Supporting Information

Monomer-Induced Switch of Stereoselectivity and Limitation of Chain Growth in Polymerization of Amine-containing Para-substituted Phenylacetylenes by [Rh(norbornadiene)Cl]$_2$

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Contents

Figure S40. In situ ^{1}H NMR spectra of polymerization of phenylacetylenes: (a) comparison of NMR spectrum between $[Rh(nbd)Cl]_2$, monomer **3** and mixture. (b) comparison of NMR spectrum between mixture and monomer **5**.

References

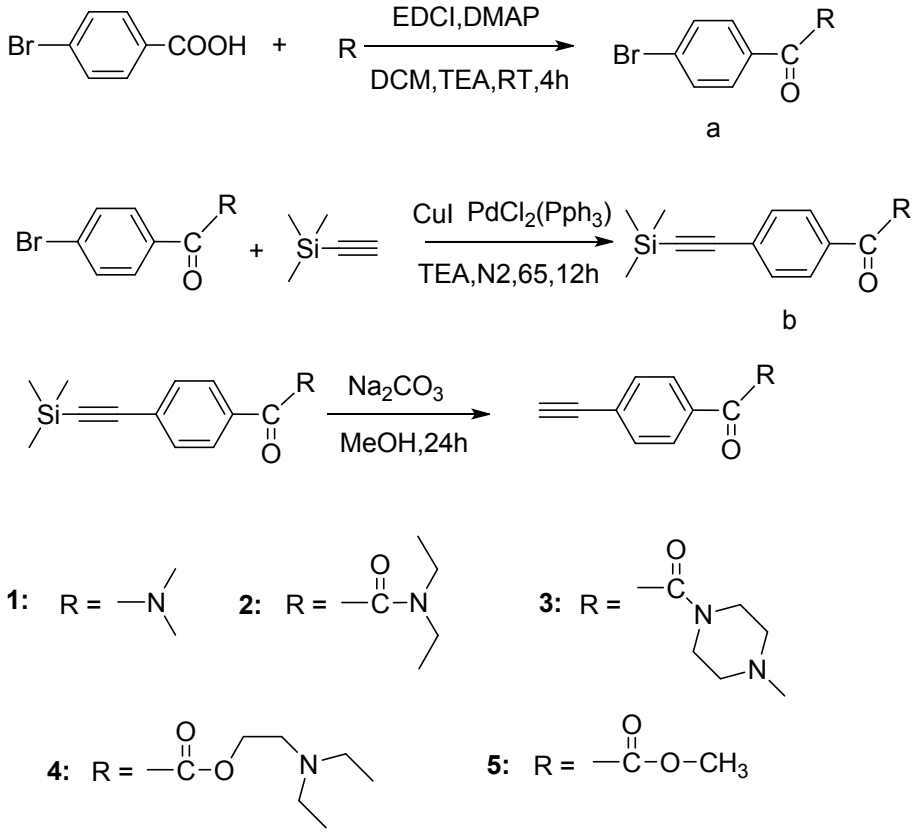
Experimental Section

Materials. Unless stated otherwise, all chemicals were obtained from commercial suppliers and used without further purification. $[Rh(nbd)Cl]_2$, Aladdin, 96%, CAS: 12257-42-0. Methyl 4-ethynylbenzoate (monomer **5**), Alfa Aesar, 97%, CAS: 3034-86-4. 4-Ethynyl-N,N-dimethylaniline (monomer **1**), Sigma Aldrich, 97%, CAS: 17573-94-3. Phenylacetylene，Alfa Aesar, 99%,CAS: 536-74-3. Chloroform-d, Methanol-d were bought from Innochem. The para-substituted phenylacetylenes bearing different amine-containing pendant groups p-CH≡CC6H4-R (**2–4**) (**2**: R = $-CON(CH_2CH_3)_2$; **3**: R = $-CON(CH_2CH_2)_2NCH_3$; **4**: R = $-COOCH_2CH_2N(CH_2CH_3)_2$) were synthesized according to the commonly used synthetic routes (see Scheme S1**)**. All monomers put into vacuum oven to drying. Polymerization in Schlenk tube in air.

Instrument. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AVANCEIII 400MHz NMR spectrometer with a BBO probe in CH_3OD. ESI-Mass Spectra were acquired on a Thermo Q-Exactive. The number-average Mw (Mn) and the dispersity (Mw/Mn) were determined by Gel Permeation Chromatography (GPC) in 5 mmol/L BrLi DMF solution at 85 ℃ at a flow rate of 1 mL/min and calibrated against narrow polydispersity

polystyrene standers. The GPC was conducted with a Waters 1515 isocratic HPLC pump and Waters 2414 refractive index detector using PPS columns. UV-Vis spectra were recorded on a TU-1901 double beam UV-Vis spectrophotometer. Fluorescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer. TGA were measured on Shimadzu DTG-60H

Synthesis.



Scheme S1. The synthetic route of monomers.

Synthesis of N,N-diethyl-4-ethynylbenzamide (2). A 100 mL flask was charged with 4-bromobenzoic acid (10 mmol, 1 equiv), EDCI (7 mmol, 0.7 equiv) and DMAP (0.5 mmol, 5% equiv), then the 50 mL DCM and the 10 mL TEA were added in the flask. The reaction mixture was activated under stirring at 0 ℃. After 1 h, diethylamine (12

mmol, 1.2 equiv) and EDCI (7 mmol, 0.7 equiv) was added. The reaction mixture was stirred at room temperature. After 4 h, crude products was separated by column chromatography (DCM : methyl alcohol = 19 : 1). Products (compound a) was prepared by the recrystallized process. Yield is 77%. Monomer **2** was prepared by Sonogashira reaction. The process was shown as following. A Schlenk tube was charged with compound a (0.5 mmol, 1 equiv), $PdCl_2(Pph_3)$ (0.015 mmol, 3% equiv), CuI (0.04 mmol, 8 % equiv), Pph_3 (0.03 mmol, 6 % equiv) and placed under nitrogen atmosphere. Anaerobic TEA (15 mL) and THF (8 mL) was added, and the reaction mixture was heated under stirring to 65 ℃. After 12 h, products were separated by flash column chromatograph. The previous product (0.1 mmol, 1 equiv), Na_2CO_3 (0.1g, 1 mmol, 10 equiv) and methanol (50 mL) were adding in 100 mL flask. The reaction mixture was stirred at room temperature. After 24 h, Na_2CO_3 was removed by filtration. Filtrate was collected and solvent was evaporated. Products were separated by flash column chromatograph. Yield is 91%. ^{1}H NMR (400 MHz, Chloroform-d): δ = 7.54 (d, *J* = 7.9 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 3.78 – 3.17 (d, 4H), 3.15 (s, 1H), 1.40 – 0.92 (d, 6H) ppm. MS (ESI): m/z calcd for $C_{13}H_{15}NO^+$ $[M]^+$: 201; found: 201.

Synthesis of (4-ethynylphenyl)(4-methylpiperazin-1-yl)methanone (3). A 100 mL flask was charged with 4-bromobenzoic acid (10 mmol, 1 equiv), EDCI (7 mmol, 0.7 equiv) and DMAP (0.5 mmol, 5% equiv), then the 50 mL DCM and the 10 mL TEA were added in the flask. The reaction mixture was activated under stirring at 0 ℃. After 1 h, 1-methylpiperazine (12 mmol, 1.2 equiv) and EDCI (7 mmol, 0.7 equiv) was added.

The reaction mixture was stirred at room temperature. After 4 h, crude products was separated by column chromatography (DCM: methyl alcohol = 19 : 1). Products (compound a) was prepared by the recrystallized process. Yield is 71%. Monomer **3** was prepared by Sonogashira reaction. The process was shown as following. A Schlenk tube was charged with compound a (0.5 mmol, 1 equiv), $PdCl_2$(Pph3) (0.015 mmol, 3% equiv), CuI (0.04 mmol, 8% equiv), Pph_3 (0.03 mmol, 6% equiv) and placed under nitrogen atmosphere. Anaerobic TEA (15 mL) and THF (8 mL) was added, and the reaction mixture was heated under stirring to 65 ℃. After 12 h, products were separated by flash column chromatograph. The previous product (0.1 mmol, 1 equiv), Na_2CO_3 (0.1g, 1 mmol, 10 equiv) and methanol (50 mL) were adding in 100 mL flask. The reaction mixture was stirred at room temperature. After 24 h, Na_2CO_3 was removed by filtration. Filtrate was collected and solvent was evaporated. Products were separated by flash column chromatograph. Yield is 87%. Compound a: ^{1}H NMR (400 MHz, Chloroform-d): δ = 7.59 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 18.1 Hz, 2H), 3.81 (b, 4H), 2.48 (b, 7H) ppm. MS (EI): m/z calcd for $C_{12}H_{15}BrN_2O^+$ $[M]^+$: 282, 284; found: 282, 284. Monomer **3** ^{1}H NMR (400 MHz, Chloroform-d): δ = 7.62 – 7.51 (m, 2H), 7.45 – 7.35 (m, 2H), 3.63 (d, *J* = 142.8 Hz, 4H), 3.16 (s, 1H), 2.34 (d, 7H) ppm. MS (EI): m/z calcd for $C_{14}H_{16}N_2O^+$ $[M]^+$: 228; found: 228.

Synthesis of 2-(diethylamino)ethyl 4-ethynylbenzoate (4). A 100 mL flask was charged with 4-bromobenzoic acid (2g, 10 mmol, 1 equiv), EDCI (1.15g, 7 mmol, 0.7 equiv) and DMAP (61 mg, 0.5 mmol, 5% equiv), then the 50 mL DCM and the 10 mL

TEA were added in the flask. The reaction mixture was activated under stirring at 0 ℃. After 1 h, 2-(diethylamino)ethan-1-ol (1.4 g, 12 mmol, 1.2 equiv) and EDCI (1.15g, 7 mmol, 0.7 equiv) was added. The reaction mixture was stirred at room temperature. After 4 h, crude products was separated by column chromatography (DCM: methyl alcohol = 19 : 1). Products (compound a) was prepared by the recrystallized process. Yield is 71%. Monomer **2** was prepared by Sonogashira reaction. The process was shown as following. A Schlenk tube was charged with compound a (123 mg, 0.5 mmol, 1 equiv), $PdCl_2(Pph_3)$ (11 mg, 0.015 mmol, 3% equiv), CuI (8 mg, 0.04 mmol, 8% equiv), Pph_3 (9 mg, 0.03 mmol, 6% equiv) and placed under nitrogen atmosphere. Anaerobic TEA (15 mL) and THF (8 mL) was added, and the reaction mixture was heated under stirring to 65 ℃. After 12 h, products were separated by flash column chromatograph. The previous product (31 mg, 0.1 mmol, 1 equiv), Na_2CO_3 (0.1g, 1 mmol, 10 equiv) and methanol (50 mL) were adding in 100 mL flask. The reaction mixture was stirred at room temperature. After 24 h, Na_2CO_3 was removed by filtration. Filtrate was collected and solvent was evaporated. Products were separated by flash column chromatograph. Yield is 90%. Monomer **2** ^{1}H NMR (400 MHz, Chloroform-d): δ = 8.00 (d, *J* = 8.2, 1.6 Hz, 2H), 7.68 – 7.45 (d, 2H), 4.41 (t, *J* = 1.4 Hz, 2H), 3.25 (s, *J* = 1.5 Hz, 1H), 2.86 (t, *J* = 6.4, 1.6 Hz, 2H), 2.64 (dd, *J* = 7.2, 1.6 Hz, 4H), 1.08 (t, *J* = 7.1, 1.5 Hz, 6H) ppm. MS (ESI): m/z calcd for $C_{15}H_{20}NO_2^+$ $[M+H]^+$: 246; found: 246.

