对基材的热性质和力学性能影响很小. 研究表明, 由于其合成简单、原料易得、光热转换效率高, 该共轭多孔聚合物是一类很有应用前景的光热转换材料.