Electronic Supporting Information

Circularly polarized light triggered enantioselective thiol-ene polymerization reaction

Guang Yang[a], Yang Y. Xu [b]*, Zi D. Zhang[c], Long H. Wang[a], Xue H. He[c*], Qi J. Zhang[a], Chun Y. Hong[a]*, Gang Zou[a]*

a: Key Laboratory of Soft Matter Chemistry, Chinese Academy of Science, Department of Polymer Science and Engineering, iChEM, University of Science and Technology of China, Hefei, Anhui 230026, China; E-mail: gangzou@ustc.edu.cn; hongcy@ustc.edu.cn

b: College of Chemistry and Materials Science, Anhui Normal University, East Beijing Rd. 1, Wuhu, Anhui 241000, China. E-mail: ahnuxyy@ahnu.edu.cn.

c: Department of Chemistry, School of Science, Tianjin University, Nankai District, 300072, Tianjin, China. E-mail: xhhe@tju.edu.cn.

Experimental Section

1. Materials.

All the pure chiral and racemic monomers, *N*-(allyloxy)carbonyl-homocysteinethiol-actone (NACHT), prop-2-yn-1-yl(2-oxotetrahydrothiophen-3-yl) carbamate (POTC), *N*-*N*-bis(2-oxotetrahydrothiophen-3-yl) adipamide (BODPA) and diallyl ethane-1,2-diyldicarbamate (DEDB) were synthesized according to the previous procedure[1]. *N,N*-dimethylpropane-1,3-diamine (DMPDA) was purchased from Aladdin Reagent Company. All other solvents and reagents were of analytical grade and used as received.

2. CPL triggered asymmetric thiol-ene and thiol-yne polymerization reaction.

The CPL (313 nm ± 10 nm), generated by Babinet-Soleil prism from ultra-high pressure mercury lamp, was used for asymmetric polymerization reactions. The light intensity of 313 nm was 20 mW/cm^2.

A typical CPL-triggered asymmetric thiol-ene polymerization procedure was carried out as following: Racemic NACHT (100 mg, 0.50 mmol) and DMPDA (64 mg, 0.63 mmol) in 1,4-dioxane (1 mL) were put into a quartz cuvette filled with nitrogen atmosphere. After 30 min for theopening of thiolactone ring, racemic allyl (1-((3-(dimethylamino)- propyl)amino)-4-mercapto-1-oxobutan-2-yl)carbamate (DPAMOC) monomers were obtained. Then above solutions were subjected to 313 nm CPL irradiation for 90 min, and the final polymer products could be obtained via precipitating by addition of diethyl ether and filtering. As the reference samples, the thiol-ene based polymerization for the thus-formed racemic monomers were proceeded upon normal UV irradiation and the linear polymers could be obtained via precipitating by addition of diethyl ether and filtering from the reaction solution. The CPL-triggered polymerization experiments for pure L- and D-type enantiomers were also proceed similarly and the optical active polymer could be obtained via precipitating and filtering methods.

Further, the CPL-triggered asymmetric thiol-ene polymerization for dithiol and divinyl functional monomers could also realized as following: Racemic BODPA (188 mg, 0.50 mmol), DEDB (114 mg, 0.50 mmol) and DMPDA (128 mg, 1.26 mmol) in 1,4-dioxane (1 mL) were put into a quartz cuvette filled with nitrogen atmosphere. The mixture were kept at room temperature for 30 min for the opening of thiolactone ring. Then the mixture solutions were directly subjected to 313 nm CPL irradiation for 90 min, and the final linear polymer products could be obtained via precipitating and filtering methods.

A typical CPL-triggered asymmetric thiol-yne polymerization procedure was carried out as following: Racemic POTC (100 mg, 0.51 mmol) and DMPDA (64 mg, 0.63mmol) in 1,4-dioxane (1 mL) were put into a quartz cuvette. After 30 min for the opening of thiolactone ring, the solutions were directly subjected to 313 nm CPL irradiation for 90 min, and the optical active hyperbranched polymer products could be obtained via precipitating and filtering methods.

3 DFT calculation. Geometries for left-handed (L) and right-handed (D) thiyl radicals were optimized with the PBE0/Def2-TZVPP theory of level. The solvent effect was evaluated by the polarizable continuum models (PCM) with the solvent 1,4-dioxane. The vertical excitation calculations were performed at the optimized ground state geometries for the lowest 30 singlet excited states using the linear response TDDFT under the same theory of level mentioned above. All calculations were performed using Gaussian 09 suit of package. The UV-visible and ECD spectra were analysed by the Multiwfn package and the full width at half maximum (FWHM) for the Gaussian broadening function equalled 0.5 eV.

4. **Chracterizations**.