Polymerization of substitute of phenyl(polyacetylene) and its derivatives (PPAs). A 25 mL Schlenk tube was charged with monomer (0.13 mmol, 1 equiv) and

$[Rh(nbd)Cl]_2$ (different equiv). Then DCM (2.6 mL) (the monomer concentration is 50 mmol/L) was added. The reaction mixture was heated at different temperature with stirring. After 2 h, the solution was diluted with 10 mL DCM. Then the PPAs were precipitated with 50 mL n-hexane. Pure PPAs was washed three times with n-hexane. The ^{1}H NMR spectrum was used to calculate the proportion of *cis*/*trans*-selectivity of the PPAs.[1, 2] The resonance of *cis* polyenic proton overlaps the resonance of aromatic proton. Multi-peak fitting method shows one cis polyenic proton at δ = 5.7 ~ 6.3 ppm, four aromatic protons, and the trans polyenic proton at δ = 6.3 ~ 8.3 ppm. *Cis* contents can be calculated by eq. (1):

$$\textit{Cis}\ \text{contents}\ (\%) \quad = \quad \frac{A_{6.2}}{At/5} \times 100 \qquad (1)$$

Where $A_{6.2}$ is the area of the polyenic proton in *cis* form and At is the total area of the olefinic and aromatic protons in the spectra. Take entry 4 (see Figure S25) as example: three protons resonances, centered at δ = 6.1 ppm (the *cis* polyenic proton), centered at δ = 6.9 ppm and δ = 7.4 ppm (the *trans* polyenic proton and four aromatic protons). According to the protons distribution of olefinic and aromatic, the configuration of PPAs have a *cis-transoid* configuration.[3]

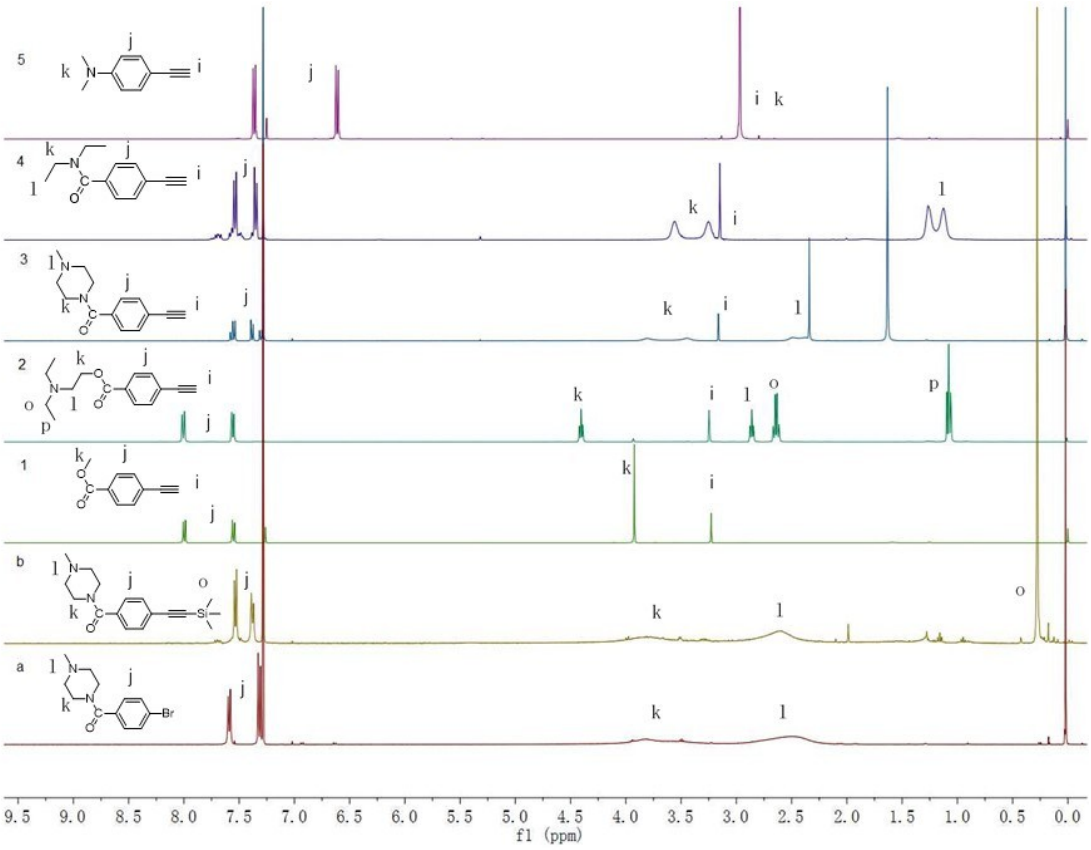


Figure S1. ^{1}H-NMR spectra of monomers in $CDCl_3$.

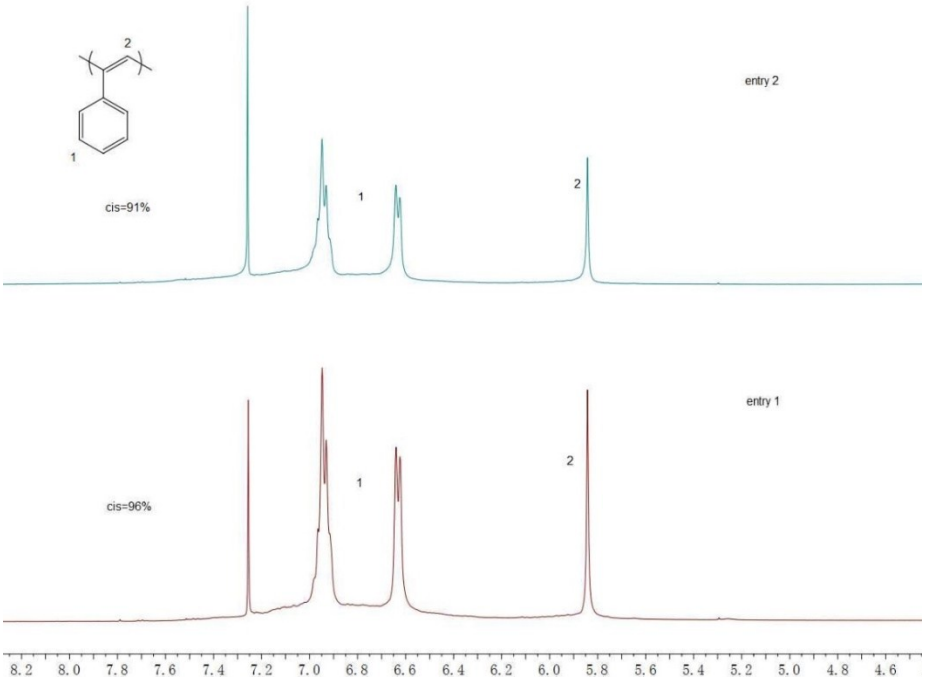
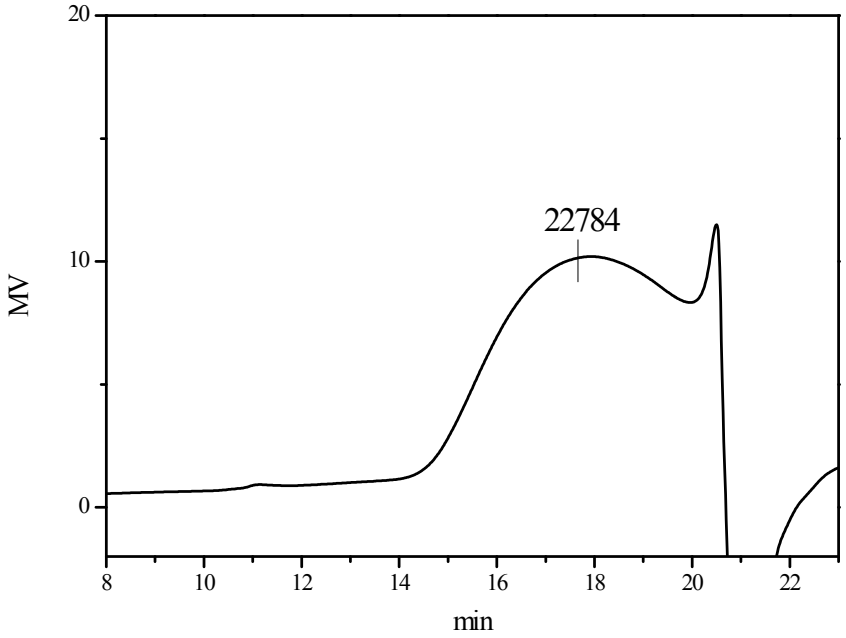


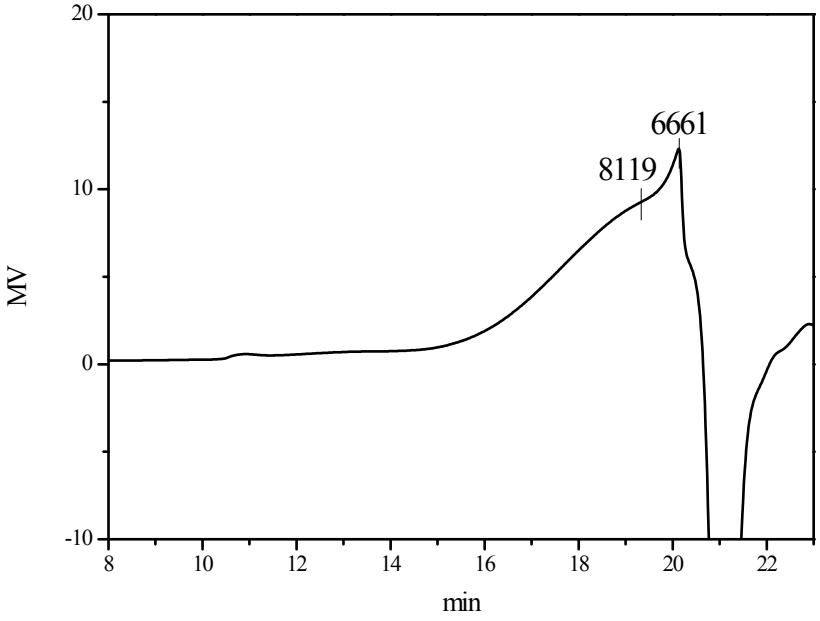
Figure S2. ^{1}H-NMR spectra of PPAs of entries 1 and 2 in Table 1 in $CDCl_3$.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.183	17.183	17.183	19623	23989	22784	28880	33668	1.203889	1.403483

Figure S3. The GPC result of PPA of entry 1 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.683	19.683	19.683	13064	15083	8119	17922	21479	1.188220	1.424047
2		20.124	20.124	20.124	6954	7014	6661	7073	7130	1.008374	1.016476

Figure S4. The GPC result of PPA of entry 2 in Table 1.

