

Supporting Information

Facile preparation of optically active helical polycarbenes with salicylate substituents and their postpolymerization modification

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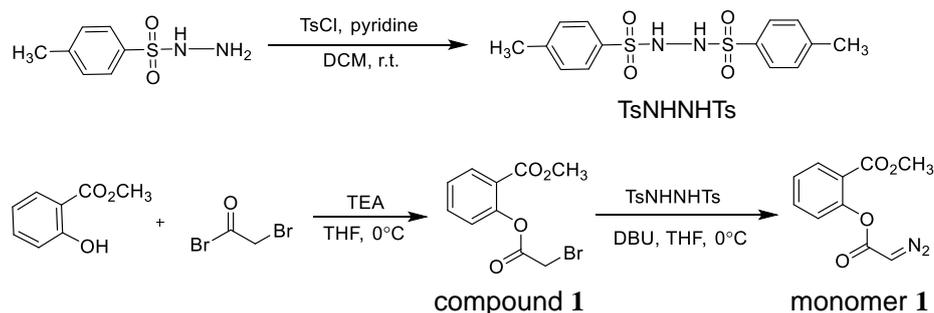
1. Measurements

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker spectrometer as denoted. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield with tetramethylsilane or residual chloroform as an internal standard. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40°C) using a series of two linear TSK gel GMHHR-H columns. The number-average molecular weight (M_n) and its polydispersity (M_w/M_n) data were reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. Fourier transform infrared (FT-IR) spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets at 25°C . Circular dichroism (CD) spectra were obtained in a 1.0 mm quartz cell using a JASCO J1500 spectropolarimeter. The UV-vis absorption spectra were recorded on a UNICO 4802 UV/vis double beam spectrophotometer. High performance liquid chromatography (HPLC) with UV-vis detector was carried out on SHIMADZU LC-20AT equipment using chiral columns. Differential scanning calorimetric (DSC) measurements were carried on a Mettler-Toledo DSC821e instrument under a nitrogen atmosphere, and samples were first heated from -50 to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$, followed by cooling to -50°C after stopping at 200°C for 3 min, and finally heating to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$.

2. Materials

All solvents were obtained from Sinopharm. Co. Ltd., and were purified by the standard procedures before use. All chemicals including π -allylPdCl and PdCl₂ were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The monomer **1**,^{1,2} the phosphine ligands L^S and L^R ,^{3,4} *N*-(2-aminoethyl)-5-(dimethylamino)-1-naphthalene sulfonamide⁵ were prepared according to reported literatures with slight modifications.

3. Experimental procedures



Scheme S1 Synthesis of monomer 1.

3.1 Synthesis of monomer 1

The monomer 1 was synthesized by three steps as shown in Scheme S1. Firstly, TsNHNHTs was prepared by the reaction between *p*-toluenesulfonyl hydrazide and *p*-toluenesulfonyl chloride as described below. A flame-dried, 500 mL round-bottomed flask fitted with a magnetic stir bar was charged with *p*-toluenesulfonyl hydrazide (18.64 g, 0.10 mol, 1.0 eq.) and *p*-toluenesulfonyl chloride (28.60 g, 0.15 mol, 1.5 eq.) in CH₂Cl₂ (100 mL). The mixed suspension was stirred at room temperature while pyridine (12 mL, 0.15 mol, 1.5 eq.) was added dropwise over 3 min. During the addition, the reaction mixture became homogenous and turned yellow. White precipitate was observed within 3 min and the reaction mixture was stirred for further 1.5 h. Diethyl ether (400 mL) and H₂O (200 mL) were added and stirred at 0°C for 15 min. The white solid which precipitates was collected in a Büchner funnel using suction filtration and washed with diethyl ether (100 mL). The solid thus obtained was dissolved in boiling methanol (400 mL). After cooling to room temperature, precipitate appeared. About 180 mL of methanol was removed by rotary evaporation and cooled to 0°C. The precipitate was collected in a Büchner funnel using suction filtration and washed with cold methanol (20 mL) and diethyl ether (100 mL) to give *N,N'*-ditosylhydrazine (TsNHNHTs) as a white solid (yield: 81%).

Secondly, the compound 1 was synthesized by reacting methyl salicylate with bromoacetyl bromide. Under a N₂ atmosphere, bromoacetyl bromide (3.90 mL, 0.045 mol, 1.5 eq.) was added dropwise to a stirred suspension of methyl salicylate (5.00 g,

0.03 mol, 1.0 eq.) and triethylamine (5.20 mL, 0.0375 mol, 1.25 eq.) in THF (70 mL) at 0 °C. The resulting mixture was stirred for 10 min at this temperature. After the addition of H₂O, the mixture was extracted with CH₂Cl₂, the combined organic phase was dried over Na₂SO₄, and evaporated to dryness to give a crude product. The obtained residue was further purified by column chromatography (petrol ether/ethyl acetate (6:1, v/v)), afforded compound **1** as a yellowish oil (yield: 67%).

Finally, the monomer **1** was prepared from compound **1** via reacting with *N,N'*-ditosylhydrazine (TsNHNHTs) in the presence of DBU. The compound **1** and TsNHNHTs (10.21 g, 0.03 mol, 1.5 eq.) was dissolved in THF (100 mL). After cooling to 0 °C, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (9 mL, 0.06 mol, 3.0 eq.) was added dropwise to the mixture, and kept stirring for 10 min at 0 °C. Then the reaction solution was quenched by the addition of saturated aqueous NaHCO₃, and extracted with diethyl ether. The combined organic phase was then washed with brine, dried over Na₂SO₄, and evaporated to dryness to give a crude product. The obtained residue was further purified by column chromatography (petrol ether/ethyl acetate (10:1, v/v)), afforded monomer **1** as a yellowish oil (yield: 61%).

The chemical structure of compound **1** was characterized by ¹H NMR, ¹³C NMR, and FT-IR (Fig. S1-S3). All the protons of compound **1** could be clearly observed in the ¹H NMR spectrum (Fig. S1), and the integration area ratio of peak a (4.17 ppm) to peak f (3.87 ppm) was 2:3, suggestive of the successful obtainment of compound **1**. The product of monomer **1** was firstly analyzed via ¹H NMR spectrum (Fig. S4). Compared with the ¹H NMR of compound **1** (Fig. S1), the signal at 4.17 ppm (peak a in Fig. S1) disappeared completely, while a new signal at 5.03 (peak a in Fig. S4) ascribed to the methyne proton next to the diazo group was detected, indicating that the monomer **1** was synthesized successfully, which was further verified via ¹³C NMR, FT-IR, and mass spectra (Fig. S5-S7).

The detailed assignments of the ¹H NMR spectra for compound **1** and monomer **1** are shown as follows:

The compound **1**: ¹H NMR (600 MHz, CDCl₃): δ 8.05–7.13 (m, 4H, ArH), 4.17 (s, 2H,

BrCH₂), 3.87 (s, 3H, OCH₃).

The monomer **1**: ¹H NMR (600 MHz, CDCl₃): δ 8.01–7.16 (m, 4H, ArH), 5.03 (s, 1H, N₂CH), 3.88 (s, 3H, OCH₃).

3.2 Polymerization of monomer **1**

3.2.1 Helix-sense-selective polymerization (HSSP) of Monomer **1.** The chiral catalyst of allylPdCl/L^R was freshly prepared by the reaction between commercial π-allylPdCl and chiral phosphine ligands. A solution of commercial available π-allylPdCl (30.1 mg, 0.082 mmol) in THF (3 mL) was treated with the phosphine ligand (L^R) (47.4 mg, 0.080 mmol) at room temperature for 30 min. Then a solution of the as-prepared allylPdCl/L^R catalyst in THF (0.18 mL, 0.027 mol/L, 0.005 mmol) was added to a solution of monomer **1** (100 mg, 0.45 mmol) in THF (0.82 mL) at 25 °C. The concentrations of the monomer **1** and the catalyst were 0.45 mol/L and 0.005 mol/L, respectively. The initial feed ratio of monomer to catalyst was 90/1 ([**1**]₀/[Pd]₀ = 90). The reaction mixture was stirred at 25 °C, and a large amount of bubbles was released upon the addition of the allylPdCl/L^R catalyst. After the polymerization solution was stirred for 30 min at 25 °C, it was precipitated into a large amount of *n*-hexane. The precipitated solid was collected by centrifugation and dried in vacuum at room temperature overnight, afforded poly-**1**₉₀(R) as a yellow solid (yield: 72%). SEC: *M*_n = 9.4 kDa, *M*_w/*M*_n = 1.17. ¹H NMR (600 MHz, CDCl₃): δ 7.76–6.64 (br, 4H, ArH), 4.82–4.41 (br, 1H, CH of main chain), 3.72–3.01 (br, 3H, OCH₃).

3.2.2 Kinetic studies. A solution of the asprepared allylPdCl/L^R catalyst in THF (0.16 mL, 0.027 mol/L, 0.0045mmol) was added to the mixture of monomer **1** (100.0 mg, 0.45 mmol) and 1,4-dimethoxybenzene (22.0 mg, 0.16 mmol) in THF (0.84 mL) via a syringe ([**1**]₀ = 0.45 M, [**1**]₀/[Pd]₀ = 100). The polymerization solution was stirred at 25 °C and was followed by measuring SEC and high performance liquid chromatography (HPLC) of the aliquots taking out from the reaction solution at appropriate time intervals. The conversion of monomer **1** was calculated based on the peak area of unreacted monomer **1** relative to that of the internal standard

1,4-dimethoxybenzene on the basis of the linear calibration curve. The M_n and M_w/M_n were estimated by SEC and reported as equivalent to polystyrene standards.

3.2.3 Preparation of atactic poly- $\mathbf{1}_m$ by PdCl₂/pyridine. Under a dry N₂ atmosphere, a mixture of PdCl₂ (2.0 mg, 0.011 mmol), pyridine (0.047 mL, 0.58 mmol) and toluene (2.5 mL) in a Schlenk tube was stirred for 30 min at room temperature. Then a solution of monomer **1** (0.312 g, 1.42 mmol) in CH₂Cl₂ (1.5 mL) was added via a syringe. The resulting mixture was stirred at 55 °C for further 18 h. Then HCl/MeOH (1 N, 8 mL), CHCl₃ (25 mL) and water (25 mL) were added. The organic phase was dried over Na₂SO₄, and evaporated to dryness. The obtained viscous oil was purified by precipitation from 1 mL of CHCl₃ into 30 mL of n-hexane. Freeze-drying of the residue using benzene afforded poly-**1**_m as a yellow solid (yield: 54%).