^{1}H-NMR spectra were recorded in 1,4-dioxane-d_8 (Alfa-Aesar) on a Bruker Avance 400 MHz. The NMR spectra were analyzed and processed by using MestReNova-6.1.1-6384 software. The molecular weights (M_W) and polydispersities (PDI) were determined by GPC performed at 35^{o}C with three linear Styragel columns and a Waters 2414 differential refractive index (RI) detector. DMF was utilized as eluent with flow rate of 1 mL/min, polystyrene was used as standard. HPLC were performed on a column of Chiralpak AD-H (Daicel Chemical Industries Ltd) using isopropanol in 0.005 M aqueous solution of n-hexane (5:95, v/v), at a flow rate of 1.0 mL/min. CD spectra of the formed polymers in acetonitrile solution (0.1 mg/mL) were characterized by using JASCO CD spectrometer J-810. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker UltraflexIII TOF/TOF mass spectrometer (Bruker Daltonics, Tnc., Billerica, MA) equip with a Nd: YAG laser(355nm). The matrix was 2-[(2e)-3-(4-ter-butylphenyl)-2-methylprop-2-enylidene]malononitrile trans-2-[3-(4-ter-butylphenyl)-2-methyl-2-propenylidene] malononitrile propanedinitrile (DCTB) in CH_2Cl_2 solution(20mg/ml), and the salt was sodium trifluoroacetate in CH_3OH solution(1mg/ml).

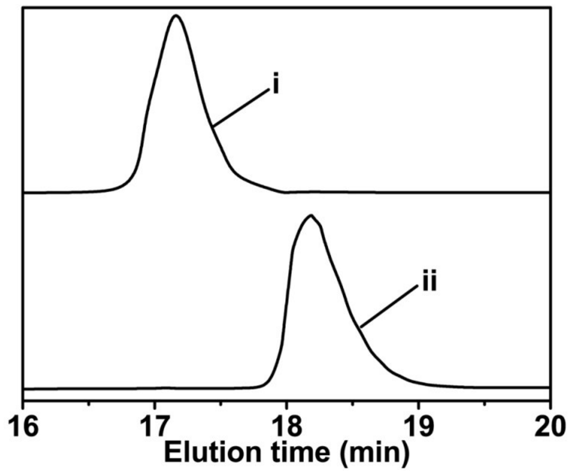

Fig. S1 HPLC characterization of (i) D- and (ii) L-type DPAMOC enantiomer monomers.

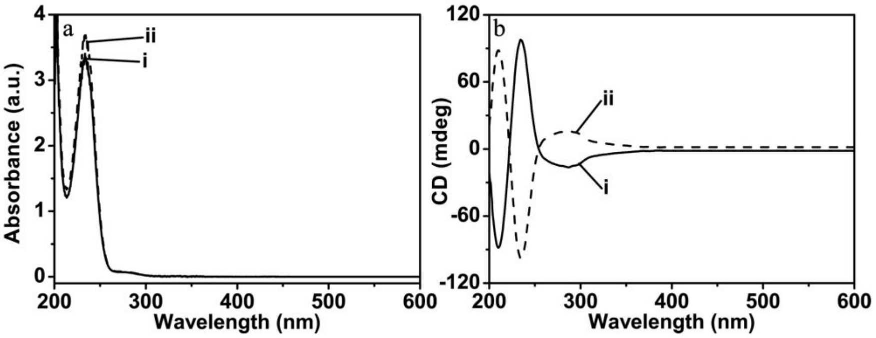

Fig. S2 (a) UV-visible and (b) CD spectra of pure (i) L- and (ii) D-type DPAMOC enantiomer monomers, respectively.

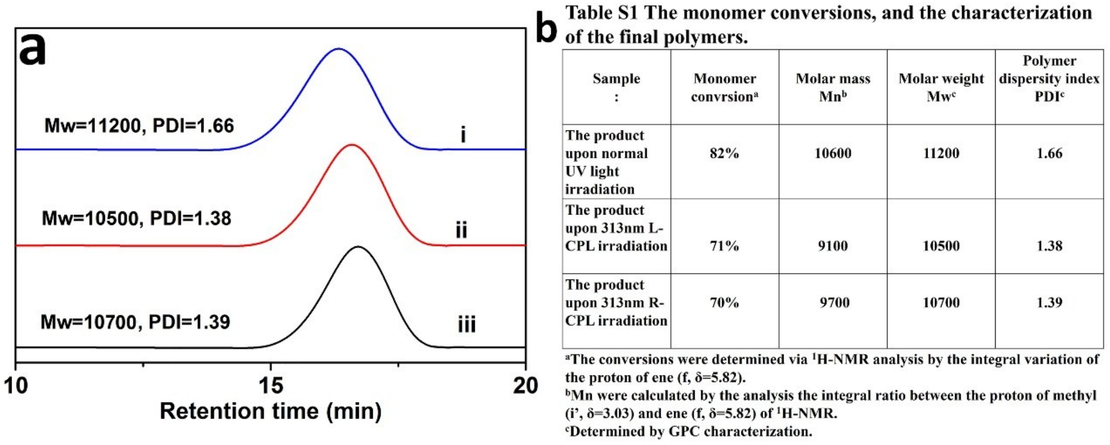

Table S1 The monomer conversions, and the characterization of the final polymers.

