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Luminescent two-way reversible shape memory polymers prepared by the hydroxyl-yne click polymerization

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Two-way reversible shape memory polymers (2W-SMPs), capable of changing their shapes reversibly, are highly desirable for many potential applications. However, the polymerization reactions used for preparing 2W-SMPs always require harsh conditions, such as metal catalysts, light irradiation and elevated temperature. Furthermore, there are rare reports on SMPs integrating with other functions, such as luminescence. Herein, luminescent 2W-SMPs of semi-crystalline PCL-based networks bearing aggregation-induced emission (AIE) moiety of tetraphenylethylene (TPE) are designed and prepared *via* an organobase-catalyzed hydroxyl-yne click polymerization under mild reaction conditions. For comparison, a TPE-free polymer network is also prepared through the same polymerization. The TPE-containing polymer network shows stronger emission than that of TPE-containing monomer because of the activation of restriction of intramolecular rotation. Both the polymer networks are able to perform excellent reversible shape motions, such as bending-unbending, coiling-uncoiling, and closing-blooming, when they are exposed to cold and warm water. By taking advantages of the shape memory and luminescence properties, the TPE-containing polymer network is used to construct a luminescent robotic gripper, which can grab and release weights with payload-to-weight ratio much higher than that of many industrial robotic grippers. Moreover, it could also be used to realize double anti-counterfeiting function. This work represents the first example of luminescent 2W-SMPs, which might be widely applied in diverse areas.

Introduction

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Shape memory polymers (SMPs) are a kind of intelligent materials that are capable of fixing their deformation shape and recovering their original one when exposed to external stimuli, such as heat,¹⁻⁴ light,^{5,6} electric field,⁷ magnetic field,⁸ microwave,⁹ ultrasound,¹⁰ solvent,¹¹⁻¹³ ion,¹⁴ and pH.^{14,15} Different from conventional one-way SMPs, which cannot reverse their permanent shape to the temporary one unless they are programmed by imposing an external force,¹⁶⁻²⁰ the two-way shape memory polymers (2W-SMPs) can automatically change between two distinguished shape upon exposure to two external stimuli.^{5,21-23} Thus, such polymers can extend the applications of SMPs in diverse areas including biomimetic

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Electronic Supplementary Information (ESI) available: Synthetic routes to dipropiolates and PCL-4OH prepolymers, structure characterization (Figures S1-S8), properties of PCL prepolymers, Thermal properties of monomers, PCL-4OH, and PCL-based networks, and the structure of used AlEgen with red emission).

Movie S1, coiling and uncoiling shape changes of $\mathsf{PCL}_{\mathsf{3600}}$ network

Movie S2, coiling and uncoiling shape changes of $\mathsf{PCL}_{\mathsf{5800}}\text{-}\mathsf{TPE}$ network

actuators,²⁴ switches,²⁵ artificial muscles,^{26,27} microrobots,^{5,28} flexible electronics,^{29,30} and so on. However, to date, most of the investigation is focused on the design and synthesis of 2W-SMPs with single function, *i.e.*, reversible shape changes, limiting their broad applications.

Thus, endowing the 2W-SMPs with additional functions, such as luminescence, may greatly expand their applications. For example, when using the SMPs with NIR-II emission as intravascular stent inside our body, we can observe where they are by their luminescence due to their excellent tissue penetration depth (>1.0 cm),³¹ which is hard to be observed by other technique.^{32,33} Another example is the anti-counterfeiting application. Although the SMPs have been commercialized in this field, they are still easily counterfeited due to the single anti-counterfeiting manner.³⁴ Luminescent SMPs might provide an alternative toward this problem, and more complicated dual anti-counterfeit purpose can be realized. Unfortunately, there is no report on semi-crystalline 2W-SMP that integrates the reversible shape deformation and luminescence ability in one system though structural color materials have been reported recently.35-37 One of the reasons may be that conventional organic fluorophores usually suffer from the aggregationcaused quenching (ACQ) effect, which makes this target challengeable.