3.3 Molecular Modeling and ECD Calculations of poly- $\mathbf{1}_{10}(R)$.⁶⁻⁸

Molecular modeling and molecular mechanics calculations (MM) were conducted with the COMPASS force field as implemented in the Materials Studio software (version 2019, Accelrys Co. Ltd.) operated using a server computer running under Windows 10. The polymer model of poly-**1**₁₀(*R*) was constructed using a Polymer Builder module in the MS Modeling software. The starting main-chain conformation of the poly-**1**₁₀ model was defined by the dihedral angle of the single bond from planarity (θ : C-C-C-C), which was set to -180° from 180° at 5° intervals in order to build all possible right-handed conformations. The structures were optimized using the geometry optimization of the Forcite module of MS with the COMPASS force field. Energy minimization was conducted until the root-mean-square (rms) values became less than 0.001 kcal/mol. The most stable right-handed helical structure was shown in Fig. S14a ($\theta = -125^\circ$).

The optimized right-handed helical structure of poly-**1**₁₀(*R*) was then further calculated using the density functional theory (DFT) method at the B3LYP-D3BJ/6-31G(d)/CPCM(THF) level in the Gaussian 16 program running under server computer, and the stimulation temperature was set at 298 K. The DFT

optimized right-handed helical structure of poly-**1**₁₀(*R*) was shown in Fig. S14b.

The UV-vis and ECD spectra for the right-handed helical poly-**1**₁₀(*R*) were calculated using the time-dependent DFT (TD-DFT) method with the B3LYP-D3BJ/6-31G(d)/CPCM(THF) level after DFT geometry optimization (Fig. S15). Ten singlet excited states of the polymer were calculated, including oscillator strength and rotatory strength. The corresponding UV-vis and ECD spectra were constructed from oscillator strength-wavelength data (for UV-vis) and rotatory strength wavelength data (for ECD) with a Gaussian function of 2685 cm⁻¹ width at half-height (from 100 nm to 600 nm) for all transitions centered at a given excitation wavelength.

Coordinates of the optimized geometry by DFT calculation:

C	-4.31034550	-3.27331609	0.82381238
C	-3.78028011	-4.15045908	-0.28297043
H	-5.37600253	-3.49989132	0.89431403
H	-3.86012136	-3.63074515	1.75374248
O	-3.09856826	-3.45041734	-1.23695986
O	-3.94967199	-5.34623827	-0.33034464
C	-2.60670201	-4.13928278	-2.33973186
C	-1.59629439	-5.07932667	-2.16823987
C	-3.08598122	-3.79754158	-3.60941946
C	-1.07407923	-5.72432758	-3.28768310
H	-1.23277876	-5.28429016	-1.16860468
C	-2.53623778	-4.45142431	-4.72243633
C	-4.12880540	-2.74473877	-3.78387816
C	-1.54890243	-5.41753543	-4.56484050
H	-0.29785549	-6.47256437	-3.16480075
H	-2.89394192	-4.18936449	-5.71048843
O	-4.99943097	-2.47313948	-2.97973029
O	-3.96459449	-2.12766385	-4.97273933
H	-1.14017743	-5.92032346	-5.43506686
C	-4.89409898	-1.08837128	-5.34294097
H	-5.23022240	-1.31201151	-6.35688797
H	-5.73276113	-1.06170690	-4.64897687
H	-4.35496812	-0.14097434	-5.32152199
C	-4.11301829	-1.75190407	0.68158701
C	-4.89591104	-0.99524943	1.75456093
H	-4.55066922	-1.46248543	-0.28046576

O	-6.03226789	-1.67530762	2.11118541
O	-4.59976092	0.06792468	2.23406396
C	-6.85196546	-1.08424462	3.06882538
C	-6.94985780	-1.72072018	4.29928712
C	-7.55189820	0.10201972	2.80571942
C	-7.77160381	-1.18078039	5.28969614
H	-6.37668158	-2.62591343	4.46801064
C	-8.35000624	0.64516281	3.82008747
C	-7.47216326	0.74329144	1.46546283
C	-8.46896217	0.00491826	5.05209893
H	-7.85576247	-1.68277288	6.24845473
H	-8.88449447	1.56834891	3.62630288
O	-7.36211524	0.13136027	0.41902184
O	-7.55129849	2.08128966	1.54188643
H	-9.10213761	0.43095278	5.82361764
C	-7.41438022	2.78057636	0.28556179
H	-7.50311388	3.83740387	0.53428238
H	-6.43972537	2.55881840	-0.15168102
H	-8.20398438	2.47919260	-0.40493798
C	-2.61224592	-1.35287563	0.68580307
C	-2.08335190	-1.48044056	2.10571059
H	-2.09036709	-2.20075230	0.24106256
O	-0.71989995	-1.38006677	2.16642290
O	-2.73274915	-1.83261411	3.06207950
C	-0.11080521	-1.95667637	3.27933238
C	0.50401030	-1.09524243	4.17457431
C	-0.09659000	-3.34982935	3.47229762
C	1.12853017	-1.60340782	5.31233134
H	0.47677807	-0.03347032	3.96972410
C	0.51953177	-3.83861290	4.63537259
C	-0.69164793	-4.28821389	2.48125020
C	1.11459291	-2.97745260	5.55330559
H	1.61227108	-0.92200958	6.00486942
H	0.53467662	-4.90793392	4.80357560
O	-1.14873549	-3.97078986	1.39322987
O	-0.66497058	-5.55940251	2.90633578
H	1.57342511	-3.38079949	6.44976667
C	-1.19240747	-6.53742208	1.98567036
H	-1.21807930	-7.47142199	2.54521455
H	-2.19175659	-6.25119222	1.65281823
H	-0.52831777	-6.62611367	1.12368013
C	-2.21772949	-0.16522461	-0.28526769
C	-3.42013478	0.68630545	-0.71475078
H	-1.96318156	-0.67807177	-1.21011140

O	-3.66656859	0.41671481	-2.04347825
O	-4.10136287	1.42545537	-0.05557240
C	-4.76083886	1.04782205	-2.63154636
C	-6.04117818	0.63042766	-2.28925039
C	-4.56003560	2.06850756	-3.56728627
C	-7.14696722	1.23926611	-2.87848542
H	-6.17152617	-0.14941270	-1.55379461
C	-5.68477926	2.69349632	-4.12530538
C	-3.22852889	2.51017884	-4.08082294
C	-6.97172219	2.27996037	-3.79253248
H	-8.14318430	0.90688420	-2.60491688
H	-5.52800071	3.49529619	-4.83903844
O	-2.93240430	3.67979301	-4.25200590
O	-2.45927980	1.47876466	-4.44704150
H	-7.83081885	2.76397703	-4.24610085
C	-1.20252890	1.82666808	-5.07182832
H	-0.75659415	0.87684856	-5.35673164
H	-1.39081643	2.45391896	-5.94653477
H	-0.56267946	2.34169430	-4.35705627
C	-0.96054368	0.66336995	0.13920987
C	-1.05642381	2.13690619	-0.23509418
H	-0.88844348	0.68329016	1.22510668
O	-0.19780621	2.85666072	0.55630832
O	-1.79937941	2.65347432	-1.02949105
C	-0.41491055	4.21955843	0.69283063
C	0.60029654	5.07952210	0.30426203
C	-1.60102045	4.69808179	1.27194105
C	0.42805576	6.45537632	0.44521802
H	1.51943793	4.66045290	-0.07996272
C	-1.76557572	6.08512735	1.38218538
C	-2.59687349	3.75826057	1.86045129
C	-0.76396688	6.96018649	0.96597697
H	1.22787795	7.12508035	0.14679088
H	-2.67866281	6.46678501	1.82355649
O	-2.34599769	2.62394741	2.22637438
O	-3.80945694	4.31921428	1.99358426
H	-0.90626163	8.03115398	1.06850437
C	-4.80469967	3.47197385	2.61061334
H	-5.74035112	4.02277553	2.53140968
H	-4.85729987	2.51701044	2.09088922
H	-4.54957868	3.30409416	3.66073789
C	0.33087256	-0.05789597	-0.37686859
C	0.23587695	-0.24858681	-1.87877110
H	0.31010404	-1.04856208	0.07050914

O	0.69905242	-1.48128327	-2.25930020
O	-0.24231239	0.54724764	-2.64278929
C	0.71611608	-1.72795157	-3.63494918
C	-0.47745469	-1.76187743	-4.34626852
C	1.94800669	-1.90688258	-4.27398402
C	-0.45261369	-1.99094102	-5.72056307
H	-1.41401530	-1.58813194	-3.83493883
C	1.95709278	-2.11656792	-5.65945024
C	3.22280271	-1.93011965	-3.49779266
C	0.76529658	-2.16657645	-6.38002773
H	-1.39016851	-2.02220912	-6.26556706
H	2.90926910	-2.24799056	-6.16193134
O	3.38299528	-2.55035520	-2.46633718
O	4.18554207	-1.21833721	-4.10727108
H	0.78789360	-2.33974632	-7.45126806
C	5.44659314	-1.15126409	-3.40567217
H	6.10661020	-0.57657584	-4.05449072
H	5.31446832	-0.64797494	-2.44806945
H	5.84825740	-2.15444402	-3.24355652
C	1.66101118	0.64231309	0.07362873
C	2.47365394	1.24468263	-1.07313169
H	1.38293711	1.48944028	0.69321856
O	2.89754686	2.48712568	-0.68843551
O	2.72056342	0.74542742	-2.14056796
C	3.65212265	3.29884777	-1.53525771
C	5.02953497	3.33910766	-1.34323561
C	3.01557431	4.19376281	-2.41144571
C	5.79176281	4.27832123	-2.03902040
H	5.49136889	2.64811410	-0.65114826
C	3.80195163	5.13164206	-3.09672293
C	1.54050624	4.16039603	-2.60523742
C	5.18116125	5.17377184	-2.91887746
H	6.86403948	4.31590175	-1.87615715
H	3.31228250	5.82732807	-3.76782759
O	0.84680844	3.17639238	-2.43516143
O	1.05192450	5.35731109	-2.97332362
H	5.77493836	5.90620723	-3.45596533
C	-0.38340663	5.41032550	-3.13638682
H	-0.61149715	6.46256329	-3.30278815
H	-0.69836055	4.80539032	-3.98703054
H	-0.87505245	5.03873788	-2.23638374
C	2.52194446	-0.21734234	1.05842836
C	2.88158643	-1.63816576	0.63975707
H	1.86102005	-0.35524492	1.91541850