Sample :	Monomer convrsion^a	Molar mass Mn^b	Molar weight Mw^c	Polymer dispersity index PDI^c
The product upon normal UV light irradiation	82%	10600	11200	1.66
The product upon 313nm L-CPL irradiation	71%	9100	10500	1.38
The product upon 313nm R-CPL irradiation	70%	9700	10700	1.39

[a] The conversions were determined via ^{1}H-NMR analysis by the integral variation of the proton of ene (f, δ=5.82).

[b] Mn were calculated by the analysis the integral ratio between the proton of methyl (i’, δ=3.03) and ene (f, δ=5.82) of ^{1}H-NMR.

[c] Determined by GPC characterization.

Fig. S3 (a) GPC characterization of the obtained polymers upon irradiation with (i) normal UV light, (ii) 313 nm L-CPL and (iii) R-CPL for 90 min. (b) Table of the monomer conversions, Mn, Mw and PDI of the polymers upon irradiation with normal UV light, 313 nm L-CPL and R-CPL, respectively.

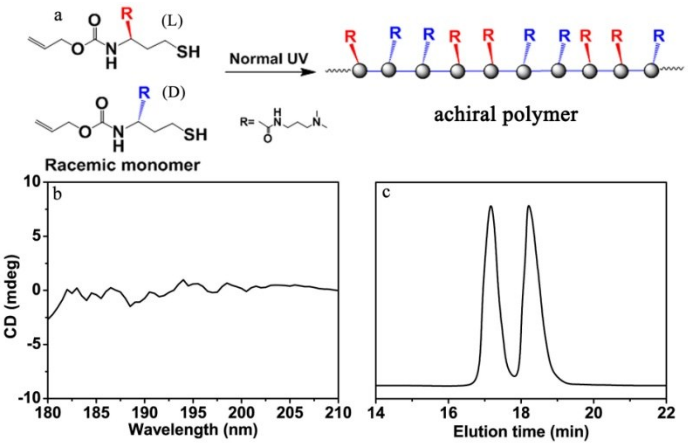

Fig. S4 (a) Chemical structures of L- and D-type DPAMOC enantiomer monomers, and schematic illustration of growing achiral polymer from racemic monomers upon irradiation with normal UV light, (b) CD signal of the final polymers by irradiation with normal UV light and (c) HPLC spectrum of the residual solution containing the unreacted L- and D-type DPAMOC enantiomer monomers.

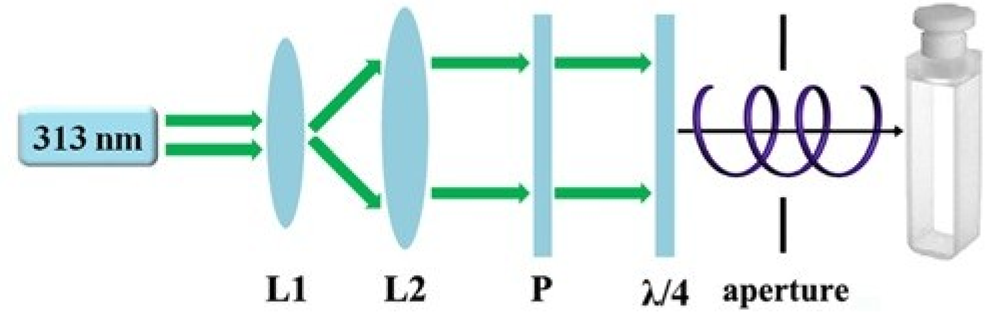

Fig. S5 Experimental set-up for the asymmetric polymerization with 313 nm CPL irradiation.

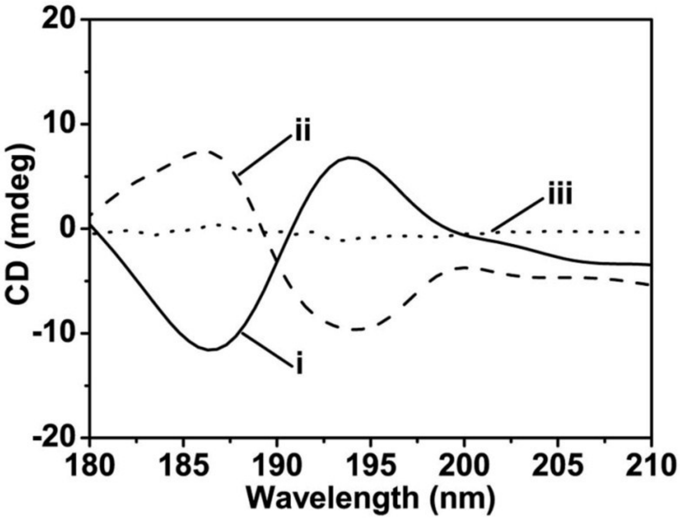

Fig. S6 CD spectra of the residual reaction solution containing the unreacted monomers and oligomers after irradiation with 313 nm (i) L- and (ii) R-CPL, and (iii) normal UV light for 90 min, respectively.