Exactly opposite to the ACQ effect, aggregation-induced emission (AIE), conceptually coined by Tang *et al.* in 2001, refers to a unique phenomenon that the luminogens show weak or non-emission in solution but emit intensely in their aggregate

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Movie S3, luminescent closing and blooming shape changes of PCL_{S800}-TPE network Movie S4, luminescent grasping and releasing actions of a robotic gripper See DOI: 10.1039/x0xx00000x

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Scheme 1. Synthesis of PCL₃₆₀₀ network (A) and PCL₅₈₀₀-TPE network (B) *via* DABCO-catalyzed hydroxyl-yne click polymerizations.

state.³⁸ Thus, the luminogens featuring AIE characteristics (AIEgens) are promisingly applicable in luminescent 2W-SMPs. Among the reported AIEgens,^{39,40} tetraphenylethene (TPE) has drawn much attention because of its simple synthetic procedures and high fluorescence quantum yield.^{41,42} Herein, TPE was used as the AIE unit to design and prepare luminescent 2W-SMPs.

In addition, to facilely prepare 2W-SMPs, efficient polymerization reactions are essential. However, most of them require harsh reaction conditions. For example, semi-crystalline polyurethane networks that show reversible shape changes were prepared by the polymerization of sensitive diisocyanates and alcohol monomers in the presence of metal catalyst.^{43,44} Furthermore, free radical polymerization of methacrylates or acrylates^{45,46} and thiol-ene reaction^{21,47} were also utilized to construct semi-crystalline polymer networks, where photoirradiation is a necessary condition. Moreover, the use of dicumyl peroxide as cross-linker to synthesize 2W-SMPs requires elevated temperature at a high pressure.^{48,49} To expand the application of 2W-SMPs, robust and powerful polymerizations, which could be performed in a meal-free manner under very mild reaction conditions, are highly needed.

Our groups have been working on the development of new polymerization reactions based on triple-bond building blocks.⁵⁰⁻⁵² Recently, we succeeded in establishing many robust alkyne-based click polymerizations, such as spontaneous thiolyne,^{53,54} spontaneous amino-yne^{50,55-57} and organobasecatalyzed hydroxyl-yne^{58,59} click polymerizations, which could be carried out under very mild reaction conditions.

Given that the ε -caprolactone (CL) is gernally used to prepare SMPs *via* the ring-opening polymerization, and the resultant poly(ε -caprolactone) (PCL) is terminated by the aliphatic hydroxyl groups,⁶⁰ we thus used them to react with TPEcontaining dipropiolate to prepare luminescent 2W-SMPs through the 1,4-diazabicyclo[2.2.2]octane (DABCO) catalyzed hydroxyl-yne click polymerization under mild reaction conditions (Scheme 1). Thanks to their dual functions, the resultant luminescent 2W-SMP could be fabricated into robotic grippers and realize double anti-counterfeiting. This work not only provides a new synthetic strategy for 2W-SMPs and enriches their family but also expands their applications by combining luminescence property.

Results and discussion

Preparation of monomers and polymer networks

TPE-free and TPE-containing dipropiolates 1 and 2 could be facilely synthesized via esterification reactions of propiolic acid and 1,6-hexanediol or 1,2-bis(4-hydroxylphenyl)-1,2diphenylethene, respectively. PCL prepolymers with 4 terminal hydroxyl groups and number-average molecular weights (M_n) of 2200, 3600, 4500 and 5800 g/mol, determined by $^{1}\mathrm{H}$ NMR analyses, were prepared by the ring opening polymerizations (Scheme S1 and Table S1, ESI⁺). The resultant prepolymers are denoted as PCL-4OH with Mn values in the subscript. For example, PCL₃₆₀₀-4OH indicates a PCL prepolymer with Mn of 3600. Furthermore, both PCL networks were facile prepared by DABCO-catalyzed hydroxyl-yne click polymerizations of PCL-4OH prepolymers and dipropiolates 1 or 2 under mild reaction conditions (Scheme 1).

Characterization of polymer networks

The molecular structures of dipropiolate **1**, TPE-containing dipropiolate **2** and PCL-4OH prepolymers were confirmed by ¹H and ¹³C NMR, and FT-IR spectroscopies, and satisfactory results were obtained (Figures S1-S8, ESI⁺). The ethynyl protons of both dipropiolates are detected at δ 2.87 and 3.04, respectively (Figures S1 and S2, ESI⁺). The resonance of methylene protons assigned to $-CH_2CO-$ and $-OCH_2-$ of the CL unit appear at δ 4.07 and 2.30, respectively (Figure S3, ESI⁺). The peak at δ 3.64 is assignable to methylene protons next to the hydroxyl group. The methylene protons of the pentaerythritol unit adjacent to reacted and unreacted hydroxyl groups are resonated at δ 4.11, and 3.59 and 3.51, respectively.