O	1.79696765	-2.45661411	0.75454058
O	3.96836833	-2.04547858	0.31922431
C	2.00884451	-3.82372307	0.60914929
C	1.53288635	-4.41520094	-0.55270286
C	2.60864611	-4.57975794	1.63137519
C	1.64220827	-5.79442441	-0.71109035
H	1.09986633	-3.78123967	-1.31521664
C	2.68718756	-5.97193597	1.45523675
C	3.19918430	-3.94697399	2.84215828
C	2.20996877	-6.57643371	0.29760463
H	1.29051243	-6.25892228	-1.62562652
H	3.14158997	-6.56929892	2.23517672
O	3.32726435	-2.74906179	3.02974917
O	3.62729287	-4.86498869	3.72895518
H	2.28942128	-7.65190244	0.17739638
C	4.33661062	-4.34909193	4.86967041
H	4.52556956	-5.21231182	5.50638673
H	5.27919983	-3.89520539	4.55230102
H	3.73277088	-3.60584134	5.39045997
C	3.77297970	0.56433559	1.57528602
C	5.00822582	0.16211707	0.78593202
H	3.62783664	1.61770014	1.33726262
O	5.95263550	-0.44069642	1.55921296
O	5.14163338	0.39133171	-0.39389498
C	6.87777333	-1.30857292	0.99070494
C	6.85849376	-2.59305930	1.52938870
C	7.75488054	-0.97011299	-0.04753791
C	7.72825102	-3.56419793	1.04375679
H	6.13162790	-2.80900678	2.30378940
C	8.60590842	-1.97332952	-0.54209181
C	7.85150773	0.40775048	-0.60579644
C	8.60401910	-3.25410486	-0.00001566
H	7.70978729	-4.56328943	1.46791338
H	9.27972997	-1.72503364	-1.35377390
O	7.76511901	1.43911810	0.03347132
O	8.10624307	0.36161177	-1.92840304
H	9.27978596	-4.00767676	-0.39146527
C	8.26512055	1.62562928	-2.59462093
H	8.68903751	1.39101700	-3.57055024
H	7.29106721	2.10424640	-2.71117355
H	8.93253498	2.27855493	-2.02875385
H	3.75626900	-0.56794582	3.44334692
C	3.92518890	0.45697209	3.09784428
C	3.02416296	1.38501679	3.88016837

H	4.93940239	0.72249615	3.40319398
O	1.97678575	1.87017690	3.12866441
O	3.16571965	1.66293762	5.04596923
C	1.32417433	3.01189793	3.59340548
C	0.09472451	2.87175601	4.21911845
C	1.86740370	4.28056680	3.32856768
C	-0.61115111	4.00737336	4.61346006
H	-0.31838059	1.88326566	4.37493171
C	1.13729817	5.40988300	3.72610170
C	3.16767285	4.43391475	2.62368524
C	-0.08802810	5.27725773	4.37126698
H	-1.57727054	3.89378731	5.09434764
H	1.53890742	6.39164190	3.51091629
O	4.03333668	3.57736556	2.53288475
O	3.29557828	5.65480983	2.07622420
H	-0.64087604	6.16266547	4.66643646
C	4.52887252	5.90389594	1.37501952
H	4.45892965	6.93443239	1.02949833
H	5.38093187	5.77787752	2.04673203
H	4.62638553	5.22069040	0.52983922

3.4 Postpolymerization modification of helical polycarbenes.

3.4.1 Postpolymerization modification of poly-1₉₀(*R*) with *n*-butylamine (amine

a). As a typical procedure, postpolymerization modification of poly-1₉₀(*R*) with amine **a** is described as follows. Under a nitrogen atmosphere, a THF (6.0 mL) solution of poly-1₉₀(*R*) ($M_n = 9.4$ kDa, 50.5 mg, 0.25 mmol of methyl salicylate group), amine **a** (0.073 mL, 0.75 mmol) and triethylamine (0.10 mL, 0.75 mmol) were placed in a Schlenk tube. After stirring at 55 °C for 24 h, CH₂Cl₂ and 1 N HCl aqueous solution were added to the mixture. The organic phase was separated using a separatory funnel, and the aqueous phase was extracted with diethyl ether. The combined organic phase was washed with water and brine, dried over Na₂SO₄, filtrated, and concentrated under reduced pressure to afford a crude product. The obtained residue was further purified by column chromatography (eluent: CHCl₃), yielded a light brown product (yield: 86%).

3.4.2 Postpolymerization modification of poly-1₉₀(*R*) with *N*-(2-aminoethyl)-5-(dimethylamino)-1-naphthalene sulfonamide (amine **b).** As a typical procedure,

postpolymerization modification of poly-**1**₉₀(*R*) with amine **b** is described as follows. Under a nitrogen atmosphere, a THF (6.0 mL) solution of poly-**1**₉₀(*R*) ($M_n = 9.4$ kDa, 50.5 mg, 0.25 mmol of methyl salicylate group), amine **b** (0.22 g, 0.75 mmol) and triethylamine (0.10 mL, 0.75 mmol) were placed in a Schlenk tube. After stirring at 55 °C for 24 h, CH₂Cl₂ and 1N HCl aqueous solution were added to the mixture. The organic phase was separated using a separatory funnel, and the aqueous phase was extracted with diethyl ether. The combined organic phase was washed with water and brine, dried over Na₂SO₄, filtrated, and concentrated under reduced pressure to afford a crude product. The obtained residue was further purified by column chromatography (eluent: CHCl₃), affording a light brown product (yield: 94%).

The M_n of the product after postpolymerization modification of poly-**1**₉₀(*R*) with amine **b** was 10.8 kDa (Fig. S24), which was a little higher than that of poly-**1**₉₀(*R*) precursor. The ¹H NMR spectrum of the product was depicted in Fig. S25, and the main-chain methyne proton of poly-**1**₉₀(*R*) at 4.68 ppm wholly disappeared, and new signals in the range of 2.35 ~ 4.36 ppm resulted from the main-chain methyne proton, methylene protons next to amide, and methyl protons of N(CH₃)₂ appeared, suggesting the efficient postpolymerization modification of poly-**1**₉₀(*R*) with amine **b**. Moreover, the chemical structure of the product was further explored by FT-IR measurement (Fig. S26). In comparison with the FT-IR of poly-**1**₉₀(*R*) precursor, new absorption at 1140 cm⁻¹ and 1308 cm⁻¹ corresponding to O=S=O vibration, as well as broad absorption ~3270 cm⁻¹ corresponding to N-H vibration could be clearly observed after postpolymerization modification. The optical property of the product was explored via UV-vis and photoluminescence (PL) spectra. The typical absorption peaks of dansyl group at 256 nm and 357 nm were observed in the UV-vis spectrum (Fig. S27). The PL spectrum of the product with excitation at 350 nm was illustrated in Fig. S28, and characteristic dansyl emission band at 503 nm appeared. The UV-vis and PL results further verified the successful obtainment of fluorescent polycarbene with dansyl substituents.

3.4.3 Postpolymerization modification of poly-**1**₉₀(*R*) with monomethoxy PEG

amine (amine c). As a typical procedure, postpolymerization modification of poly-**1**₉₀(*R*) with amine **c** ($M_n = 2.0$ kDa) is described as follows. Under a nitrogen atmosphere, a THF (6.0 mL) solution of poly-**1**₉₀(*R*) ($M_n = 9.4$ kDa, 50.5 mg, 0.25 mmol of methyl salicylate group), amine **c** ($M_n = 2.0$ kDa, 1.54 g, 0.75 mmol) and triethylamine (0.10 mL, 0.75 mmol) were placed in a Schlenk tube. After stirring at 55 °C for 24 h, dialysis purification (buffer solution: deionized water, cut-off: 8-14 kDa), obtained as a light yellow product after freeze-drying (yield: 81%).

The M_n of the product after postpolymerization modification of poly-**1**₉₀(*R*) with amine **c** was 101.6 kDa (Fig. S29), which was much higher than that of poly-**1**₉₀(*R*) precursor, indicating the successful obtainment of the polymer brush. The ¹H NMR spectrum of the polymer brush was shown in Fig. S30. It can be seen that the signals at 4.68 ppm and 6.64 ~ 7.76 ppm correspondingly ascribed to the main-chain methyne proton and phenyl protons of poly-**1**₉₀(*R*) disappeared, whereas new signals at 3.63 ppm and 3.36 ppm resulted from the methyne proton of the backbone, and methylene and methyl protons of PEG side chains appeared, suggesting the success of the preparation of the polymer brush, which was further confirmed via FT-IR measurement (Fig. S31).

Table S1 Results for the preparation of polycarbenes with Pd(II) complexes as catalysts.^a

entry	Polymers ^b	M_n^c (kDa)	M_w/M_n^c	yield ^d (%)	hse(%) ^e
1	poly- 1 ₃₀ (<i>R</i>)	4.8	1.20	61	48
2	poly- 1 ₆₀ (<i>R</i>)	7.9	1.19	65	77
3	poly- 1 ₉₀ (<i>R</i>)	9.4	1.17	72	86
4	poly- 1 ₁₀₀ (<i>R</i>)	10.1	1.19	78	89
5	poly- 1 ₁₂₀ (<i>R</i>)	11.2	1.18	63	94
6	poly- 1 ₁₅₀ (<i>R</i>)	13.1	1.21	71	99
7	poly- 1 ₁₈₀ (<i>R</i>)	14.9	1.20	68	100
8	poly- 1 ₃₀ (<i>S</i>)	4.7	1.21	63	51
9	poly- 1 ₆₀ (<i>S</i>)	8.1	1.19	68	79
10	poly- 1 ₉₀ (<i>S</i>)	9.5	1.18	73	90
11	poly- 1 ₁₀₀ (<i>S</i>)	10.3	1.18	74	93
12	poly- 1 ₁₂₀ (<i>S</i>)	11.6	1.19	65	98
13	poly- 1 ₁₅₀ (<i>S</i>)	12.9	1.20	68	100
14	poly- 1 ₁₈₀ (<i>S</i>)	14.8	1.21	72	100

^aThe polymers were prepared according to Scheme 1. ^bThe initial feed ratio of monomer to catalyst. ^cThe M_n and M_w/M_n values were calculated via SEC using polystyrene standards. ^dIsolated yields. ^eThe helix-sense excess (hse) of each sample was estimated by comparison of the g_{220} value of each sample with the maximum g_{220} value.