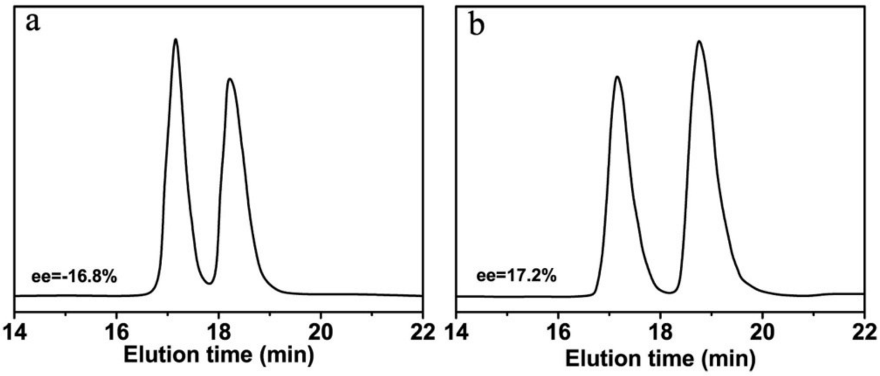

Fig. S7 HPLC spectra of the residual reaction solution containing the unreacted monomers and oligomers after irradiation with 313 nm (a) L- and (b) R-CPL for 90 min, respectively.

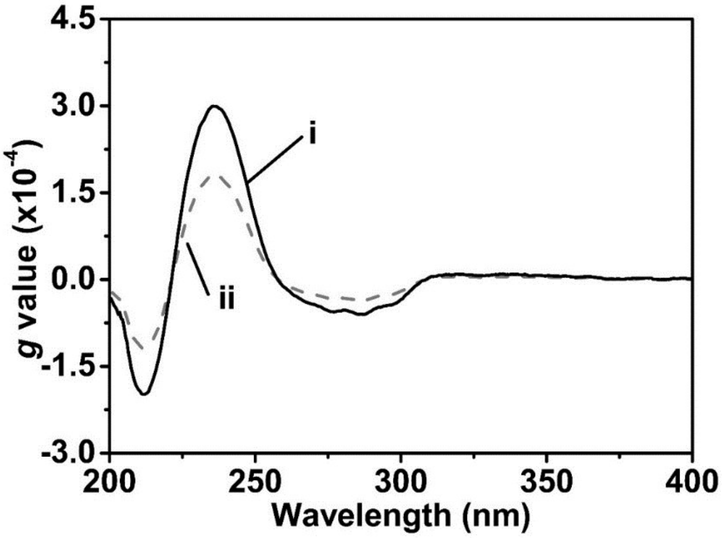

Fig. S8 The g factor of (i) the obtained polymers irradiated with 313 nm L-CPL for 90 min (with16.8% excess of L-type chiral enantiomers in the polymer chain) and (ii) the mixture chiral monomers solution with the same enantiomeric excess (with16.8% excess of L-type chiral enantiomers).