Their molecular structures were further confirmed by ¹³C NMR spectra. Dipropiolate **1** show C=C carbon resonances at δ 74.86 and 74.69 (Figure S5, ESI⁺), and those of TPE-containing dipropiolate **2** at δ 74.11, 76.64 (*Z*-configuration) and 76.84 (*E*-configuration), respectively (Figure S6, ESI⁺). The resonance peaks of carbon atoms of carbonyl group appear at δ 173.58, while that of the carbons adjacent to the hydroxyl groups emerge at δ 62.60 in the spectrum of PCL₃₆₀₀-4OH (Figure S7, ESI⁺). These results indicate that the above monomers and prepolymers were synthesized successfully.

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Figure 1. FT-IR spectra of dipropiolate **1** (A), TPE-containing dipropiolate **2** (B), PCL₃₆₀₀-OH prepolymer (C), PCL₃₆₀₀ network (D), and PCL₅₈₀₀-TPE network (E).

Polymer networks were only characterized by FT-IR spectroscopy because they cannot be dissolved in any organic solvents. As shown in Figure 1, the absorption peaks of dipropiolates associated with C=C and =C-H stretching vibrations are observed at 2111 and 3229 cm⁻¹, respectively, and the absorption at 3545 cm⁻¹ is assignable to the stretching vibrations of -OH group in PCL-4OH prepolymers. In the networks, the absorption peaks associated with the stretching vibrations of -OH and C=C groups almost disappear and that of C=C appears at 1624 cm⁻¹, indicative of the occurrence of hydroxyl-yne click polymerization.

Thermal properties of PCL-4OH prepolymers and networks

The thermal stabilities of PCL-4OH prepolymers and networks were measured by TGA. As indicated in Figure S9 (ESI⁺), the decomposition temperatures (T_{d} , 5% weight loss) of all samples are above 300 °C. Moreover, all polymer residues are very low (below 2 wt%) except PCL₅₈₀₀-TPE network because of its containing aromatic TPE units.

The melting and crystallization behaviors of PCL-4OH prepolymers and networks were investigated by DSC analysis, and their curves are depicted in Figures 2, S10 and S11 (ESI⁺). Both of melting temperatures (T_m) and crystallization temperatures (T_c) of PCL-4OH prepolymers increase with an increase in their molecular weights. T_m values of PCL₃₆₀₀-4OH and PCL₅₈₀₀-4OH were recorded to be 43 and 48 °C, while their T_c values are 21 and 25 °C, respectively. Compared with PCL-4OH prepolymers, T_c values of PCL₃₆₀₀ and PCL₅₈₀₀-TPE networks are decreased to -9 and -12 °C, respectively, due to the constrained polymer chain diffusion and conformational rearrangement. Moreover, the T_m values decreased to 33 and 41 °C, respectively, because of lower crystal size and more defects.⁶¹ It is worth noting that a weak crystallization peak at -19.5 °C was observed in the heating curve of PCL₅₈₀₀-TPE, indicating that TPE slows down the crystallization rate of PCL chains. The reason might be that during crystallization of PCL chains, TPE units are expelled out to the surface of the crystal lamellae and finally resided on the



Figure 2. DSC curves of heating (A) and cooling (B) processes of PCL-4OH prepolymers and PCL-based networks.

surface of PCL crystals, thus slowing down the arrangement rate of PCL chains into lattice.⁴¹

Photophysical properties

Thanks to their containing TPE units, the photoluminescence (PL) of TPE-containing dipropiolate **2** and PCL₅₈₀₀-TPE network were studied. As shown in Figure 3, **2** shows an emission peak at 470 nm, whereas, PCL₅₈₀₀-TPE network exhibits a slightly redshifted peak at 475 nm. Moreover, the absolute PL quantum yields (Φ_F) values of PCL₅₈₀₀-TPE network, **2**, and PCL₃₆₀₀ network in their film states were measured to be 4.5, 1.5 and 0.4%, respectively. The higher Φ_F value of PCL₅₈₀₀-TPE network than that of **2** is probably because TPE units are covalently incorporated in the polymer chains, which lead to the restriction of the intramolecular rotation of their phenyl rings and activation of more radiative transition.



Figure 3. Photoluminescence spectra of the films of TPEcontaining dipropiolate **2** and PCL₅₈₀₀-TPE network (λ_{ex} = 280 nm).