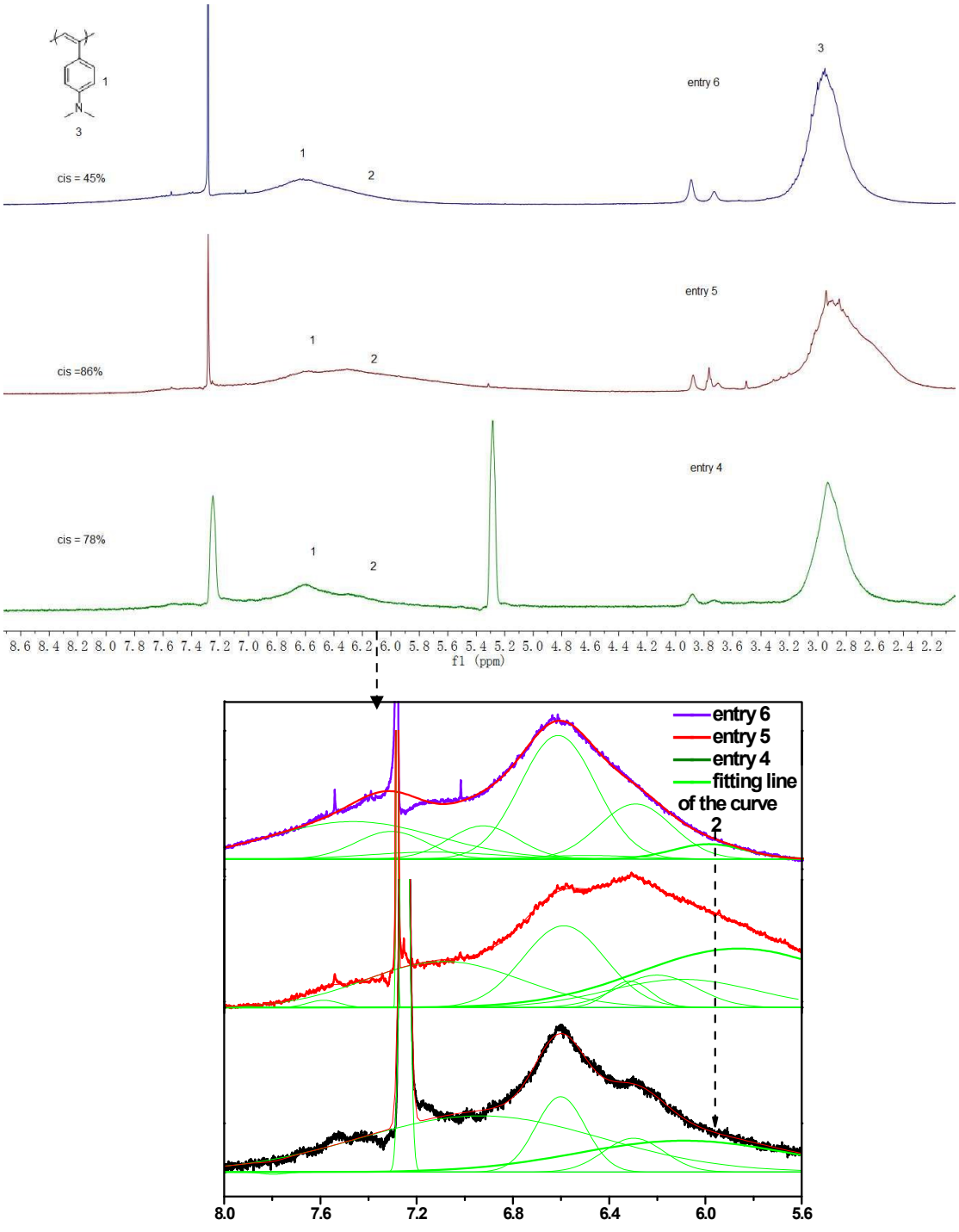
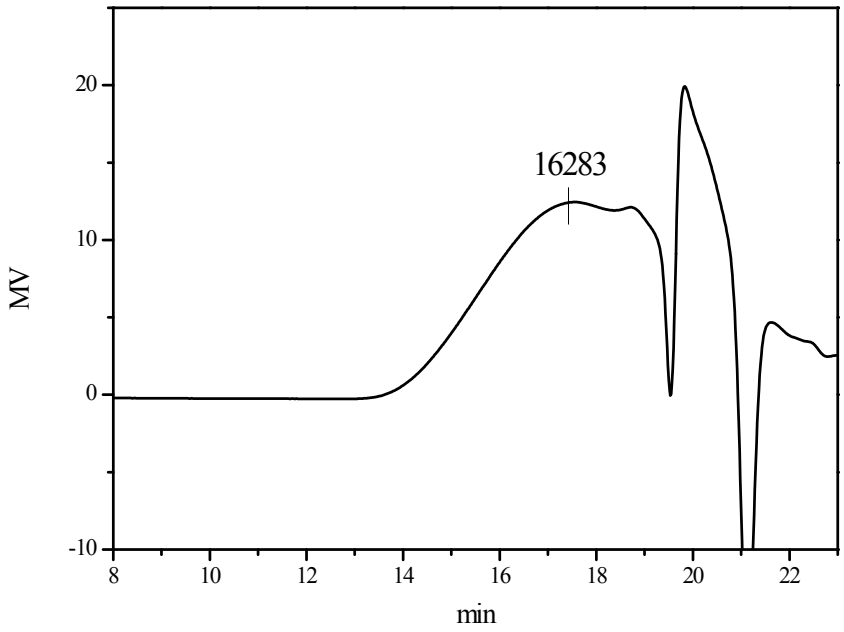


Figure S5. ^{1}H-NMR spectra of PPAs of entries 4–6 in Table 1 in $CDCl_3$.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.417	17.417	17.417	15095	19911	16283	26447	33701	1.328217	1.692564

Figure S6. The GPC result of PPA of entry 4 in Table 1.

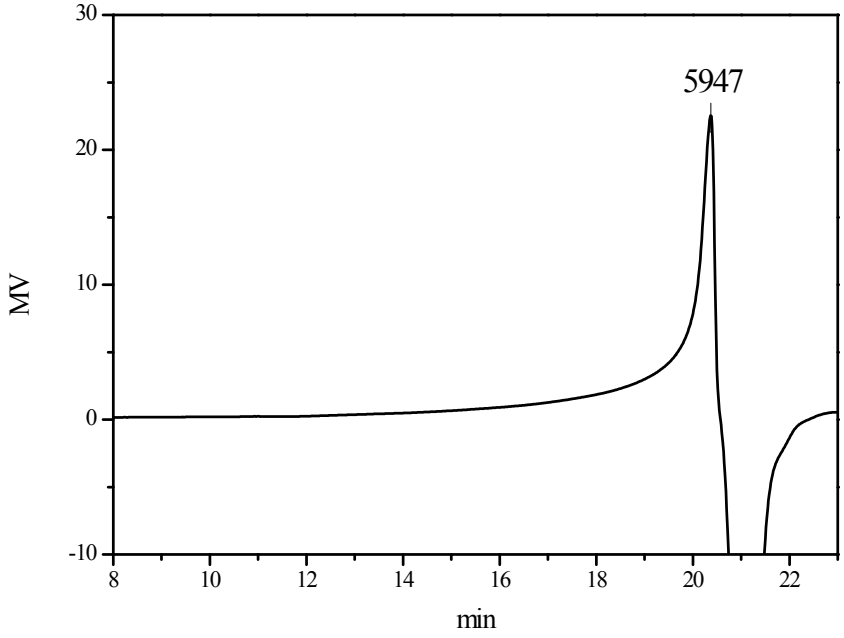


Figure S7. The GPC result of PPA of entry 5 in Table 1.

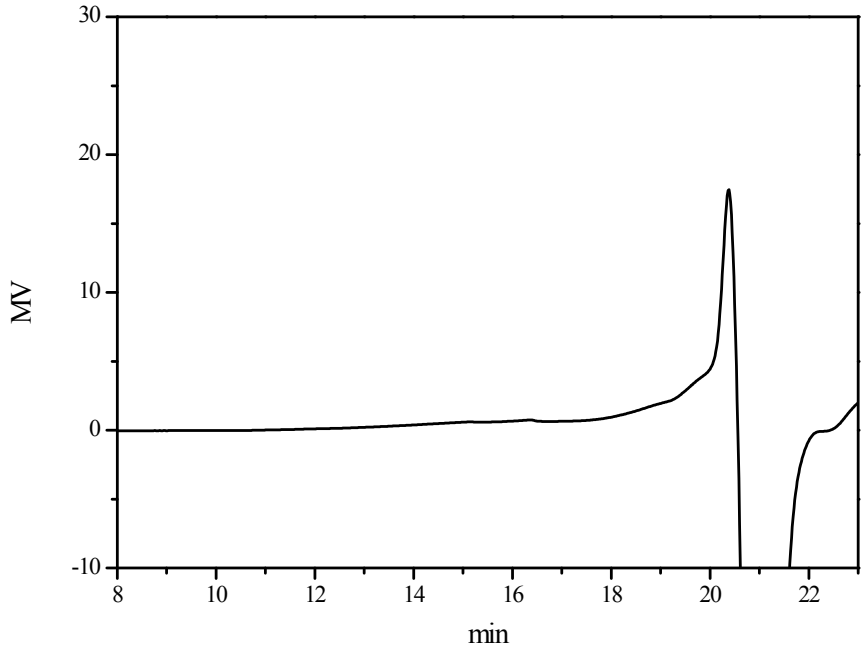


Figure S8. The GPC result of PPA of entry 6 in Table 1.