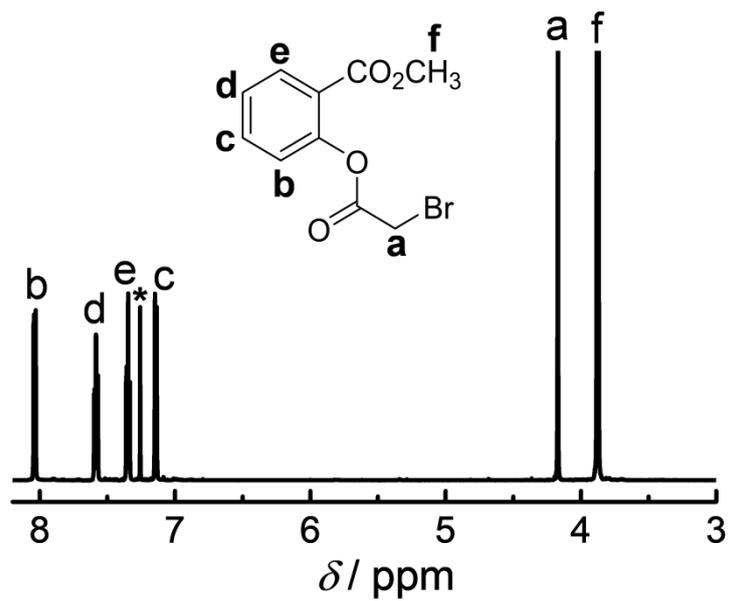


Fig. S1 ^1H NMR spectrum of the compound 1. (CDCl_3)

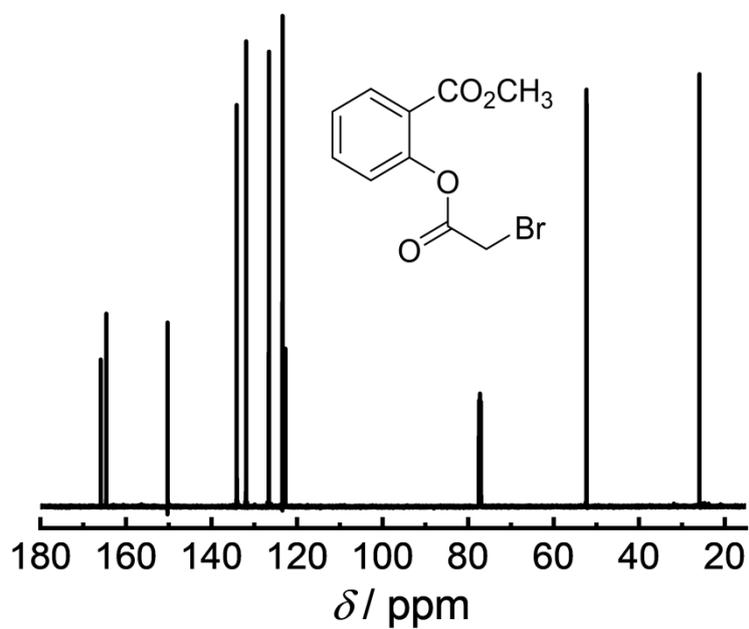


Fig. S2 ^{13}C NMR spectrum of the compound 1. (CDCl_3)

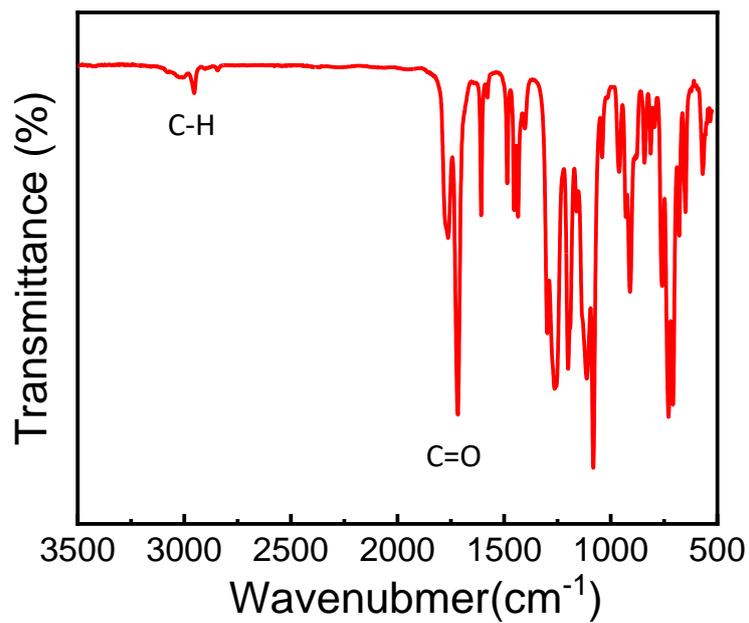


Fig. S3 FT-IR spectrum of the compound 1.

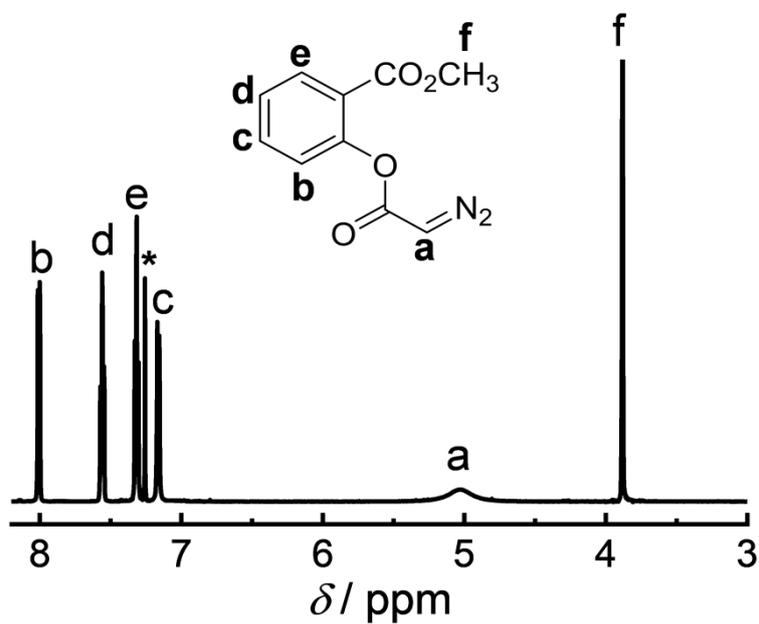


Fig. S4 ¹H NMR spectrum of the monomer 1. (CDCl₃)

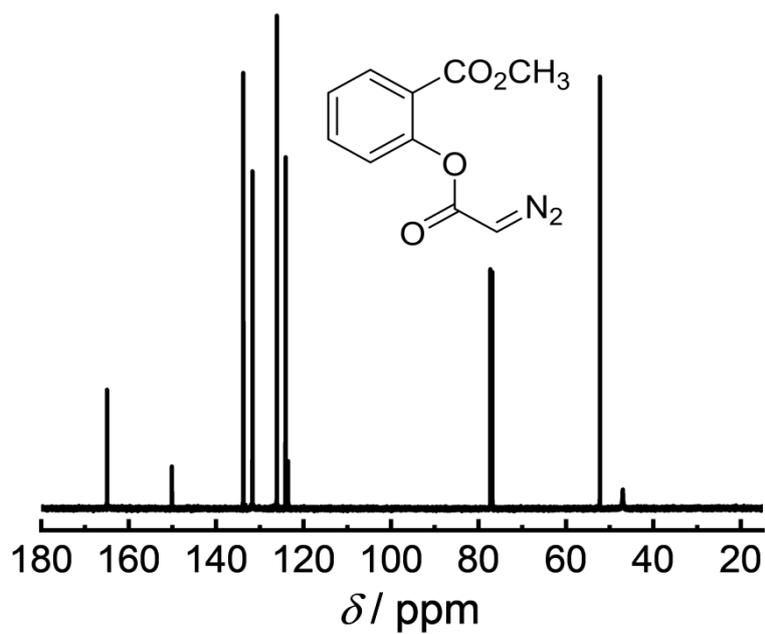


Fig. S5 ^{13}C NMR spectrum of the monomer **1**. (CDCl_3)

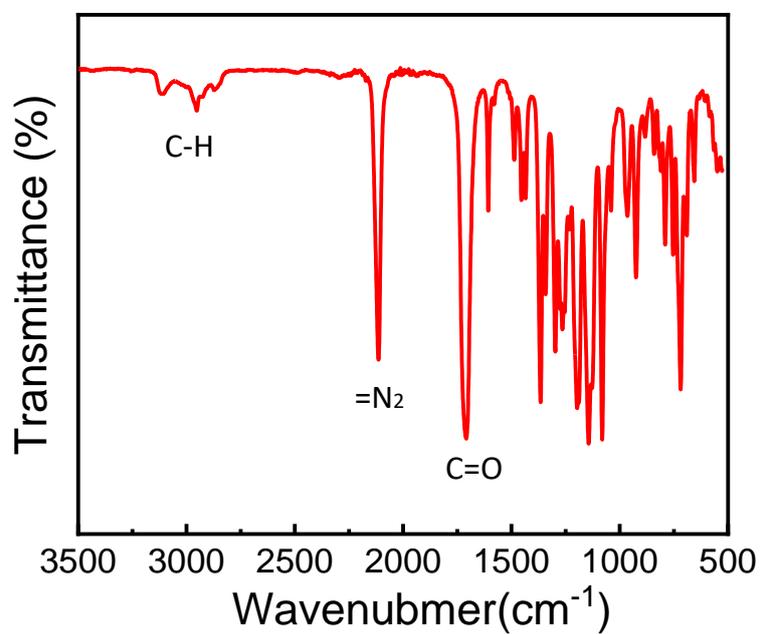


Fig. S6 FT-IR spectrum of the monomer **1**.