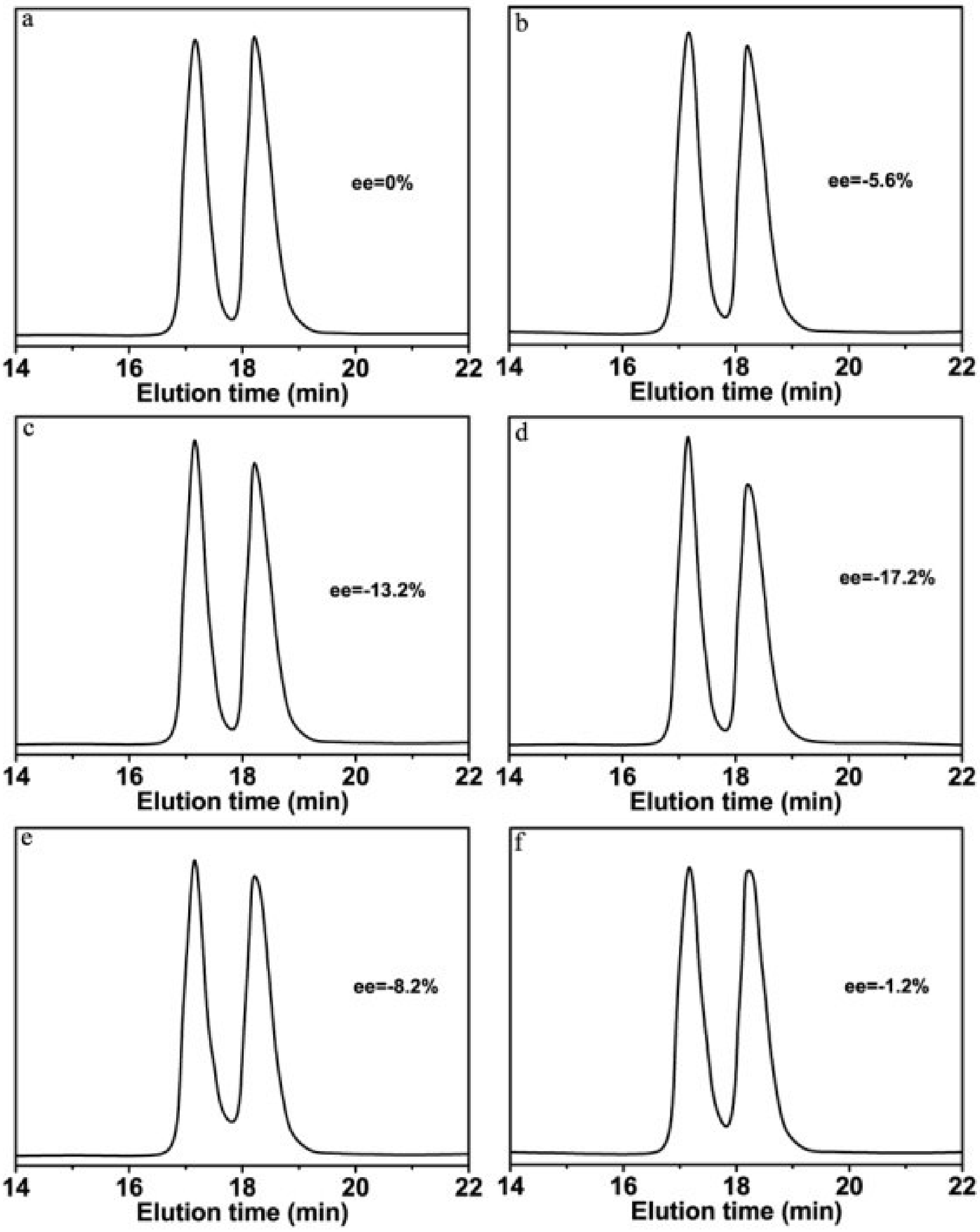

Fig. S9 HPLC spectra of the residual solution containing unreacted L- and D-type chiral monomers after irradiation with 313 nm L-CPL for (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min and (f) 150 min, respectively.

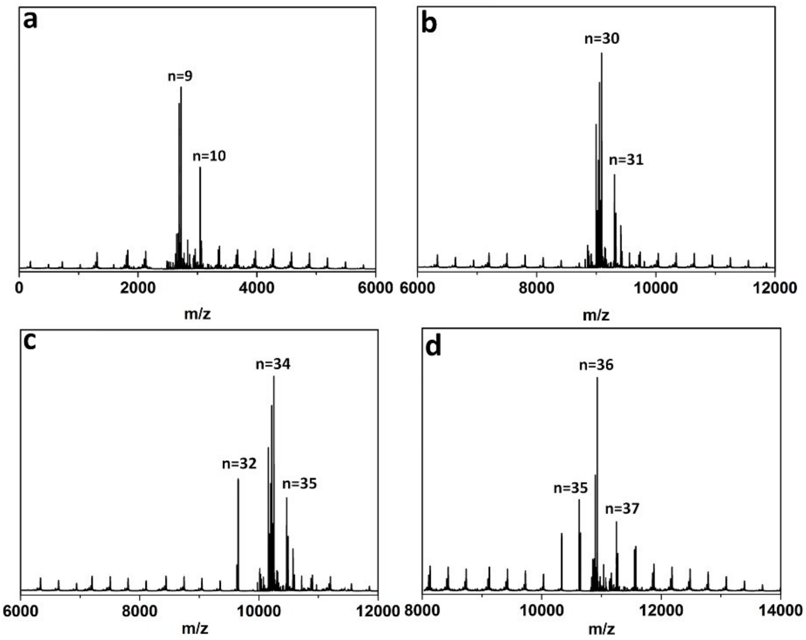

Fig. S10 Matrix-assisted laser desorption ionization time-of-flight mass spectra of the products obtained upon irradiation with 313 nm L-CPL for (a) 30 min, (b) 60 min, (c) 120 min and (d) 180 min, respectively.