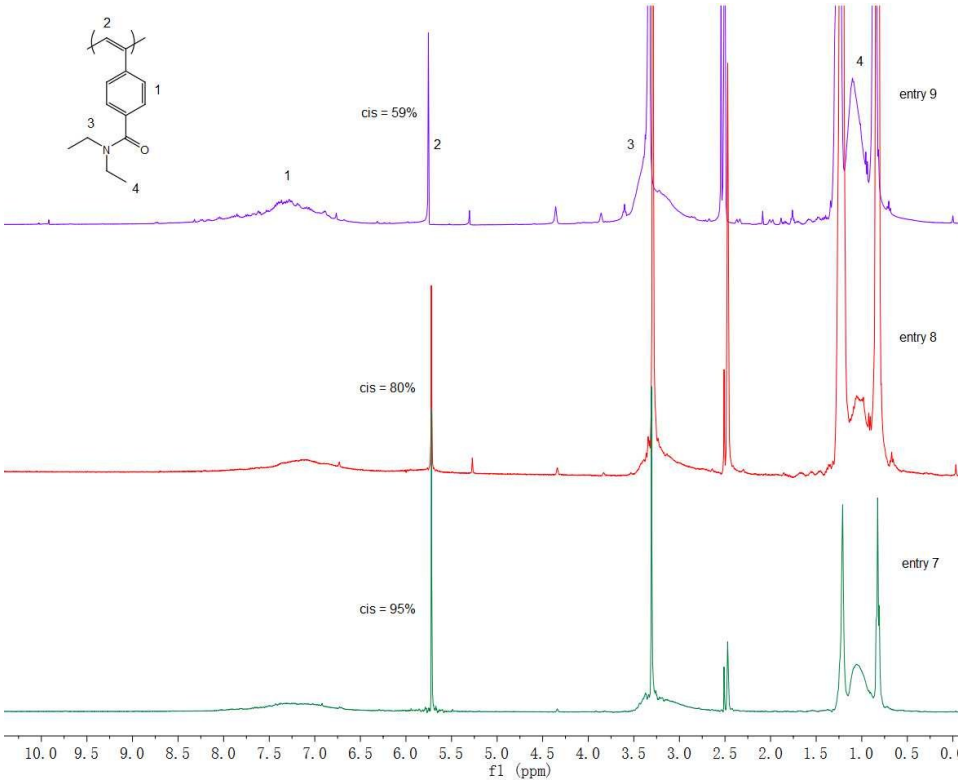
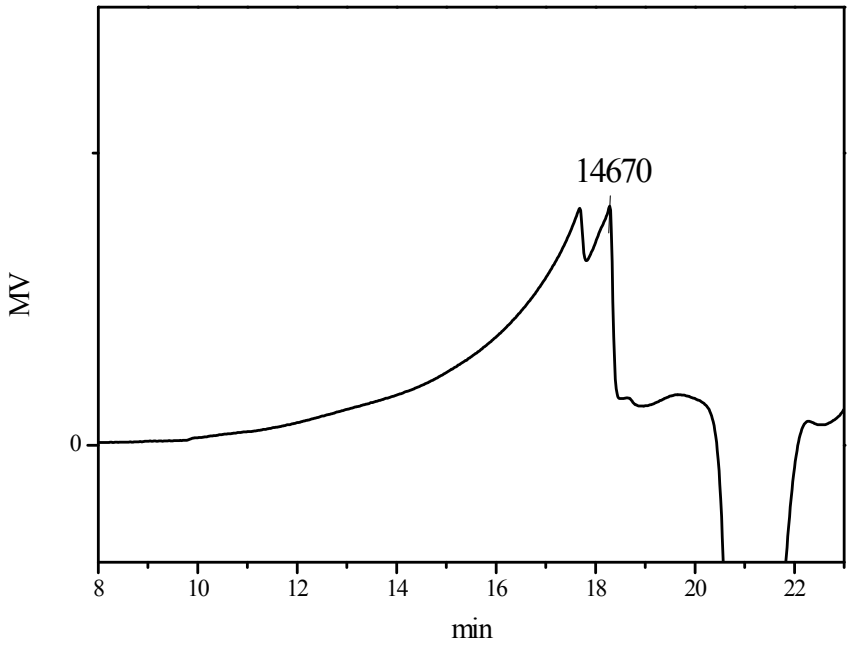


Figure S9. ^{1}H-NMR spectra of PPAs of entries 7–9 in Table 1 in (CD3)2SO.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.275	18.275	18.275	22680	27011	14670	34290	44784	1.269488	1.657994

Figure S10. The GPC result of PPA of entry 7 in Table 1.

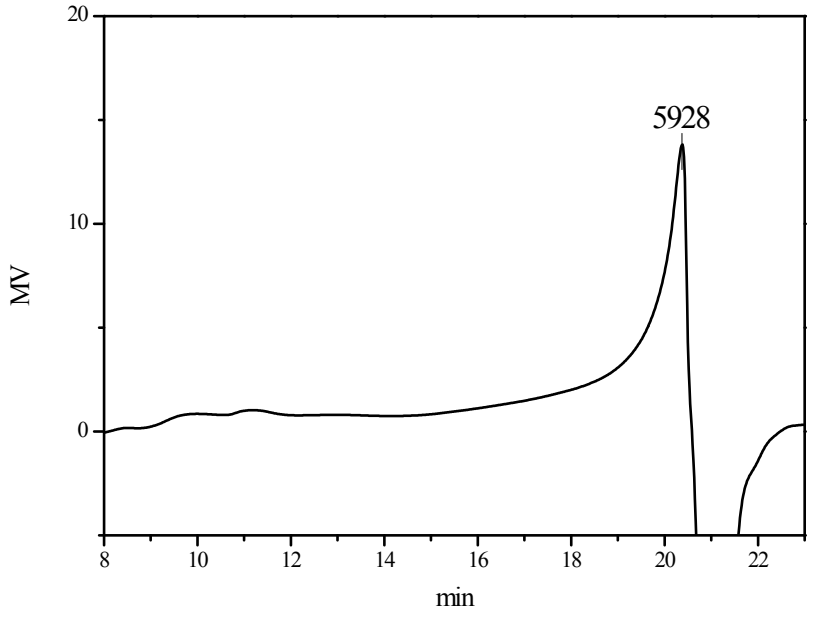
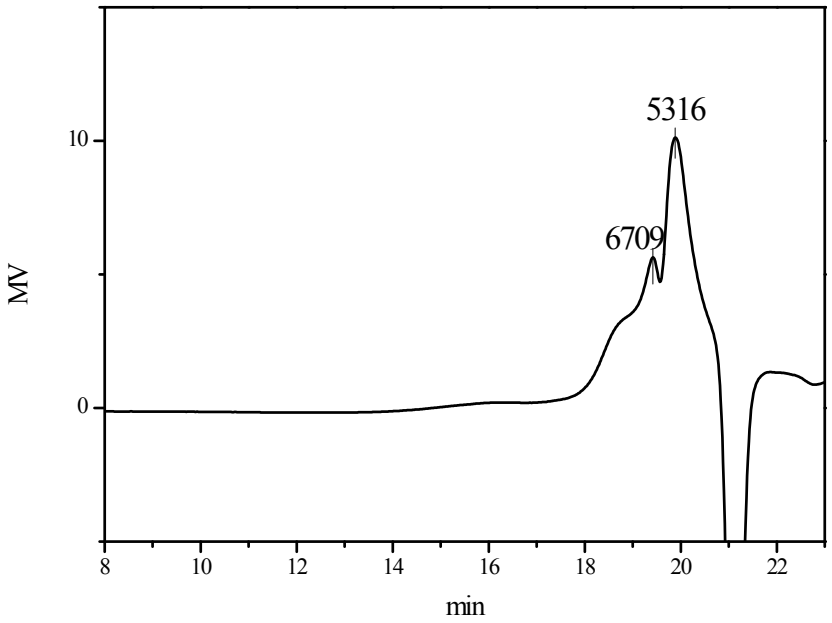


Figure S11. The GPC result of PPA of entry 8 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.421	19.421	19.421	7902	8174	6709	8475	8800	1.036913	1.076640
2		19.890	19.890	19.890			5316				

Figure S12. The GPC result of PPA of entry 9 in Table 1.

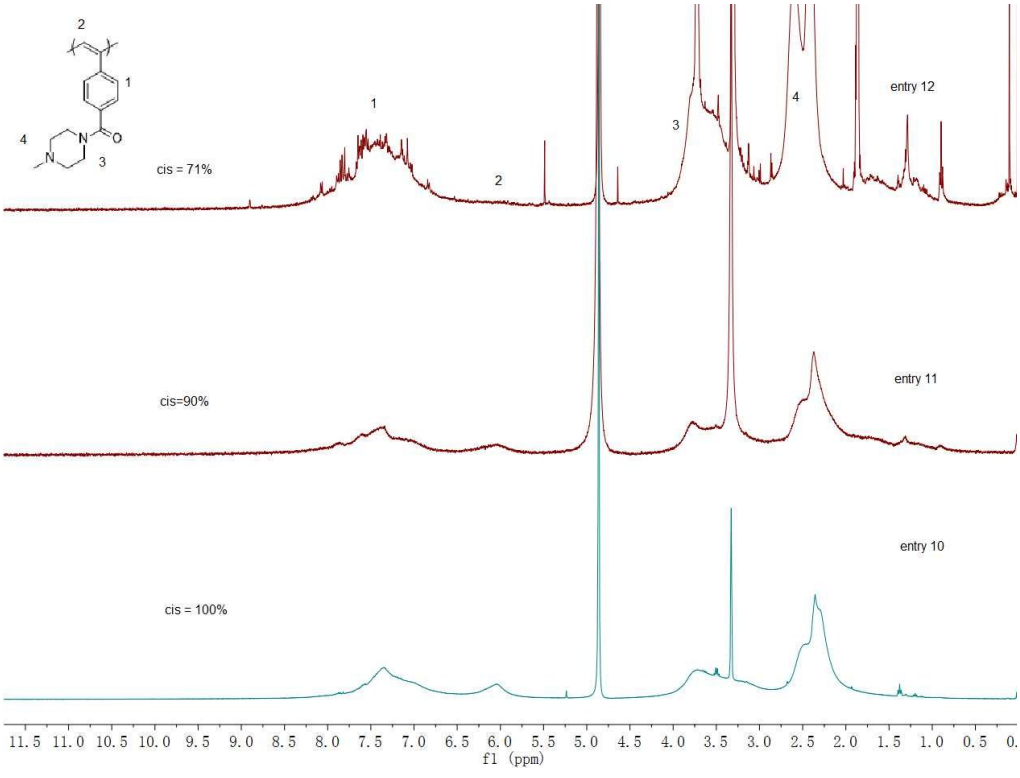
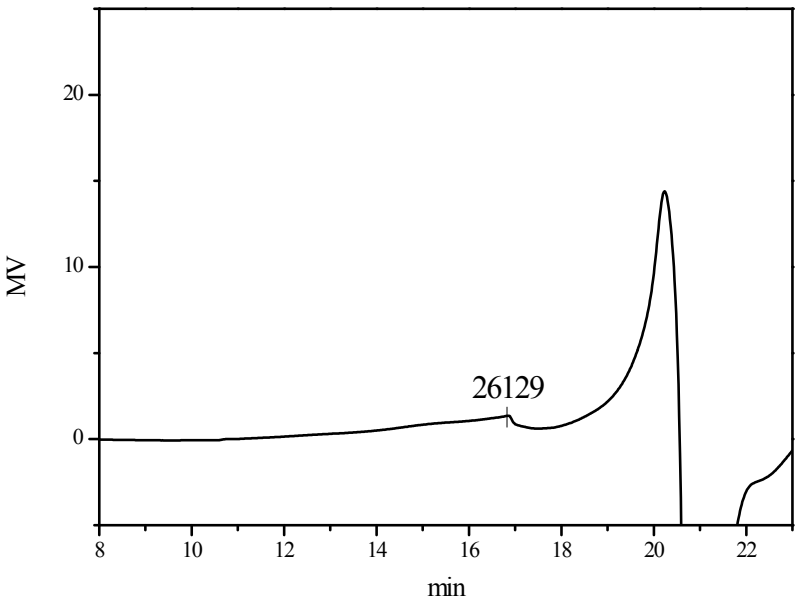