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Reversible shape memory behaviours and luminescent properties

The thermal property measurement shows that PCL_{2200} network exhibits weak crystallization peak, while the degree of crystallinity of PCL_{4500} and PCL_{5800} networks is too high, thus, PCL_{3600} network manifests the best shape memory effect due to its suitable crystallinity degree.^{44,46} Notabley, when TPE units are incorporated, PCL_{5800} -TPE network possess a better reversible shape change than PCL_{3600} -TPE network. The reason is that the TPE units are expelled out of lamellar of polymer crystals,⁴¹ thus inhibiting the crystallization of polymers and leading to a slower crystallization rate and a lower crystallinity degree of the former. Thus, PCL_{5800} -TPE network was selected to show its luminescent two-way reversible shape memory effect (2W-SME) and PCL_{3600} network was used as comparison.

The 2W-SMEs under stress-free condition of $\mathsf{PCL}_{\!3600}$ and PCL₅₈₀₀-TPE networks are shown in Figure 4 and Movies S1-S3 (ESI⁺) in water baths. Based on the results of thermal property measurement, 33 and 39 °C were selected as actuation temperatures (T_As) for PCL₃₆₀₀ and PCL₅₈₀₀-TPE networks, respectively, because they are in the range of melting temperatures. while 0 °C was used to cool them for crystallization, which is below their T_cs.²¹ As shown in Figure 4A, different original shapes of PCL₃₆₀₀ network were programmed into V and flower ones in 70 °C water bath for melting crystals of PCL networks and then placed into an ice-water bath to fix them. Once the samples were heated to 33 °C and cooled to 0 °C, different reversible shape transformations, such as bendingunbending, coiling-uncoiling, and closing-blooming shape changes, were realized. PCL₅₈₀₀-TPE network behaves similarly to PCL₃₆₀₀ network between 0 and 39 °C (Figure 4B) and strong emission was also observed under 365 nm UV light irradiation (Figure 4C).

Soft robotic gripper for grasping and releasing capability

The luminescent 2W-SMPs might have potential applications owing to their dual functions of luminescence and reversible shape memory properties. For example, the coiling-uncoiling shape changes of the luminescent 2W-SMPs incorporated NIR II fluorophores with deep tissue penetration might be used as intravascular stent. The sample would uncoil when it is implanted into blood vessel and can be traced by its luminescence. It would coil and thus can also be removed easily by cooling blood vessel.

Furthermore, they could also be used to fabricate nanorobots to perform complex operations by their reversible shape changes, and their position can also be traced through detecting its luminescence. To address this possible application, we designed a micro-gripper from two long strips of PCL₅₈₀₀-TPE network. The strips were first placed in a 70 °C water bath and programmed to a closed bending shape. The gripper was used to grasp screws, which are pre-coated with a red-emissive AIEgen (the structure is shown in Figure S12, ESI⁺),⁶² in an icewater beaker (0 °C) and release them to a warm water beaker (39 °C). Under the irradiation of 365 nm UV light, the gripper gives a blue emission, and the screws are red emissive (Figure 5A). When the gripper was immersed in warm water, each



Reversible shapes f various reversible shape changes illing, and blooming-closing) in atures. (A) PCL₃₆₀₀ network and (B) field, and (C) PCL₅₈₀₀-TPE network amp. Scale bar: 1.0 cm. bartial melting of PCL crystals b. Next, when the gripper was beended and grasped the screw of PCL chains. Afterward, the warm water bath to make the

Figure 4. Photograph illustration of various reversible shape changes (bending-unbending, coiling-uncoiling, and blooming-closing) in water baths with different temperatures. (A) PCL_{3600} network and (B) PCL_{5800} -TPE network under bright field, and (C) PCL_{5800} -TPE network under irradiation of a 365 nm UV lamp. Scale bar: 1.0 cm.

branch unbented due to the partial melting of PCL crystals (Figure 5B and Movie S4, ESI⁺). Next, when the gripper was placed in an ice-water bath, it bended and grasped the screw owing to the recrystallization of PCL chains. Afterward, the system was lifted and put in a warm water bath to make the gripper unbent again and release the screw. Repeating this process, another crew could be grasped and released. The same processes of PCL₅₈₀₀-TPE network were also demonstrated under bright field as a control, which is shown in Figure 5C. Ti is worth noting the gripper with the weight of 0.25 g can grasp and release various screws with weights up to 37 g, which is 148-fold higher than that of the polymer gripper. Moreover, this payload-to-weight ratio is much higher than many industrial robotic grippers.⁶³