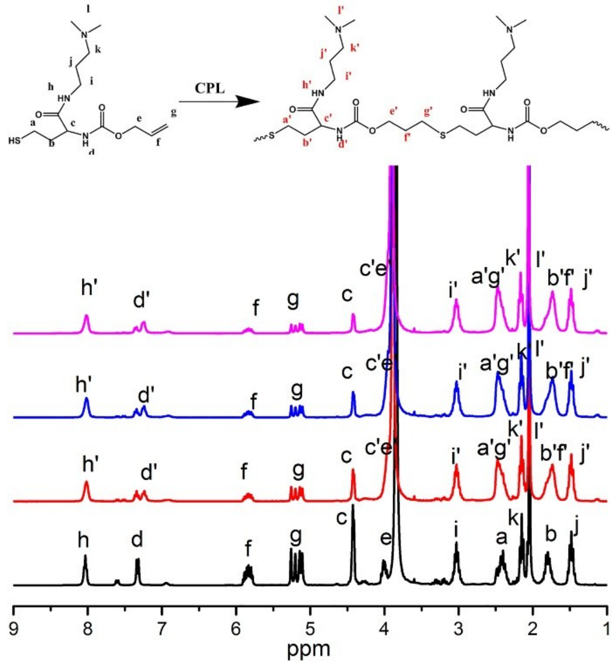

Fig. S11 ^{1}H-NMR spectra recorded *in situ* for (i) racemic DPAMOC and the mixture in DMSO-d_6 under irradiation with 313 nm L-CPL for (ii) 60 min (iii) 120 min and (iv) 180 min, respectively.

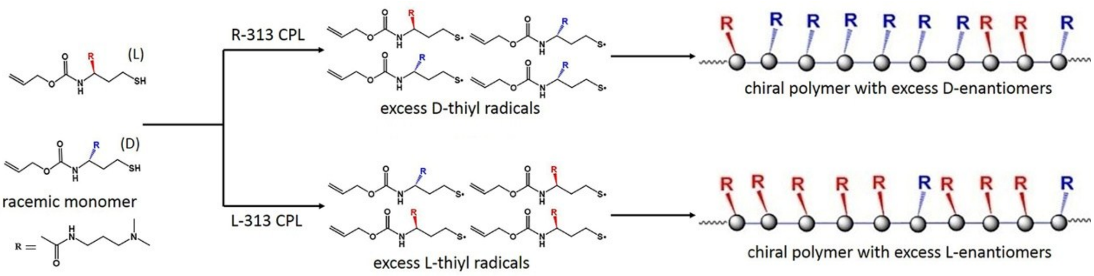

Fig. S12 Scheme for the possible thiol-ene based asymmetric polymerization procedure upon irradiation with 313 nm CPL.

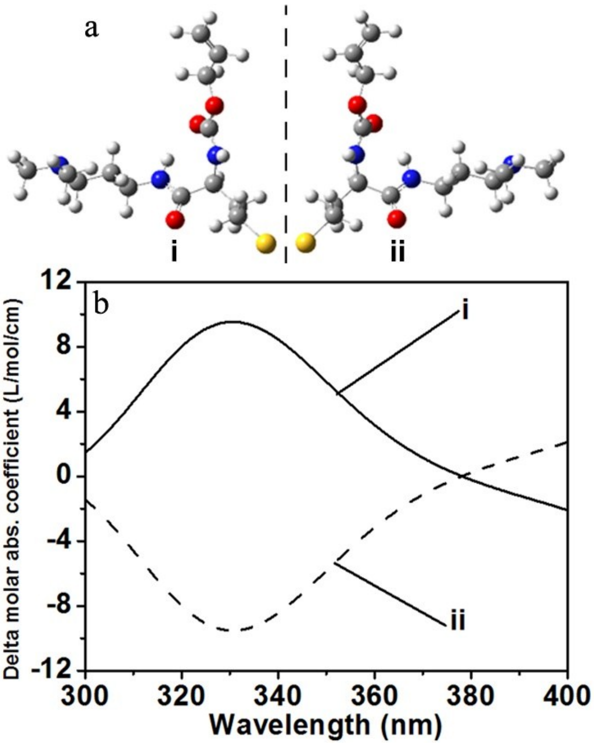

Fig. S13 (a) Optimized geometries of two enantiomers: (i) L- and (ii) D- intermediate thiyl radical. (b) Theoretical electronic CD spectra of the intermediate chiral radicals: (i) L- and (ii) D-thiyl radical by TDDFT computation.