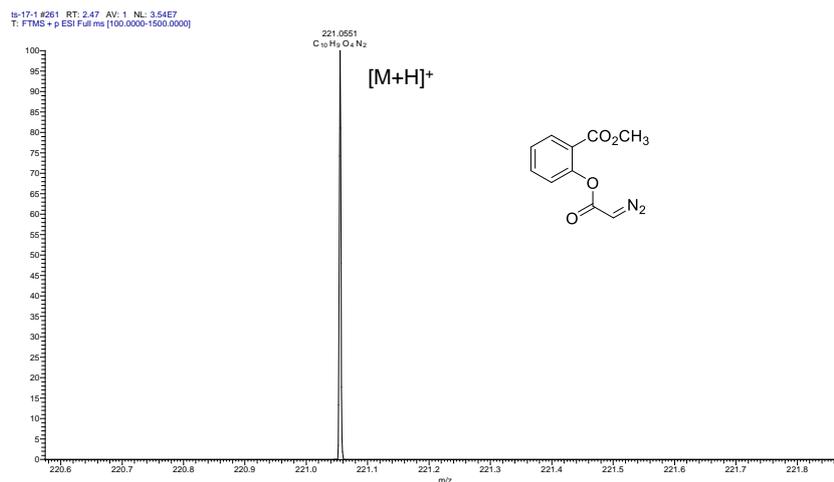


Fig. S7 HRMS(ESI-FT) spectrum of the monomer **1**.

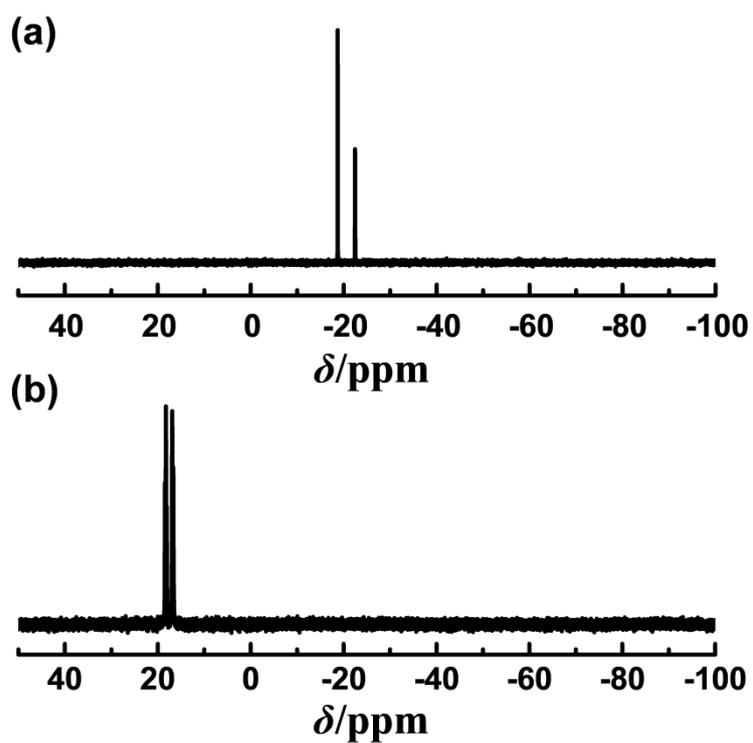


Fig. S8 ³¹P NMR spectra of (a) the chiral L^R ligand and (b) the chiral Pd(II) complex.
(THF- d_8)

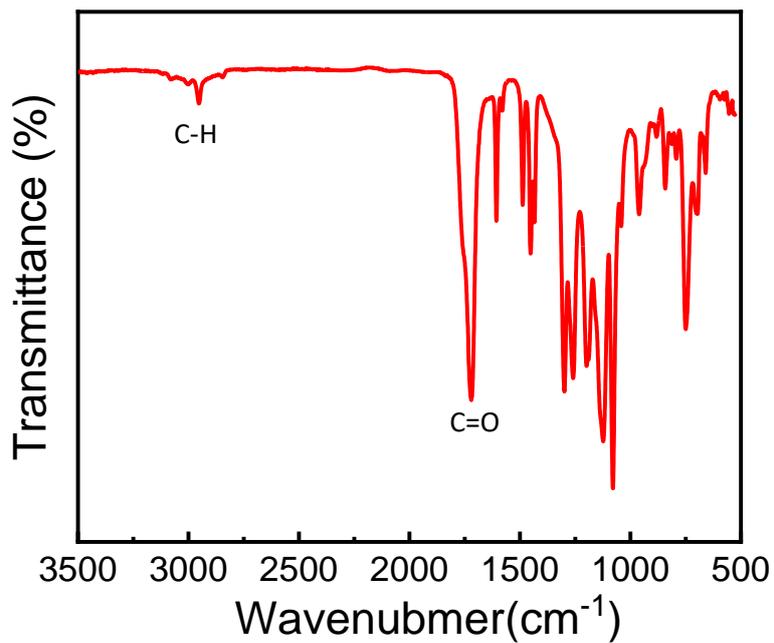


Fig. S9 FT-IR spectrum of poly-190(R).

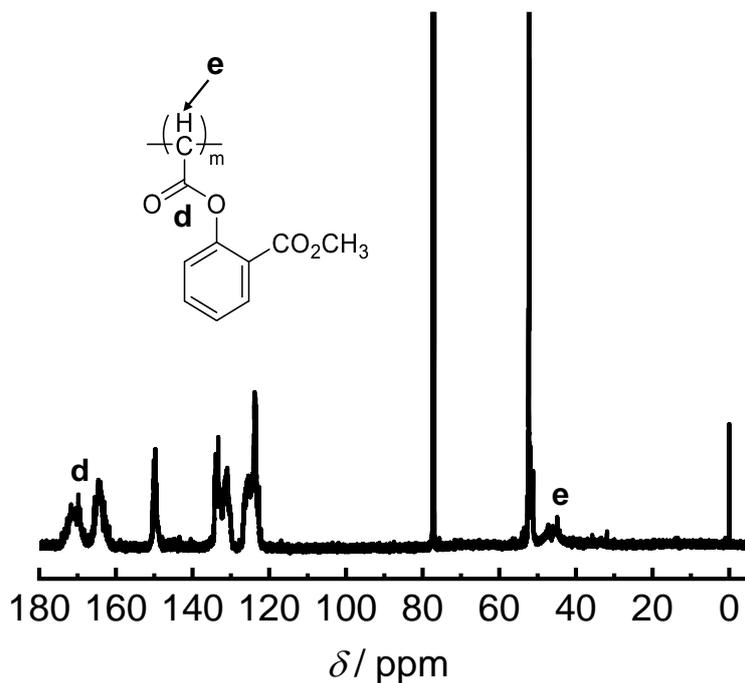


Fig. S10 ^{13}C NMR spectrum of atactic polycarbene prepared by the polymerization of monomer **1** with $\text{PdCl}_2/\text{pyridine}$ as the catalyst. (CDCl_3)

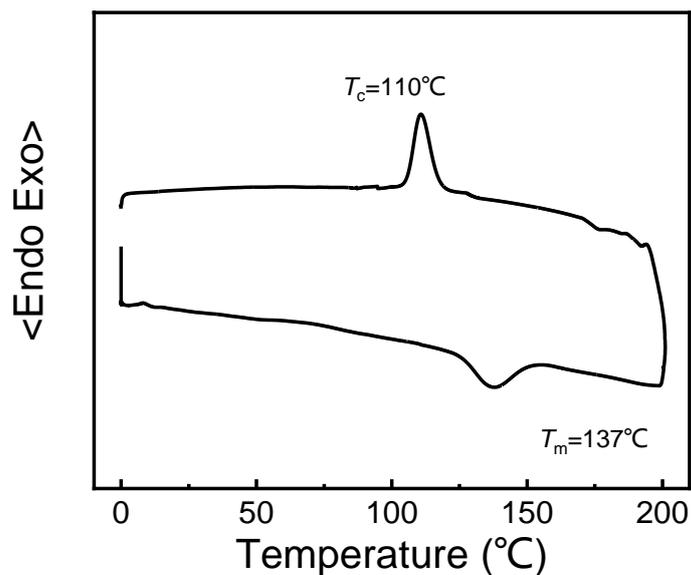


Fig. S11 DSC curves of poly-190(R) in the cooling run and second heating run.

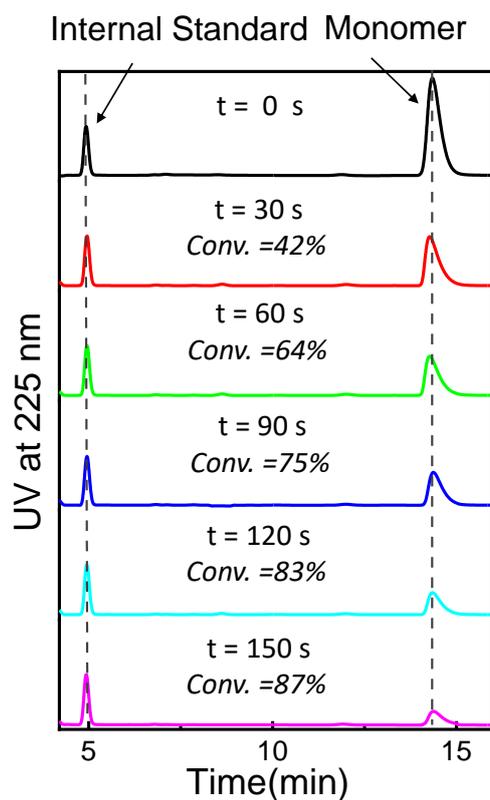


Fig. S12 Time-dependent HPLC curves for the polymerization of monomer 1 with the presence of 1,4-dimethoxybenzene as internal standard. HPLC conditions: column: OD-H; eluent: *n*-hexane/isopropanol = 9/1 (v/v); eluent rate: 0.50 mL/min.