Double anti-counterfeiting

SMPs have been used in the field of anti-counterfeiting because of their shape changing ability upon heating. For example, an injected film sheet with convex-concave patterns or words is pressed into the plane at the temperature above its transition temperature, which become invisible under such temperature. Published on 29 September 2020. Downloaded on 10/15/2020 3:23:27 AM

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Figure 5. (A) Schematic and (B and C) photograph illustration of a robotic gripper made of PCL₅₈₀₀-TPE network showing grasping and releasing capability. The photos in panel B were taken under a 365 nm UV lamp irradiation. Scale bar: 1.0 cm.



Figure 6. Photographs showing the double anti-counterfeiting capability of a luminescent SMP. (A, C) After sealing with an SMP word; (B, D) After heating using a heating gun at 50 °C. Scale bar, 0.5 cm.

The patterns or words would reappear again when the system is heated to above its transition temperature. However, such technique is still easily counterfeited due to the single anticounterfeiting way.⁶⁴

If another parameter is furnished to the anti-counterfeiting system, the safety will be enhanced. Thanks to the luminescence and shape memory property of PCL_{5800} -TPE network, we tried to apply it in dual anti-counterfeiting area. As shown in Figure 6, its film was first sealed with the characters of "SMP" in a 70 °C water bath, followed by placing in an ice-water bath to fix the patterns. As expected, this sealed film shows dual anti-counterfeit capability. It is emissive upon UV irradiation, and the sealed characters would disappear upon heating by a heat gun at about 50 °C. Thus, PCL5800-TPE shows great advantages over traditional single anti-counterfeit materials.

Conclusions

The first examples of luminescent PCL-based 2W-SMPs, which were prepared by the organobase-catalyzed hydroxyl-yne click polymerization under mild reaction conditions, are presented. Compared with PCL-4OH prepolymers, PCL-based networks show reduced T_m s and crystallinity degrees. The introduction of TPE units into polymer network can further reduce the crystallinity degree and enhance the emission compared with its monomer **2**. The PCL₃₆₀₀ network is able to perform reversible bending-unbending, coiling-uncoiling, and closing-blooming motions. Whereas, PCL₅₈₀₀-TPE network can not only behave the same as PCL₃₆₀₀ network but also shows luminescent

reversible shape transformation under UV light irradiation. A robotic gripper made of PCL_{5800} -TPE network can grasp a crew which weight could be 148-fold higher than itself, in cool water and release in warm water automatically. Moreover, PCL_{5800} -TPE network demonstrated a dual anti-counterfeiting properties of luminescence and shape change. Thus, this work offers a new strategy to develop smart materials by integrating more functions into one system.

Experimental Section

Materials. 1,4-Diazabicyclo[2.2.2]octane (DABCO), N,N'dicyclohexylcarbodiimide (DCC), pentaerythritol, and 1,6purchased from TCI. 4hexanediol were Methoxybenzophenone, ε -caprolactone (CL), and 4dimethylaminopyridine (DMAP) were purchased from Energy. TiCl₄, BBr₃, and stannous octoate were bought from Aladdin. Propiolic acid and TsOH were purchased from Macklin and HWRK Chem, respectively. Tetrahydrofuran (THF) was distilled under nitrogen at normal pressure from sodium benzophenone ketyl immediately prior to use. Dichloromethane (DCM), N,Ndimethylformamide (DMF) and dimethylsulfoxide (DMSO) are ultra-dry reagents purchased from Energy.

Characterization

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 F3 at a heating rate of 20 °C/min under nitrogen. Differential scanning calorimetry (DSC) measurements were carried out on a DSC Q800 (TA Instruments) at a heating rate of 10 °C/min. Fourier transform infrared spectroscopy (FT-IR) was used to confirm the reaction of dipropiolate and hydroxyl groups using a Bruker Vector 33 FTIR spectrometer with an ATR (attenuated total reflectance) mode. All spectra were scanned 32 times in the range 400 – 4000 cm⁻¹ at a 4 cm⁻¹ resolution. ¹H and ¹³C spectra were performed on a Bruker Avance 500 MHz NMR spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS, δ = 0) as an internal reference. SEC coupled with successively connected refractive index and UV detectors was conducted in THF at 35 °C using two identical PL gel columns (5 µm, MIXED-C) at a flow rate of 1.0 mL min⁻¹and polystyrenes with different molcular weights were used as standards. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Absolute

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fluorescence quantum yields were performed on a Hamamatsu C11347-11 Quantaurus-QY.