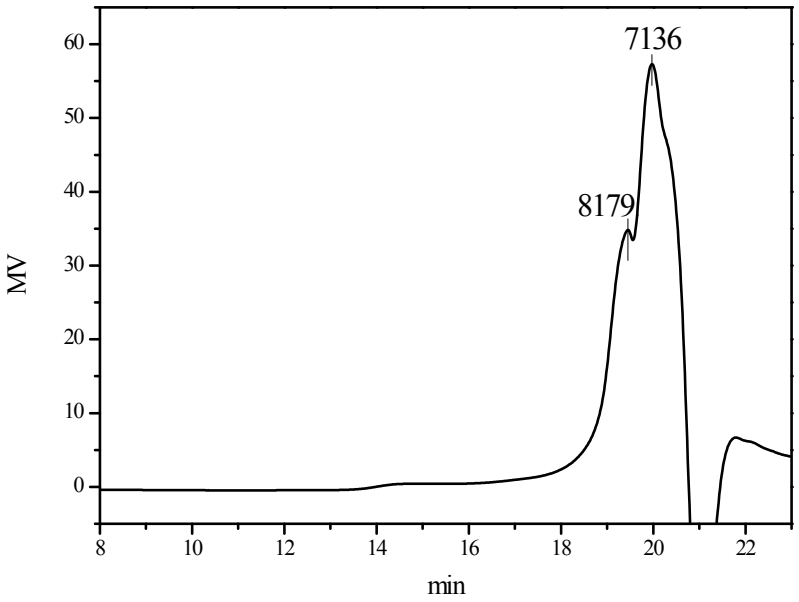
Figure S13. ^{1}H-NMR spectra of PPAs of entries 10–12 in Table 1 in CD_3OD.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.846	16.846	16.846	37071	41885	26129	48146	55389	1.149486	1.322396
2		20.235	20.235	20.235	7036	7302	6331	7646	8082	1.047126	1.106777

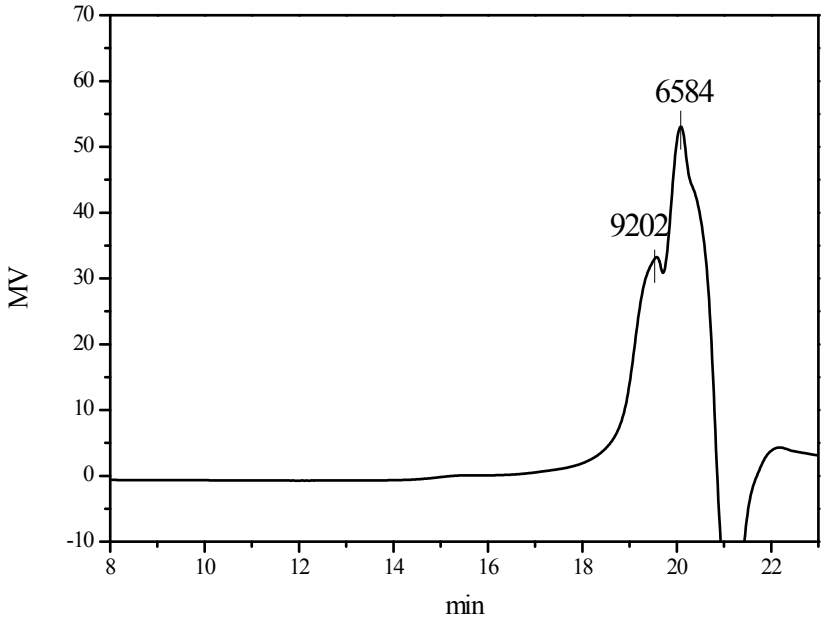
Figure S14. The GPC result of PPA of entry 10 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.667	19.667	19.667	1116(	12380	8179	14260	16850	1.151901	1.361093
2		19.973	19.973	19.973	6443	6569	7136	6692	6810	1.018687	1.036579

Figure S15. The GPC result of PPA of entry 11 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.396	19.396	19.396	10649	11061	9202	11612	12333	1.049848	1.115021
2		20.150	20.150	20.150	6460	6610	6584	6761	6911	1.022894	1.045538

Figure S16. The GPC result of PPA of entry 12 in Table 1.

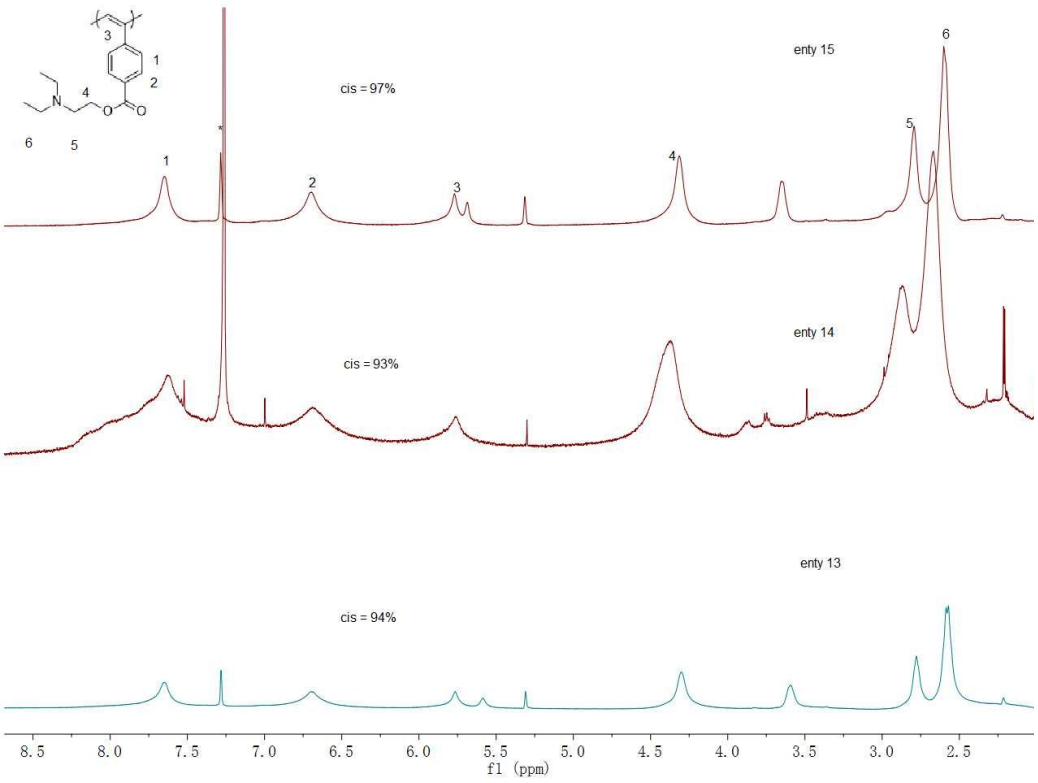
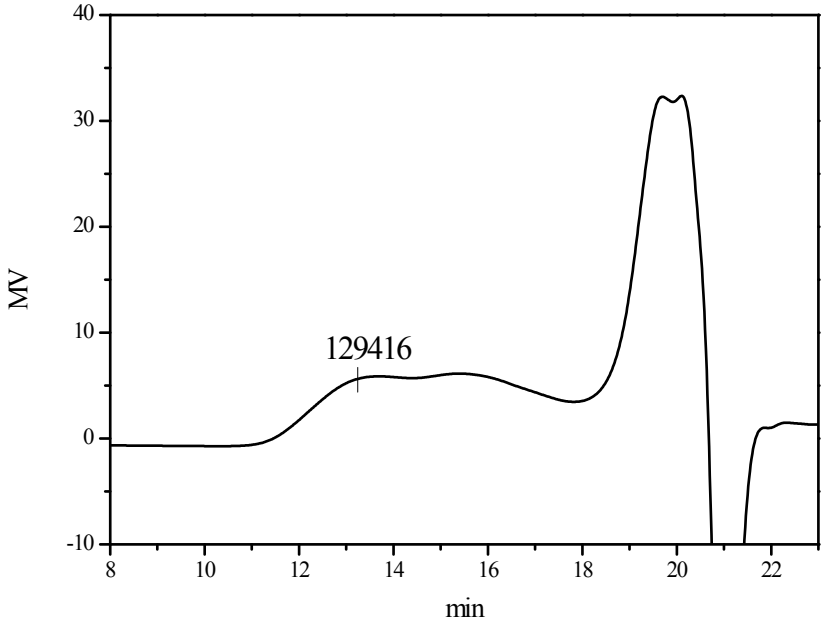


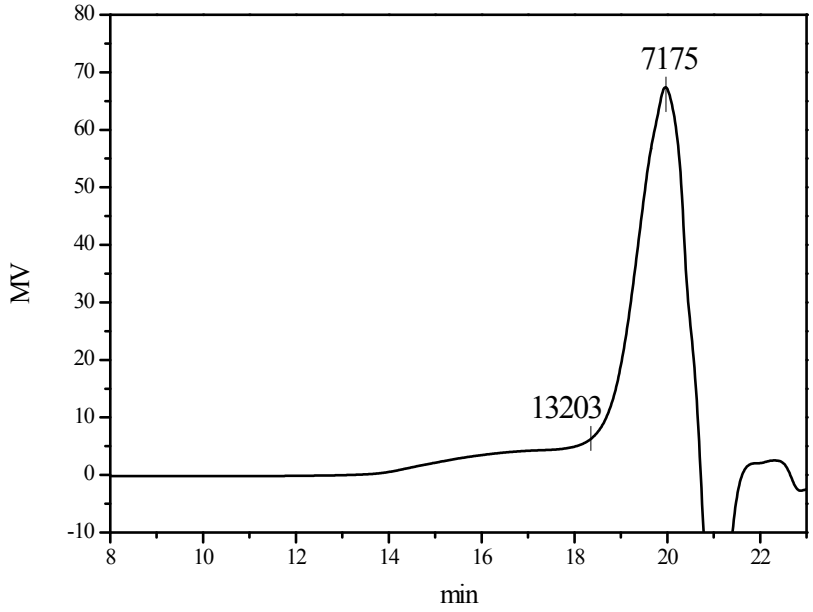
Figure S17. ^{1}H-NMR spectra of PPAs of entries 13–15 in Table 1 in $CDCl_3$.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.433	13.433	13.433	67405	107854	129416	164635	220861	1.526459