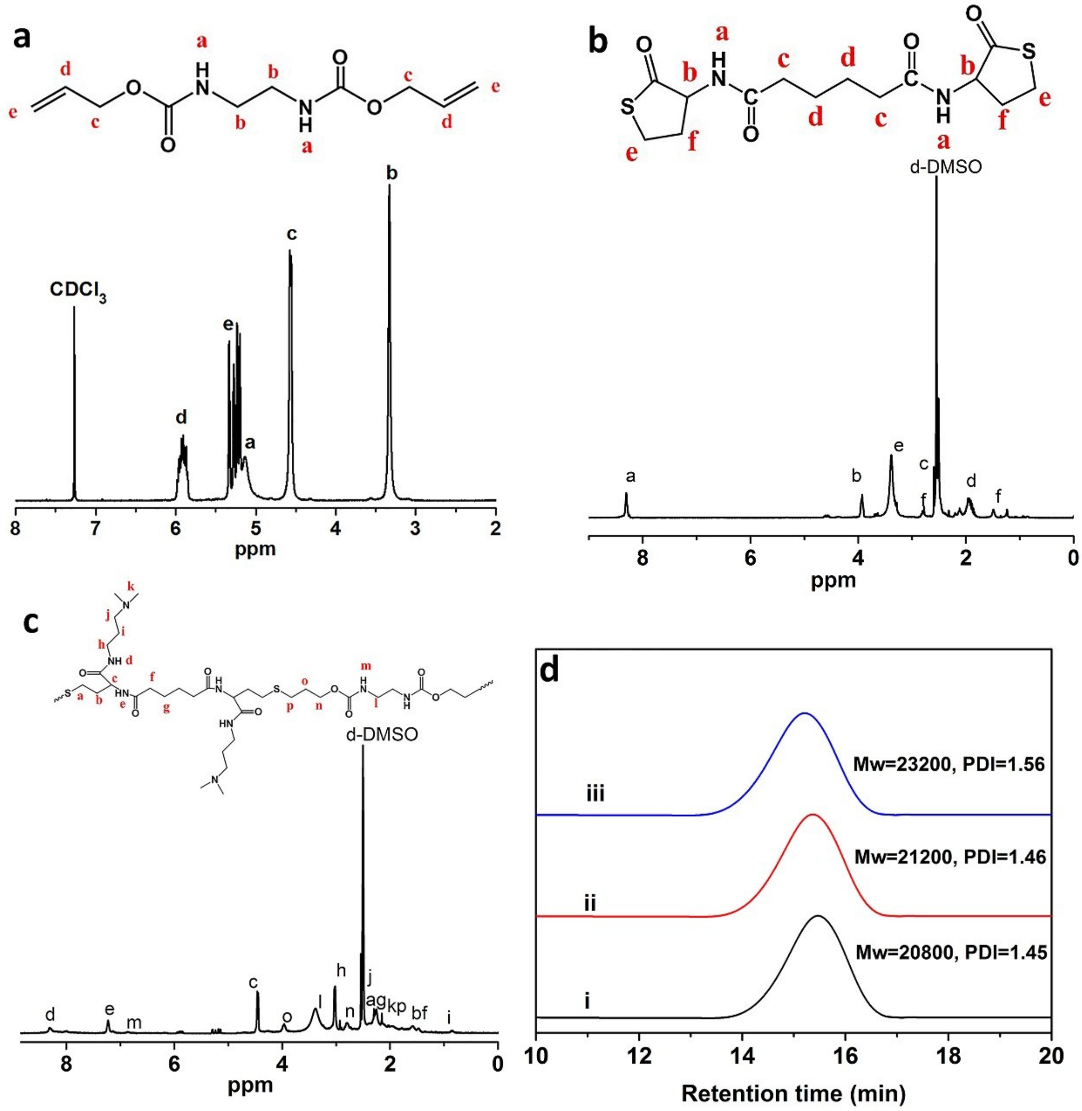

Fig. S14 Molecular structures and the ^{1}H-NMR spectra of (a) diallyl ethane-1,2-diyldicarbamate (DEDB) in CDCl$_3$, (b) *N-N*-bis(2-oxotetrahydrothiophen-3-yl)adipamide (BODPA) in *d6*-DMSO and (c) final polymer products through the asymmetric thiol-yne polymerization in *d6*-DMSO after irradiation with 313 nm L-CPL for 90 min. (d) the GPC trace of final obtained products upon irradiation with (i) 313 nm L-CPL , (ii) R-CPL, and (iii) normal UV light for 90 min, respectively.

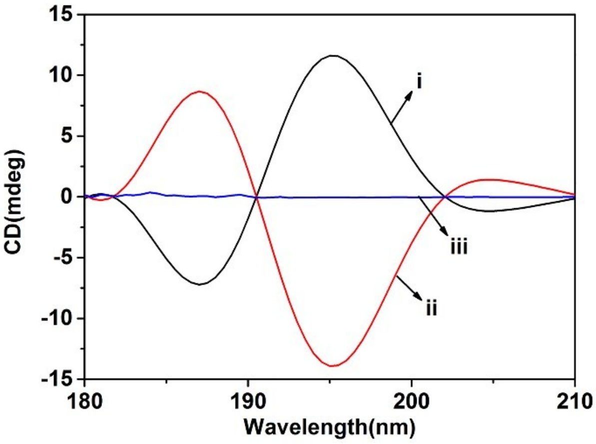

Fig. S15 CD spectra of the of the final obtained polymers after irradiation with (i) 313 nm L-CPL , (ii) R-CPL and (iii) normal UV light for 90 min, respectively.