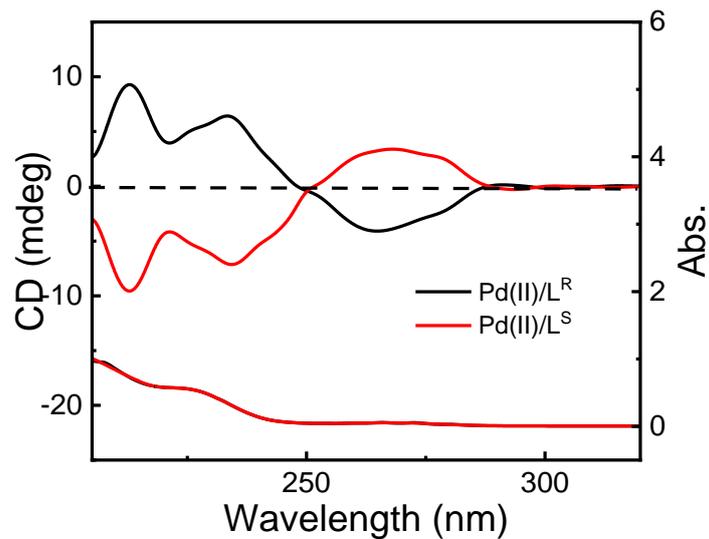


Fig. S13 CD and UV-vis spectra of Pd(II)/L^R and Pd(II)/L^S recorded in THF at 25 °C
(c = 0.2 mg/mL).

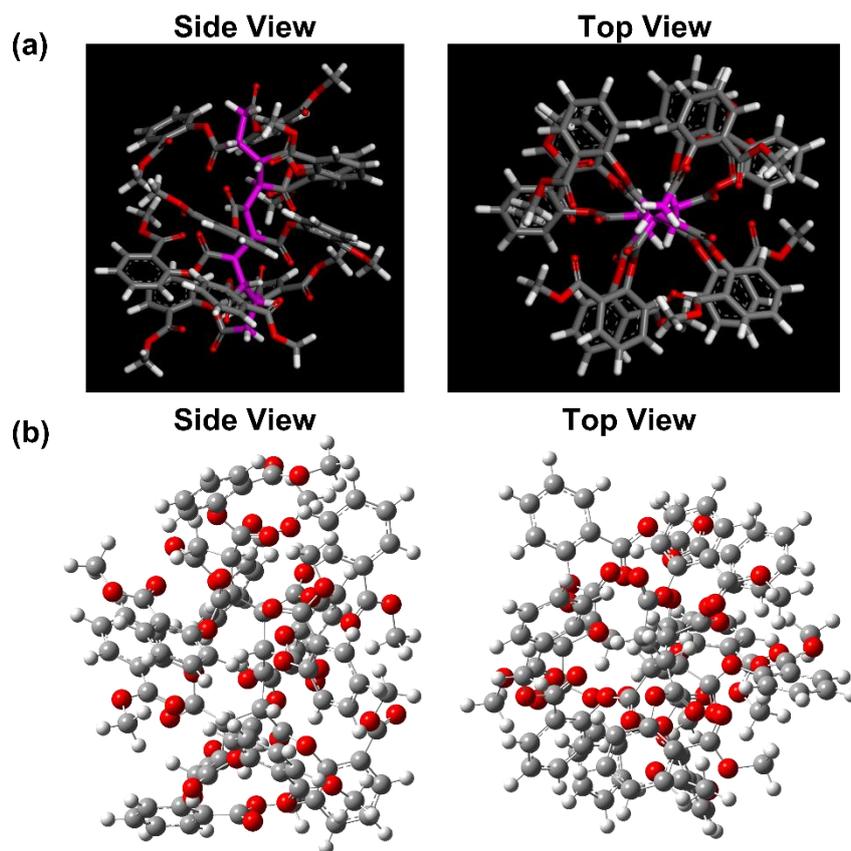


Fig. S14 (a) The most stable optimal right-handed helical structure of poly-1₁₀(R) by COMPASS force field. (b) Optimal structure of poly-1₁₀(R) by DFT calculation at B3LYP-D3BJ/6-31G(d)/CPCM(THF) level at 298 K.

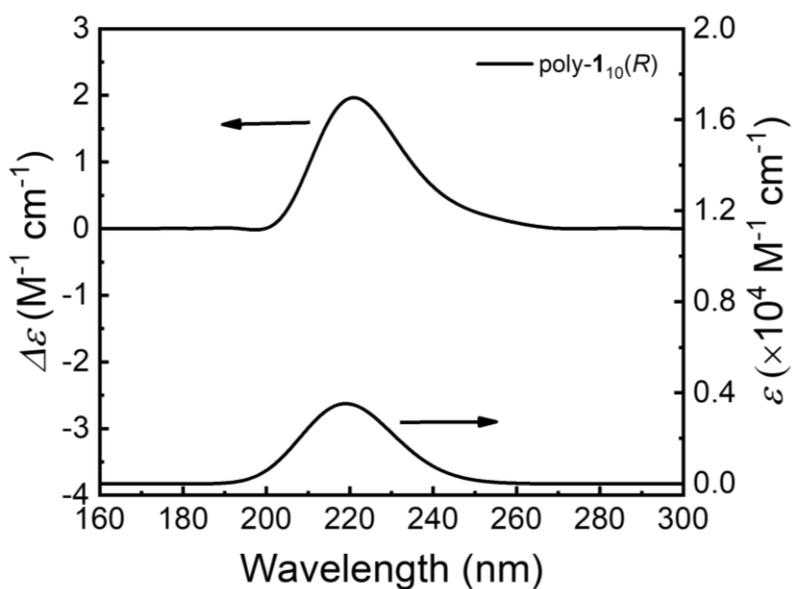


Fig. S15 TD-DFT Calculated ECD (top) and absorption (bottom) spectra of poly-**1**₁₀(*R*) at B3LYP-D3BJ/6-31G(d)/CPCM(THF) level at 298 K.

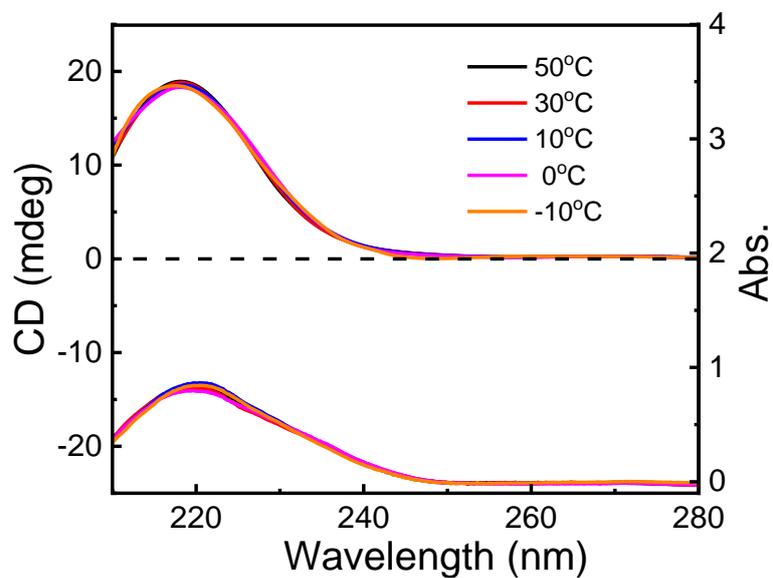


Fig. S16 CD and UV-vis spectra of poly-**1**₁₅₀(*R*) in THF at different temperatures.

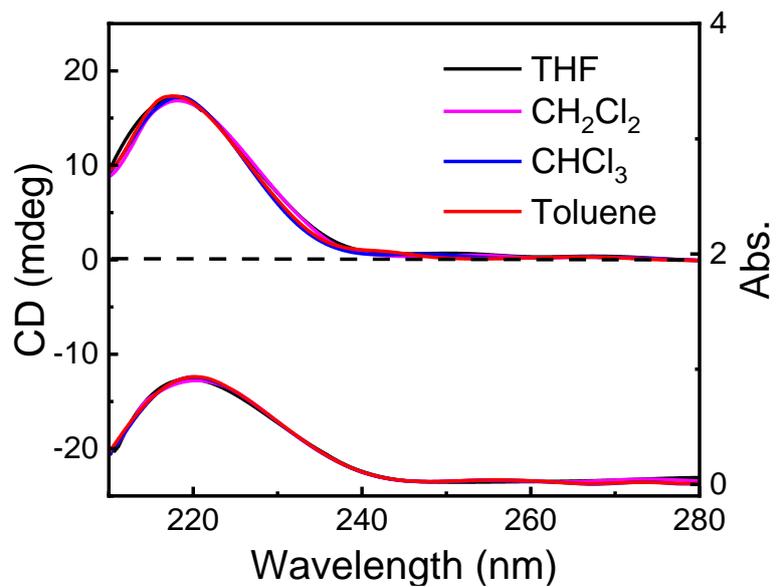


Fig. S17 CD and UV-vis spectra of poly-1₁₅₀(R) in different solvents at 25°C.

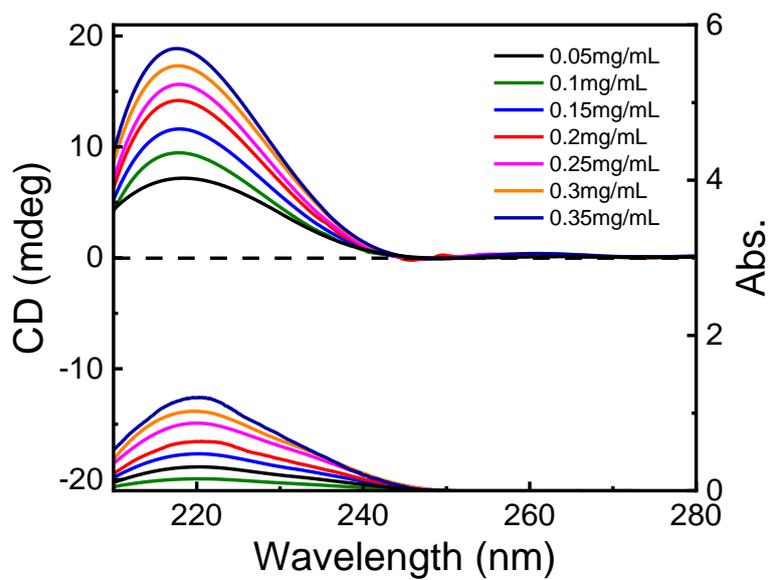


Fig. S18 CD and UV-vis spectra of poly-1₁₅₀(R) in THF at different concentrations.