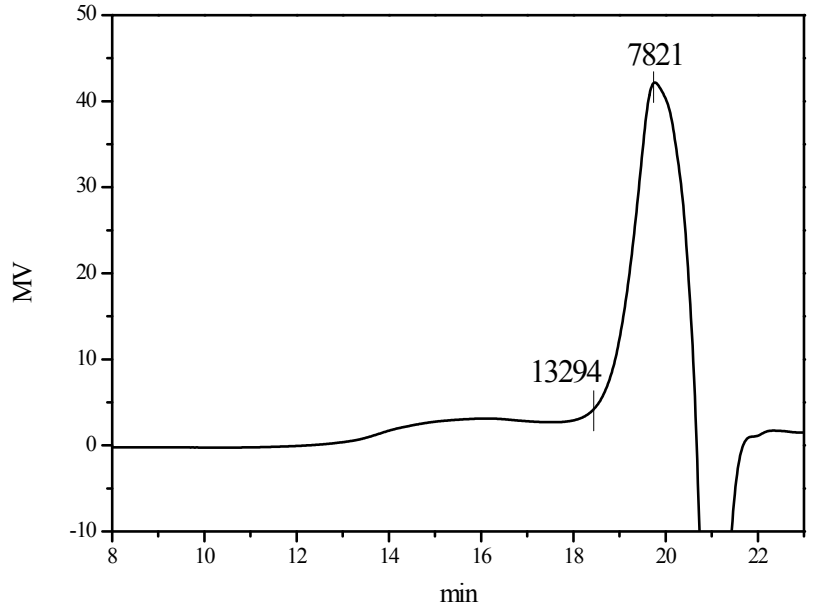
Figure S18. The GPC result of PPA of entry 13 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.533	18.533	18.533	24626	33350	13203	48745	69842	1.461632	2.094232
2		19.961	19.961	19.961	7619	7985	7175	8389	8818	1.050531	1.104348

Figure S19. The GPC result of PPA of entry 14 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.517	18.517	18.517	27613	40165	13294	60816	85064	1.514162	2.117869
2		19.768	19.768	19.768	7674	8045	7821	8453	8885	1.050674	1.104418

Figure S20. The GPC result of PPA of entry 15 in Table 1.

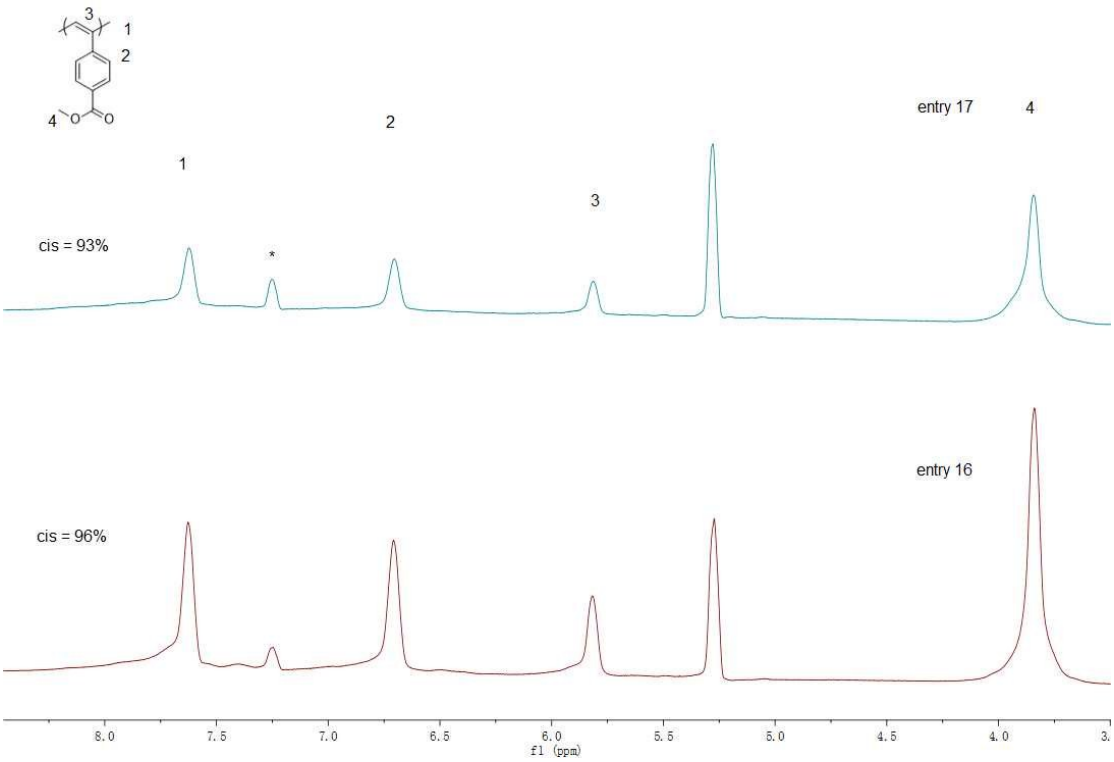
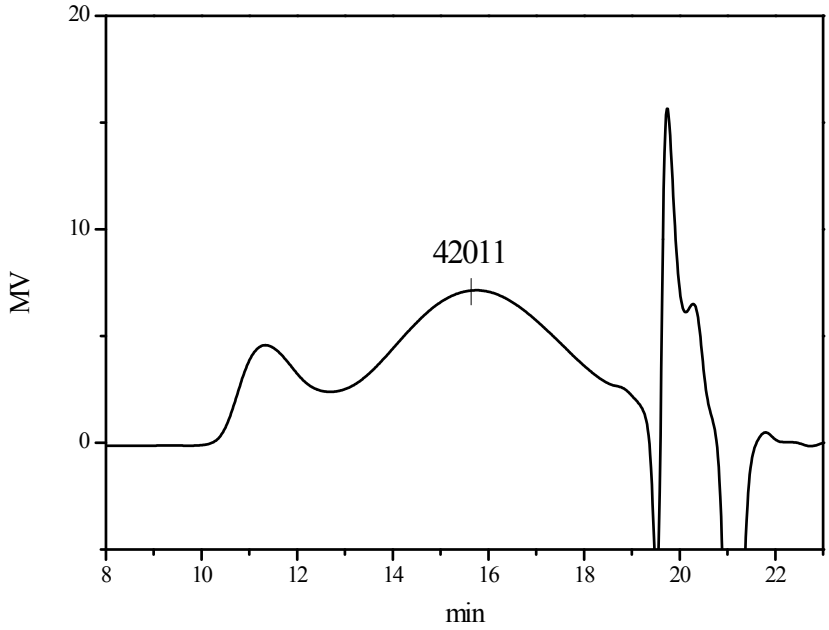


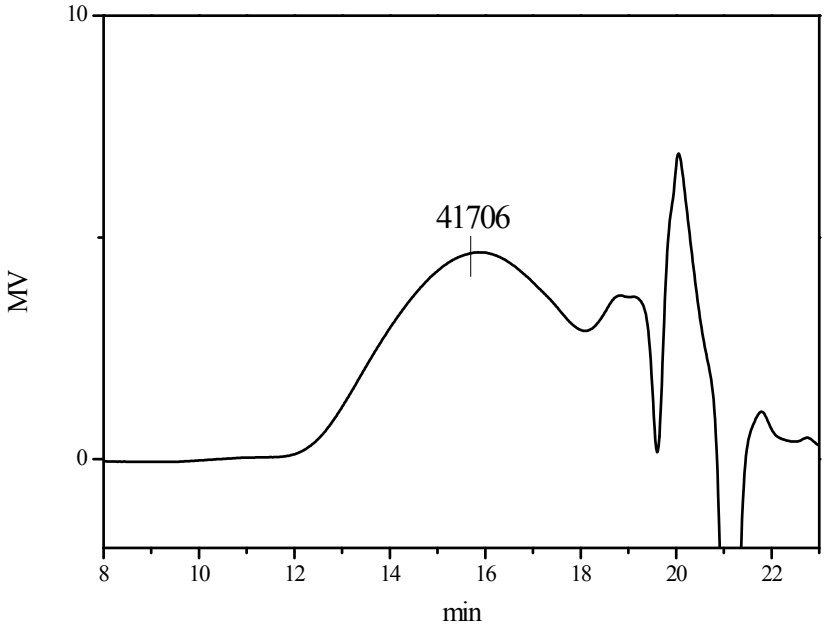
Figure S21. ^{1}H-NMR spectra of PPAs of entries 16–17 in Table 1 in $CDCl_3$.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.717	15.717	15.717	41487	138324	42011	412433	606189	2.981653	4.382397

Figure S22. The GPC result of PPA of entry 16 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.733	15.733	15.733	28894	49410	41706	79746	113196	1.613941	2.290932

Figure S23. The GPC result of PPA of entry 17 in Table 1.

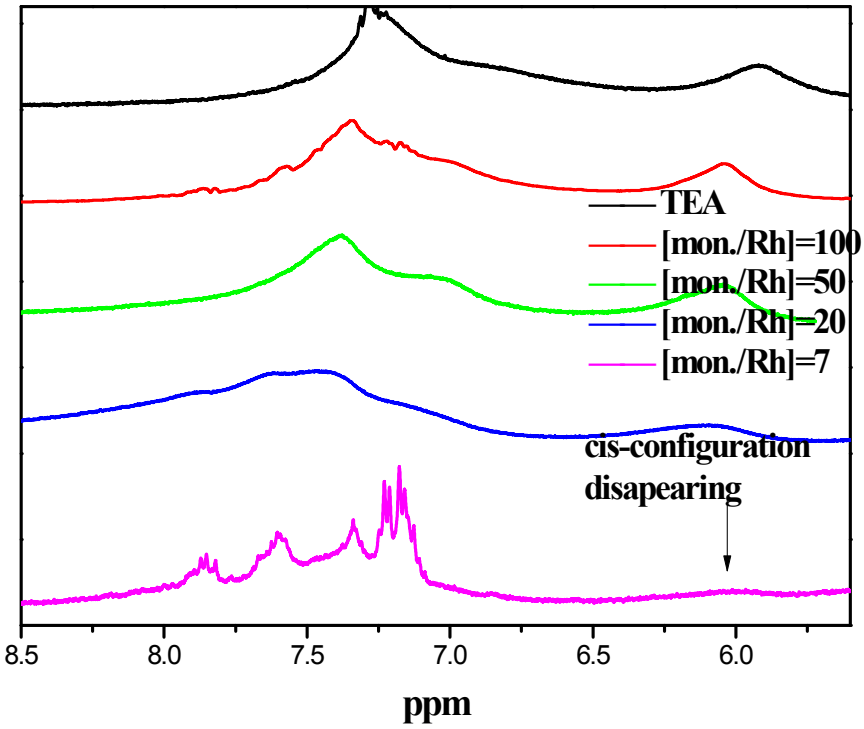


Figure S24. Part of ^{1}H NMR spectra of PPAs of entries 1–4 in Table 2 in CD_3OD.