Synthesis of monomers (Scheme S1, ESI+)

1,6-Hexanediol dipropiolate

1,6-Hexanediol dipropiolate (dipropiolate 1) was synthesized according to the procedures in our previously reported work.65 1,6-Hexanediol (3.54 g, 30 mmol), propiolic acid (5,6 mL, 90 mmol), TsOH (1.03 g, 6mmol), and 100 mL of dry toluene were successively added in a 250 mL round-bottom flask equipped with a Dean-Stark apparatus. The mixture was refluxed for 12 h. After stopping the reaction, the solution was concentrated by a rotary evaporator and then extracted with DCM three times. The organic layer was dried overnight with anhydrous magnesium sulfate (MgSO₄) and then filtered. After solvent evaporation, the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 v/v). Dipropiolate 1 was obtained as white powders in 78.5 % yield (5.24 g). FT-IR (KBr disk), u (cm⁻¹): 3228, 2946, 2874, 2112, 1698, 1477, 1250, 1077, 965, 904, 773, 713, 606, 424. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 4.19 (t, 4H), 2.88 (s, 2H), 1.70 (m, 4H), 1.42 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 152.92, 74.69, 66.30, 28.31, 25.55.

1,2-Bis(4-hydroxyphenyl)-1,2-diphenylethene (compound 3)

This compound was synthesized via a McMurry coupling. 4-Hydroxy-benzophenone (4.95 g, 25.0 mmol) and zinc powder (6.54 g, 100.0 mmol) were placed into a flask equipped with a condenser. Anhydrous THF (70 mL) was added into the flask after exhausting-refilling process for three times. TiCl₄ (4.1 ml, 37.5 mmol) was added dropwise into the mixture after being placed in an ice-water bath. The mixture was refluxed overnight. Afterward, the reaction was guenched by the addition of 10% aqueous solution of NaHCO₃. The mixture was filtered and then extracted with DCM for three times. The organic layer was dried with anhydrous MgSO₄ overnight and then filtered. After solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (3:1, v/v) as eluent. The product was obtained after drying under vacuum overnight. The compound **3** was obtained as white powders in 54.0% yield (2.46 g). FT-IR (KBr disk), u (cm⁻ ¹): 3530, 3401, 3024, 1608, 1509, 1438, 1334, 1256, 1170, 823, 701. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.13 – 7.10 (m, 6H), 7.05 – 7.01 (m, 8H), 6.93 – 6.89 (m, 4H), 3.03 (d, 1.79H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 150.82, 148.45, 143.14, 141.94, 140.55, 132.53, 131.42, 128.09, 127.02, 120.55.

4,4'-(1,2-Diphenylethenylene)diphenyl dipropiolate (TPEcontaining dipropiolate 2)

Compound 3 (2.0 g, 5.5mmol), DCC (5.78 g, 28 mmol), DMAP (0.56 g, 28 mmol), and TsOH (1.03 g, 6mmol) were added to 20 mL DCM in a round-bottom flask equipped with a magnetic stir bar and placed in an ice-water bath. Propiolic acid (1.1 mL, 16.5 mmol) in 20 mL of DCM was added dropwise to the system under vigorous stirring. The reaction was carried out at room temperature for 12 h. Afterward, the reacted mixture was filtered and extracted with DCM. After the organic layer was dried over MgSO₄ and removing the solvent every tick ot any evaporation, the crude product was Dputfied 9/by Teologian chromatography on silica gel using petroleum ether/ethyl acetate (10:1, v/v) as eluent. TPE-containing dipropiolate 2 was obtained as white powders in 37.2% yield (0.95 g). FT-IR (KBr disk), υ (cm⁻¹): 3265, 3242, 2987, 2350, 2124, 1719, 1501, 1214, 1076, 1018, 915, 811, 750, 699. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 7.14 - 7.07 (m, 6H), 7.06 - 6.98 (m, 8H), 6.94 - 6.87 (m, 4H), 3.04 (d, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 150.68, 148.42, 143.00, 141.74, 140.41, 132.42, 131.26, 127.95, 127.81, 120.59, 120.42.