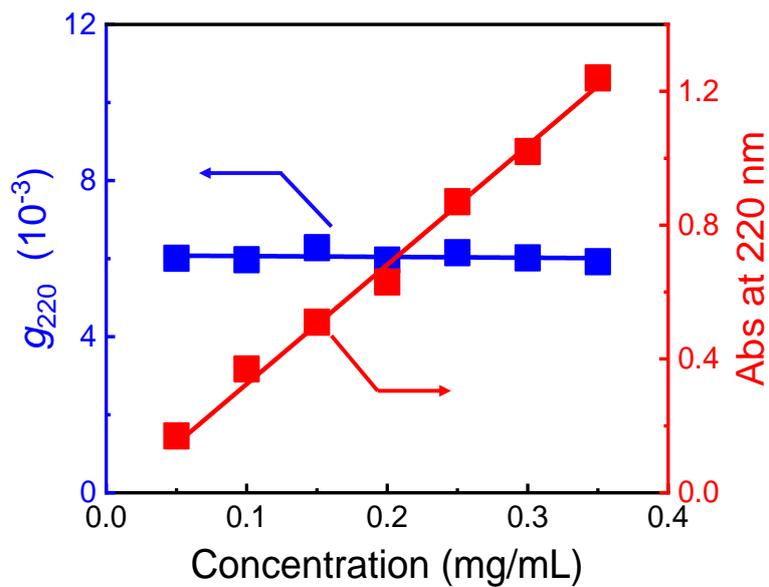


Fig. S19 Plots of CD and g_{220} values of poly-1₁₅₀(R) at different concentrations.

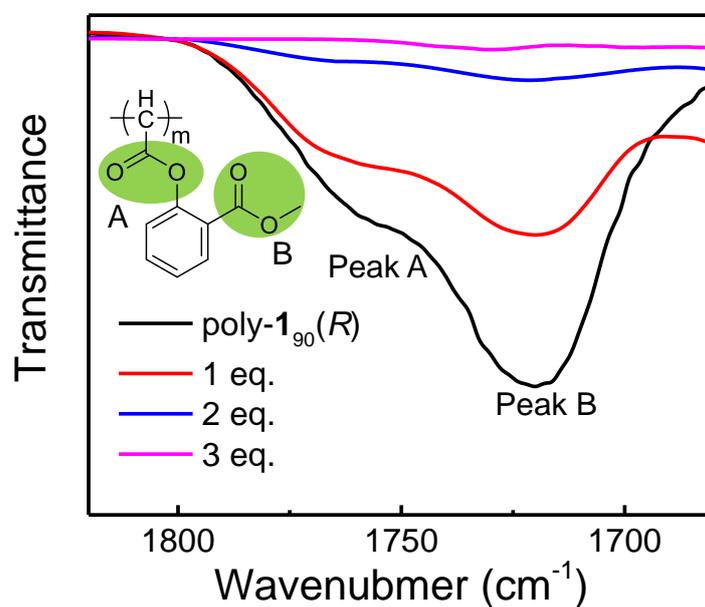


Fig. S20 FT-IR spectra for the postpolymerization modification of poly-1₉₀(R) before and after aminolysis with 1 eq., 2 eq., and 3 eq. of amine **a**.

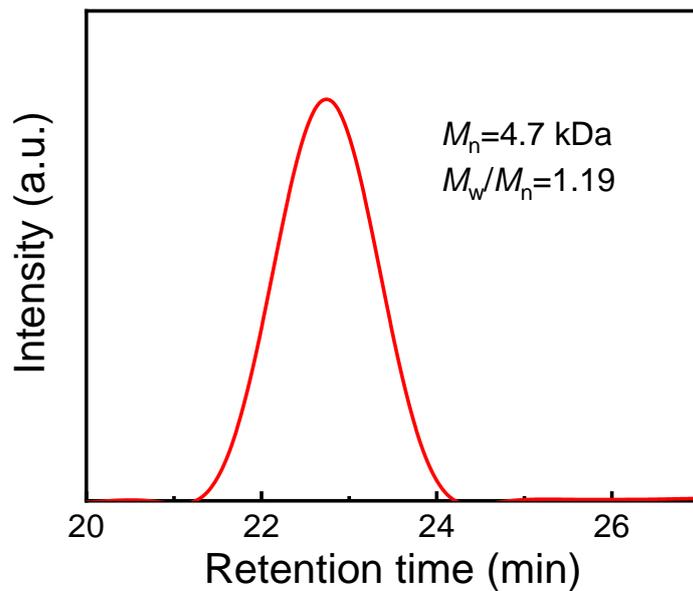


Fig. S21 SEC trace of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **a**. SEC condition: eluent = THF, temperature = 40 °C.

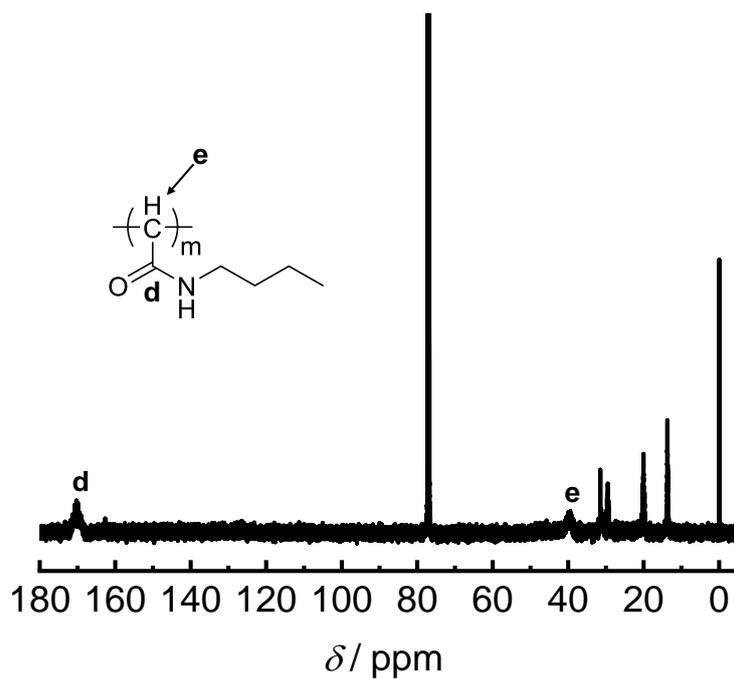


Fig. S22 ¹³C NMR spectrum of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **a**. (CDCl₃)

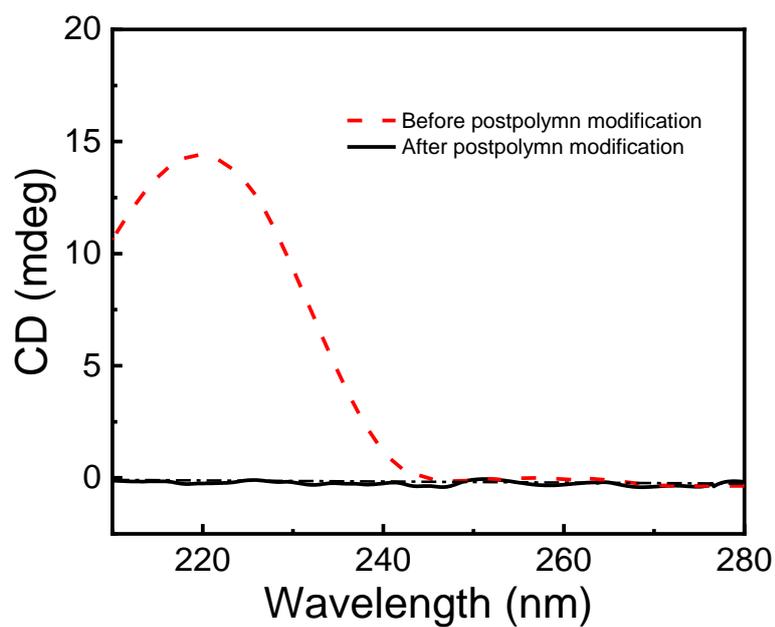


Fig. S23 CD spectra of poly-190(*R*) (a) before and (b) after postpolymerization modification with *n*-butylamine measured in THF solution at room temperature.

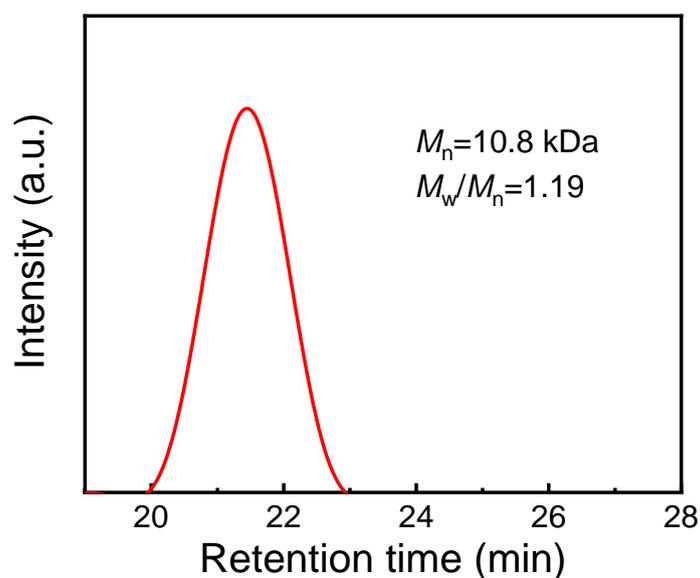


Fig. S24 SEC trace of the product of postpolymerization modification of poly-190(*R*) with amine **b**. SEC condition: eluent = THF, temperature = 40 °C.