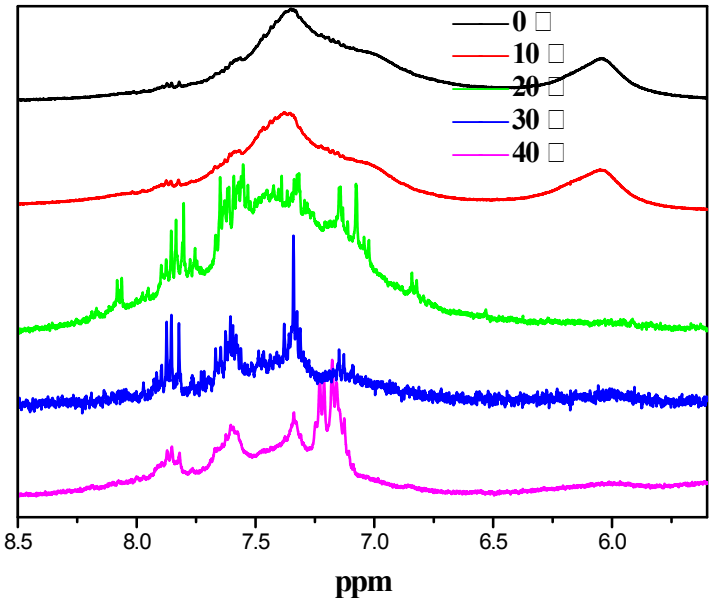
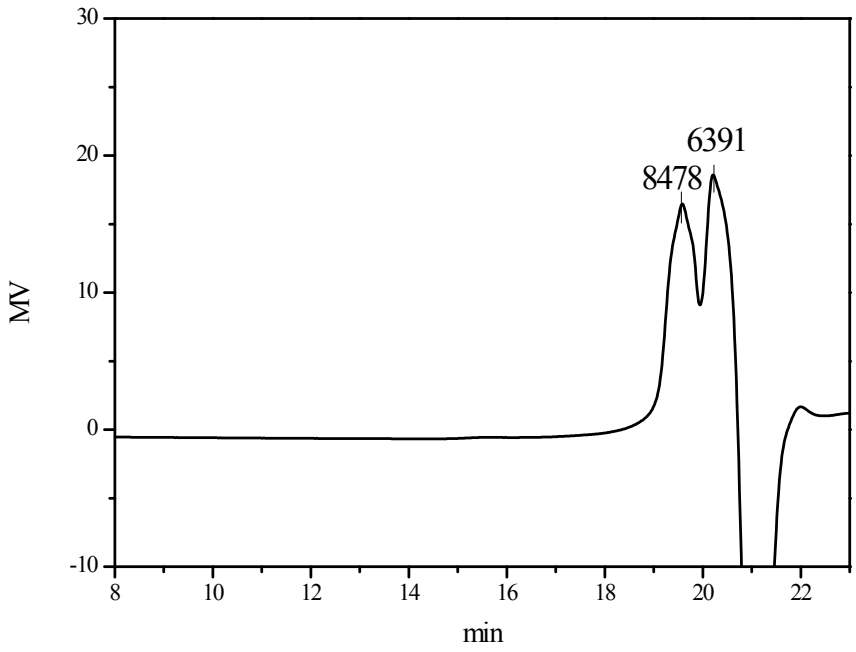


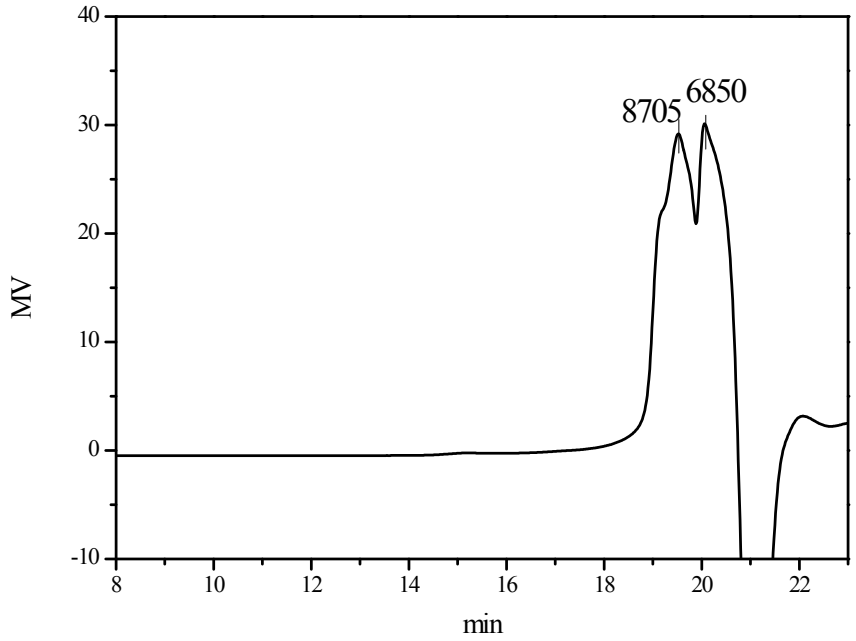
Figure S25. Part of ^{1}H NMR spectra of PPAs of entries 4–8 in Table 2 in CD_3OD.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.585	19.585	19.585	10532	12609	8478	16323	21576	1.294497	1.711086
2		20.214	20.214	20.214	5990	6042	6391	6093	6144	1.008516	1.016869

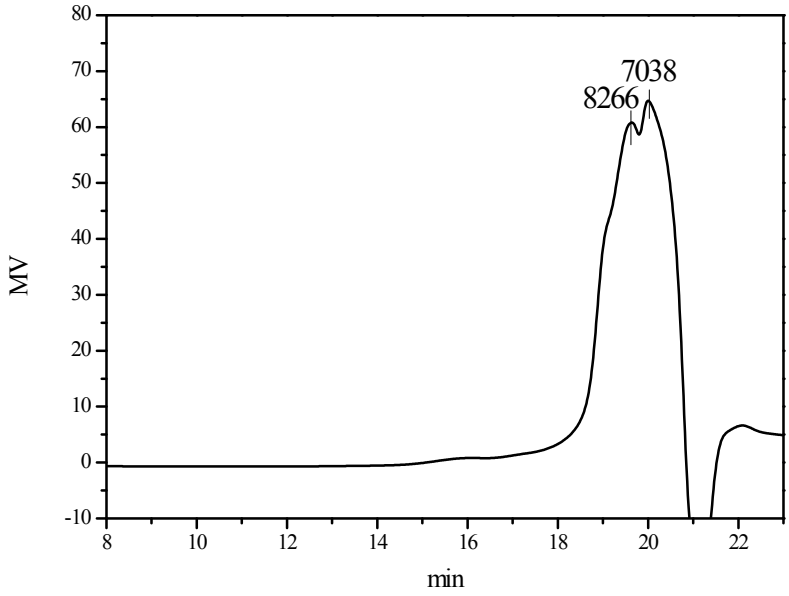
Figure S26. The GPC result of PPA of entry 1 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.524	19.524	19.524	9576	10238	8705	11223	12620	1.096243	1.232605
2		20.063	20.063	20.063	6051	6115	6850	6177	6238	1.010212	1.020129

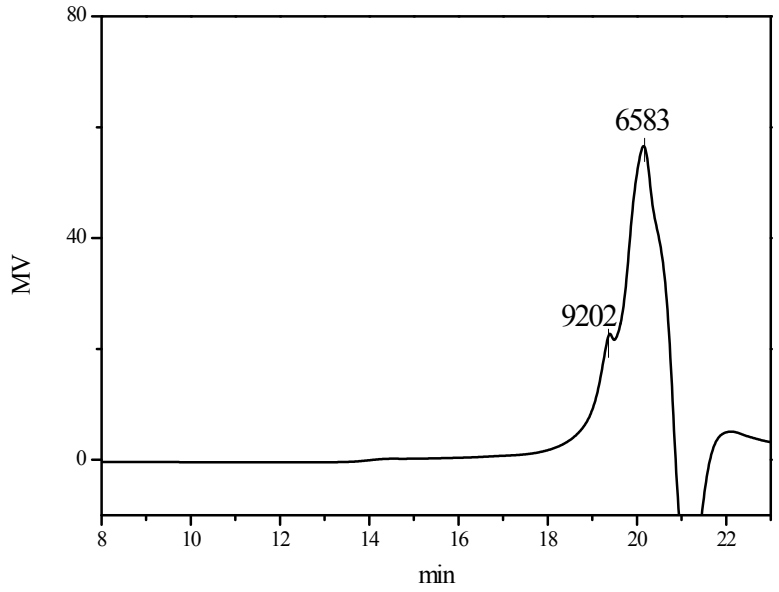
Figure S27. The GPC result of PPA of entry 2 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.643	19.643	19.643	10089	11233	8266	14174	21041	1.261830	1.873106
2		20.004	20.004	20.004	6309	6408	7038	6506	6600	1.015210	1.029830

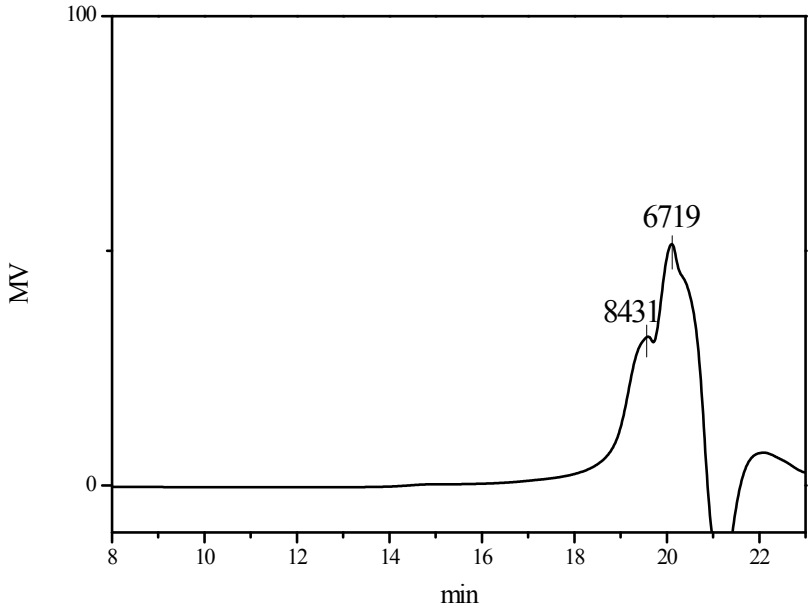
Figure S28. The GPC result of PPA of entry 3 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.396	19.396	19.396	11373	12002	9202	12795	13739	1.066060	1.144767
2		20.150	20.150	20.150	6303	6491	6583	6679	6862	1.028935	1.057039