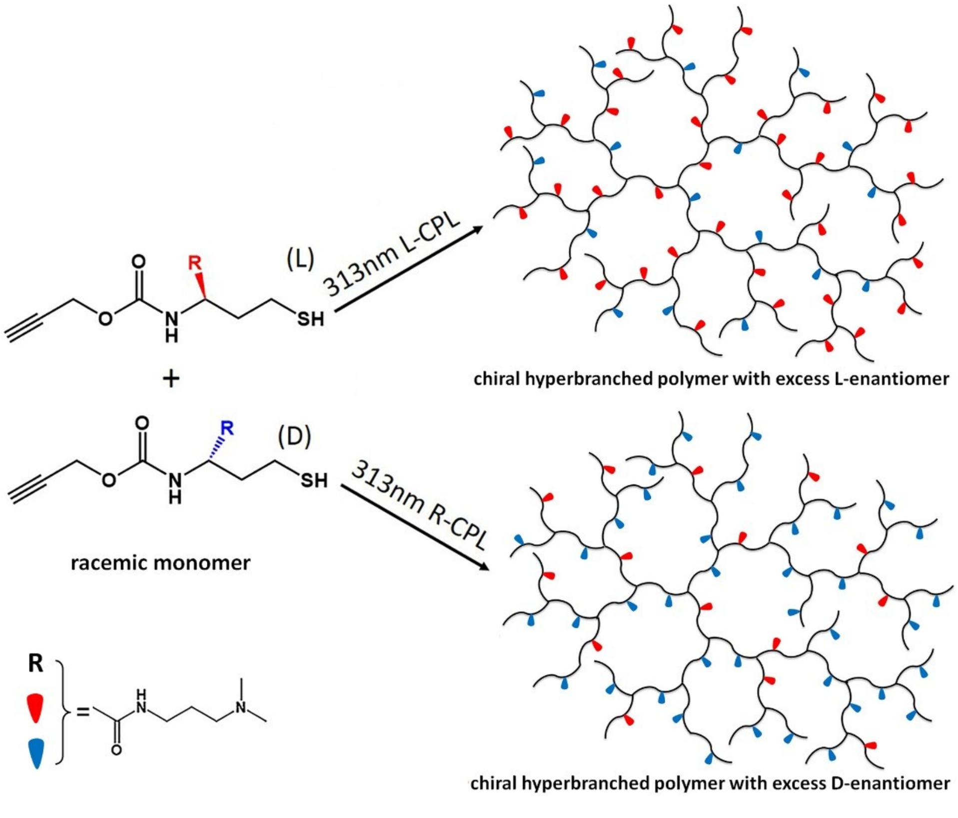

Fig. S16 Molecular structures and the synthetic route of growing chiral hyper-branched polymers.

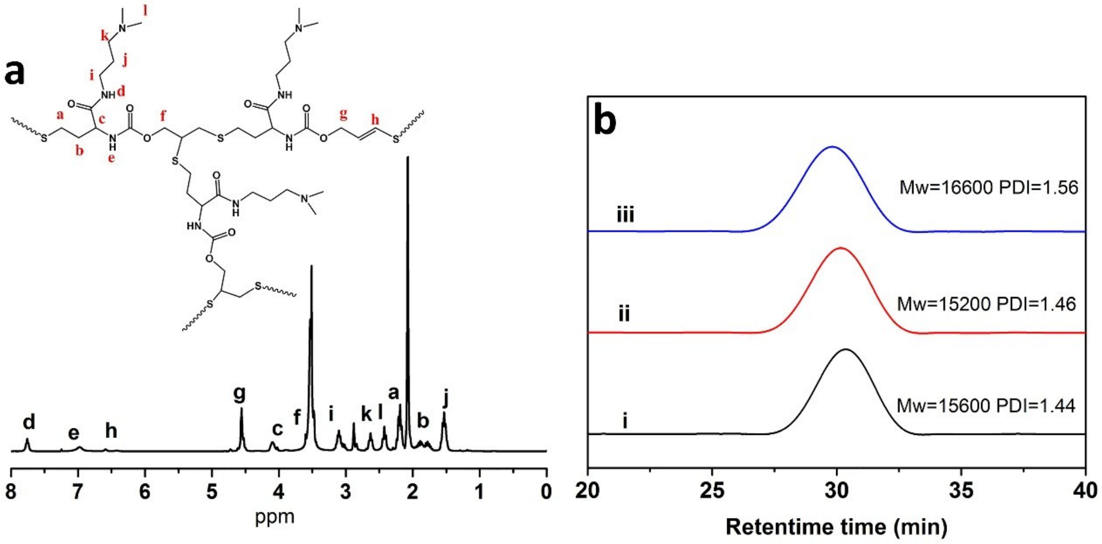

Fig. S17 (a) Molecular structure and the ^{1}H-NMR spectrum of final hyperbranched products through the asymmetric thiol-yne polymerization in DMSO-d_6 and the (b) GPC trace of final hyperbranched products under irradiation with (i) 313 nm L-CPL, (ii) R-CPL and (iii) normal UV light for 90 min, respectively.

References

1. Espeel P, Goethals F, Du Prez FE (2011) One-pot multistep reactions based on thiolactones: extending the realm of thiol-ene chemistry in polymer synthesis. *J Am Chem Soc* 133(6):1678-1681.