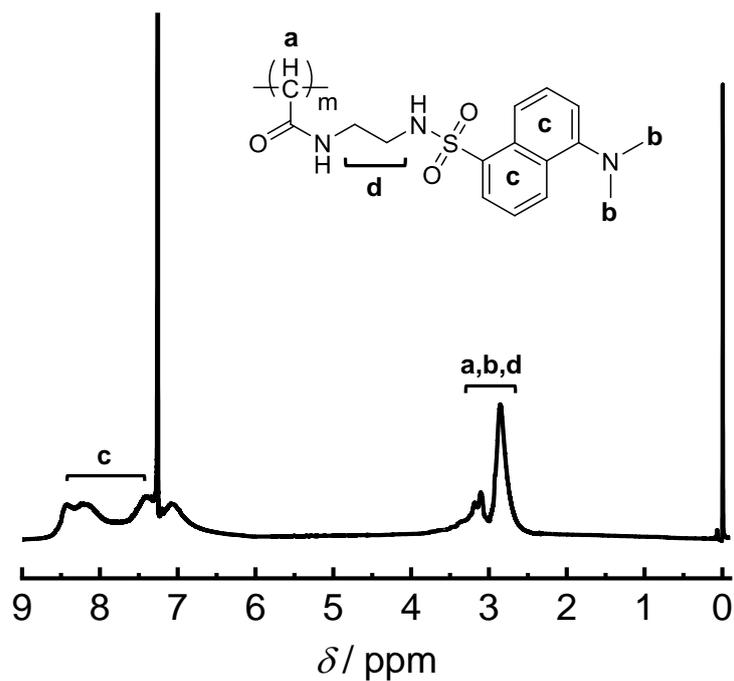


Fig. S25 ¹H NMR spectrum of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **b**. (CDCl₃)

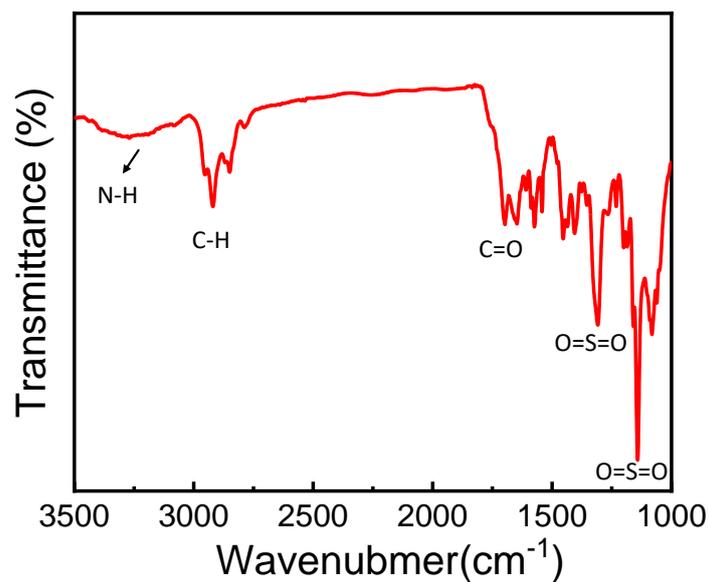


Fig. S26 FT-IR spectrum of the product of the postpolymerization modification of poly-**1**₉₀(*R*) with amine **b**.

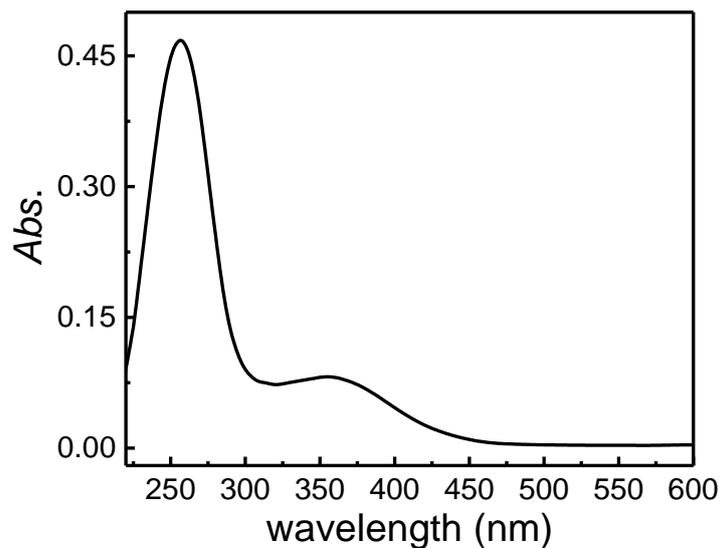


Fig. S27 UV-vis absorption spectrum of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **b** measured in THF at 25 °C.

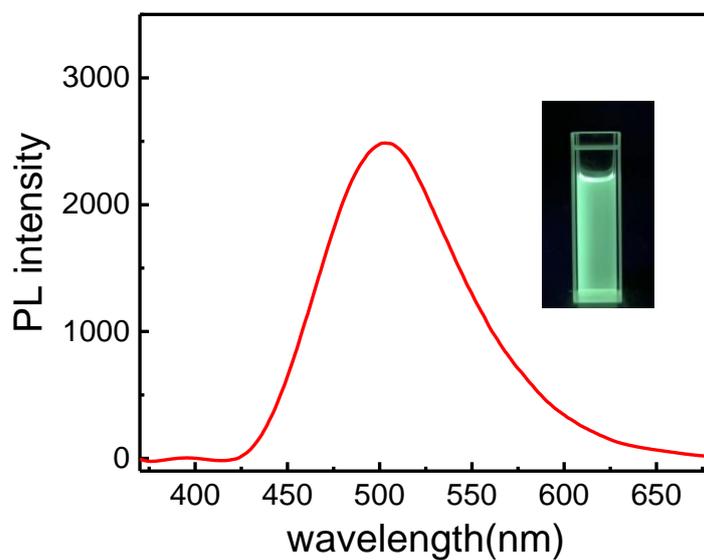


Fig. S28 PL spectrum of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **b** excited at 350 nm in THF at 25 °C (inset: photographs of the product under UV light at 365 nm).

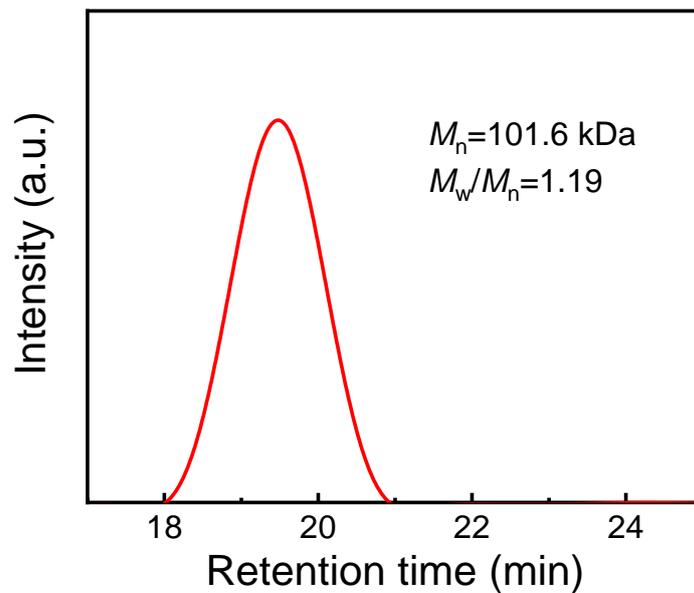


Fig. S29 SEC trace of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **c**. SEC condition: eluent = THF, temperature = 40 °C.

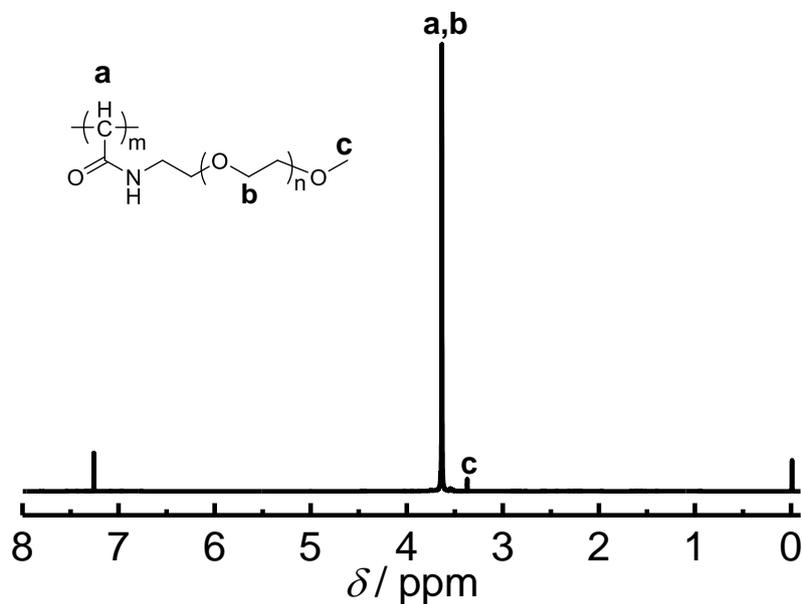


Fig. S30 ¹H NMR spectrum of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **c**. (CDCl₃)

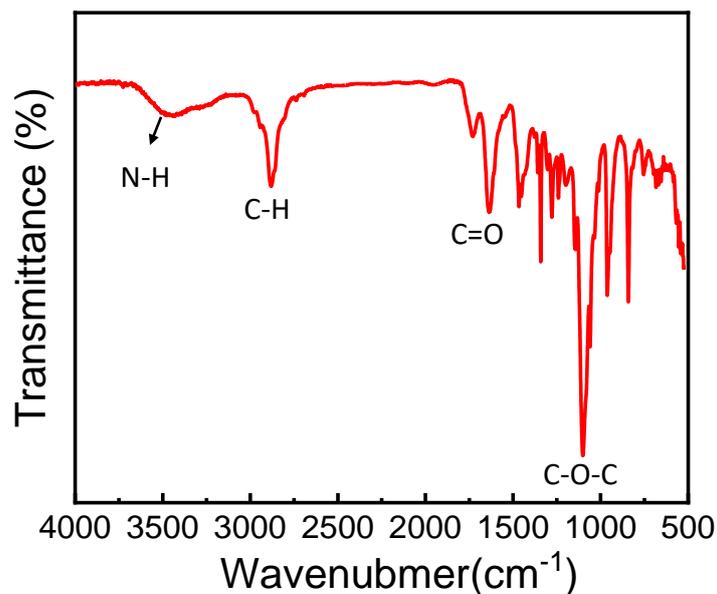


Fig. S31 FT-IR spectrum of the product of postpolymerization modification of poly-**1**₉₀(*R*) with amine **c**.

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