Synthesis of PCL-4OH prepolymers

A typical synthetic protocol of PCL-4OH prepolymer (M_p = 3600 g/mol) is addressed here. Pentaerythritol (0.204 g, 1.5 mmol) was added into a Schlenk tube equipped with a magnetic stir bar. The tube was stoppered with rubber septa, and an exhausting-refilling process was repeated three times. CL (2.91 mL, 25.50 mmol) was subsequently added via a syringe under nitrogen into the reaction vials. The vials were then placed into a preheated oil bath at 130 °C. After 5 min, Sn(Oct)₂ (0.02 mL) was injected into the mixture, which was stirred for 12 h. The polymerization was terminated by exposing to air and adding excess of chloroform. The crude polymer solution was precipitated from methanol and dried under vacuum at 30 °C for 24 h. The product was obtained as white powders in 49.9% yield (1.60 g). PCL₂₂₀₀-OH (1.56 g), PCL₄₅₀₀-OH (2.14 g), and PCL₅₈₀₀-OH (2.44 g) prepolymers were obtained with yields of 47.7%, 68.3%, and 69.1%, respectively, by the same synthetic procedures.

The number-average molecular weight (Mn) of PCL-4OH prepolymers is calculated by using the following expressions:⁶⁰

$$N = \frac{4S_i}{S_i + S_o + S_p}$$
(1)
$$L_n = \frac{S_m + S_n}{S_n}$$

$$=\frac{S_{\rm m}+S_{\rm n}}{S_{\rm n}} \tag{2}$$

$$M_{\rm n} = 114.14 \times N \times L_{\rm n} + 136$$
 (3)

where S denotes the integral area of proton signal, N is the average arm number, L_n is the average number of CL units for each arm. Four PCL prepolymers with different molecular weights were obtained. Moreover, M_n and polydispersity index (D) were also measured by size exclusion chromatography (SEC). The results are summarized in Table S1 (ESI⁺). PCL₃₆₀₀-OH prepolymer: FT-IR ATR mode, *u* (cm⁻¹): 3544, 2944, 2863, 1721, 1470, 1418, 1398, 1366, 1294, 1240, 1175, 1107, 1044, 961, 934, 840, 730. ¹H NMR (500 MHz, CDCl₃) δ (TMS, ppm): 4.14 – 4.09 (d, 6H), 4.09 - 4.02 (t, 57H), 3.69 - 3.60 (t, 6H), 3.60 - 3.55 (d, 1H), 3.58 - 3.47 (d, 1H), 2.40 - 2.25 (m, 63H), 1.74 - 1.50 (m, 133H), 1.46 – 1.30 (m, 63H). ¹³C NMR (125 MHz, CDCl₃) δ (TMS, ppm): 64.16, 62.63, 34.15, 32.35, 28.37, 25.55, 24.60.

Preparation of polymer networks via hydroxyl-yne click polymerization reaction

PCL₃₆₀₀-4OH (500 mg, 0.139 mmol,), dipropiolate 1 (61.7 mg, 0.277 mmol), and 2.4 mL THF were mixed in a dry vial under

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vigorous stirring. DABCO (3.1 mg, 0.027mmol) in 100 μ L THF solution was added into the mixture. The vial was stirred for 30 s and then poured into Teflon molds (rectangular shape: 2.0 × 6.0 cm, flower shape with five petals). The system was allowed to set in a fume hood for 2 days and then removed from the mold. The obtained polymer is denoted as PCL₃₆₀₀ network. FT-IR ATR mode, v (cm⁻¹): 2942, 2864, 1729, 1623, 1463, 1391, 1357, 1326, 1158, 1129, 1038, 965, 819, 736.

PCL₅₈₀₀-4OH prepolymer was used to prepare a TPEcontaining polymer network (denoted as PCL₅₈₀₀-TPE network). The procedures are similar with those of PCL₃₆₀₀ network, except that the mixture was stirred only for 10 s and then poured into Telfon molds due to the higher reactivity of TPEcontaining dipropiolate **2**. The structures of the polymer networks are shown in Figure 1. FT-IR ATR mode, *u* (cm⁻¹): 2942, 2863, 1728, 1623, 1504, 1462, 1391, 1358, 1261, 1234, 1159, 1095, 806, 734, 701.

Conflicts of interest

There are no conflicts to declare.

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