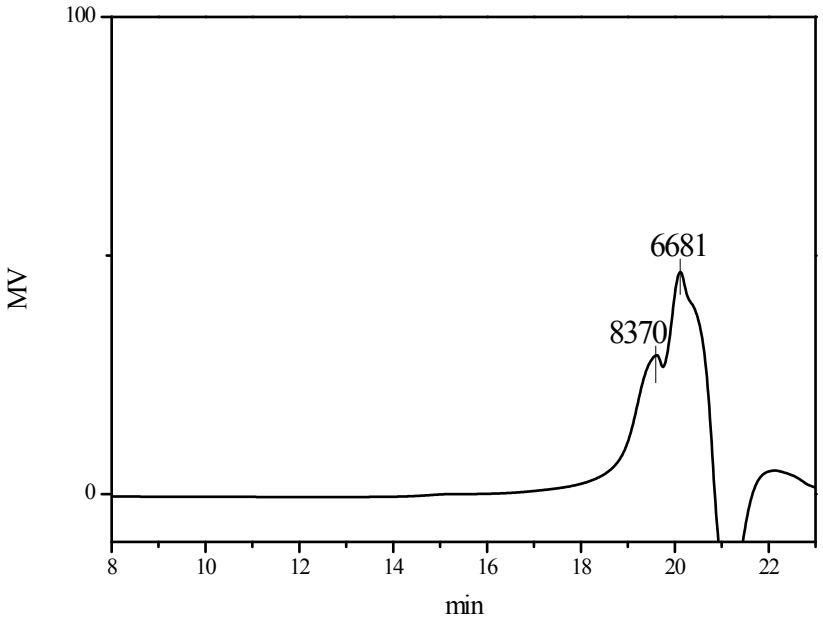
Figure S29. The GPC result of PPA of entry 4 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.597	19.597	19.597	11040	12195	8431	13883	16086	1.138408	1.319066
2		20.105	20.105	20.105	6107	6251	6719	6392	6526	1.022496	1.044003

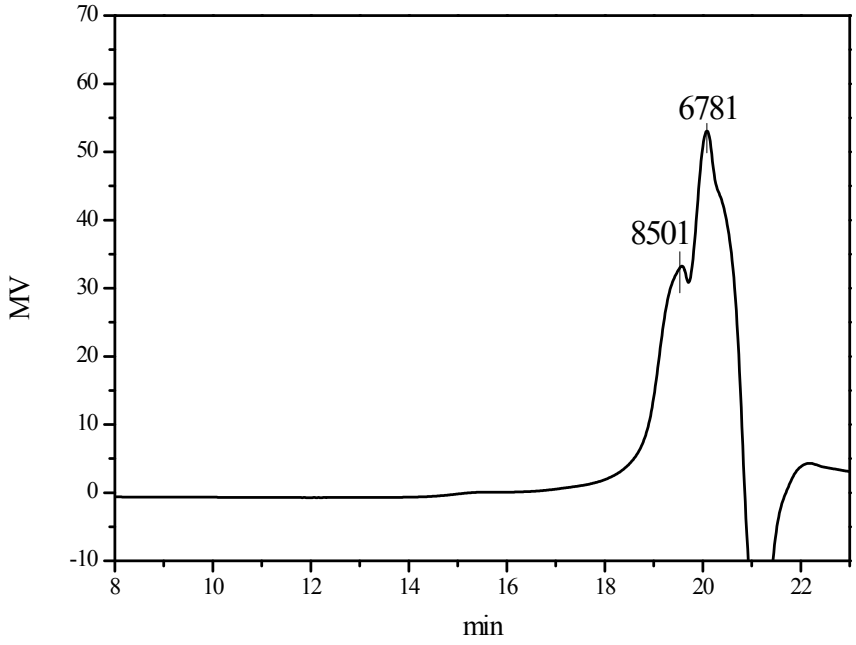
Figure S30. The GPC result of PPA of entry 5 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.614	19.614	19.614	11090	12392	8370	14290	16733	1.153218	1.350334
2		20.118	20.118	20.118	6043	6175	6681	6303	6426	1.020780	1.040676

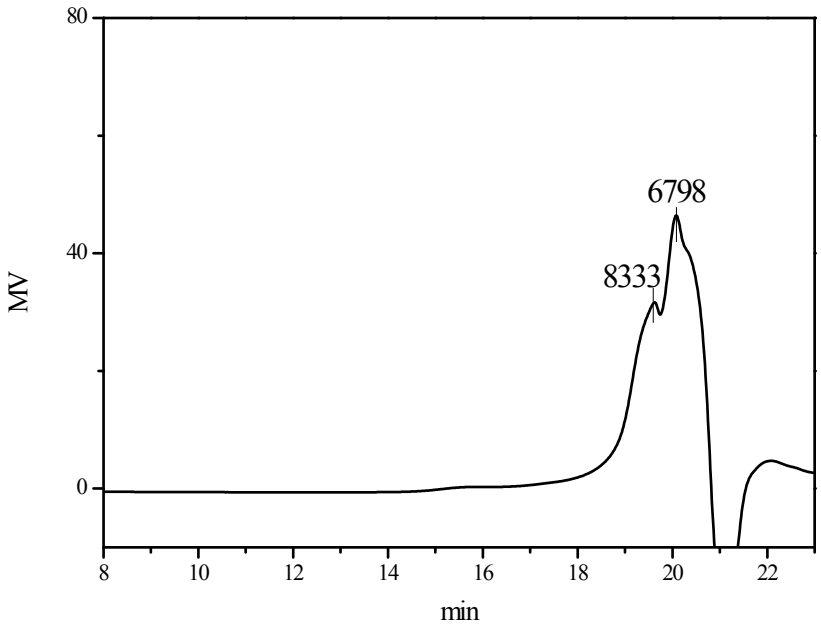
Figure S31. The GPC result of PPA of entry 6 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.576	19.576	19.576	11973	14655	8510	19448	26089	1.327069	1.780244
2		20.085	20.085	20.085	6127	6257	6781	6385	6506	1.020321	1.039738

Figure S32. The GPC result of PPA of entry 7 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		19.624	19.624	19.624	10789	12006	8333	13824	16231	1.151418	1.351865
2		20.080	20.080	20.080	6095	6210	6798	6323	6431	1.018107	1.035454

Figure S33. The GPC result of PPA of entry 8 in Table 2.

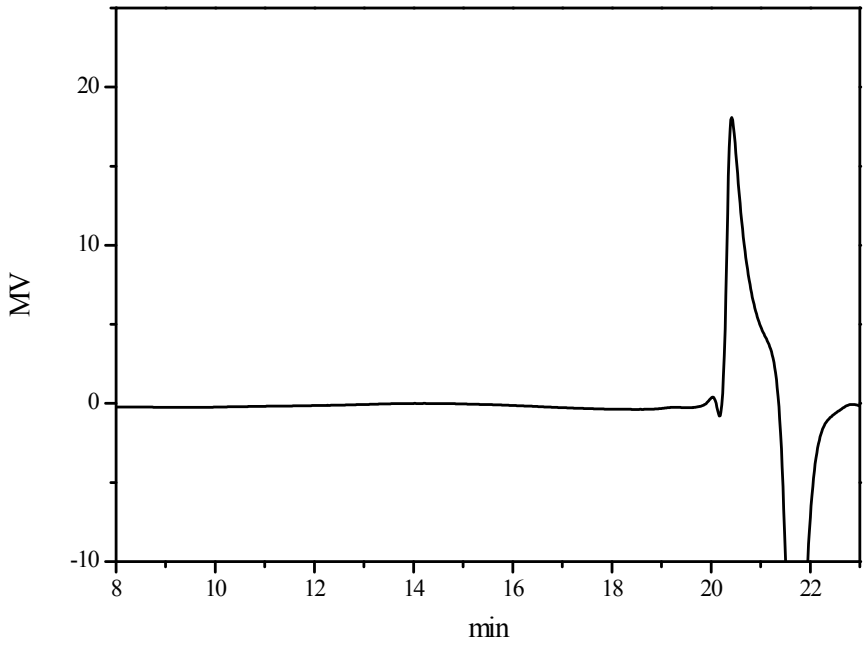
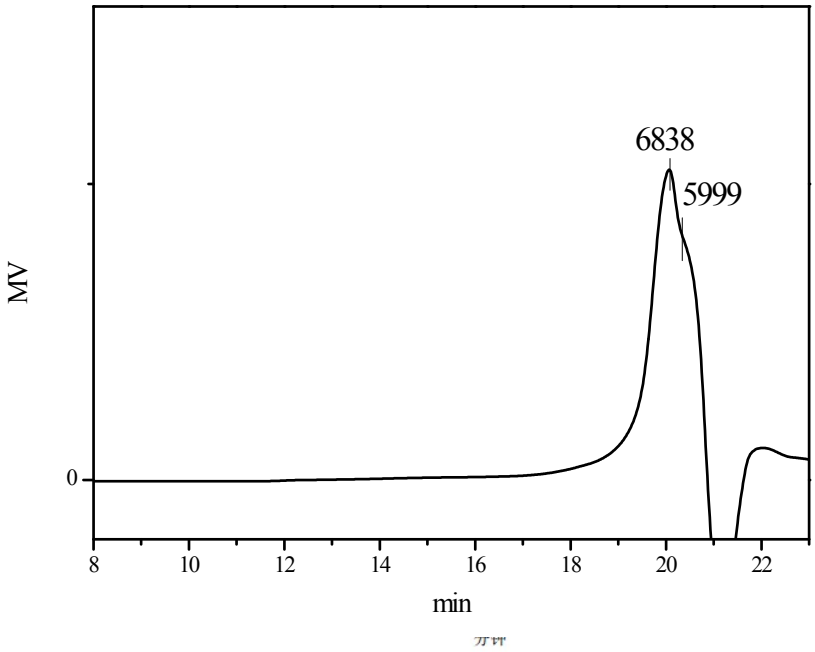


Figure S34. The GPC result of PPA of entry 9 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.067	20.067	20.067	8111	8771	6838	9710	10939	1.107000	1.247109
2		20.350	20.350	20.350	5279	5318	5999	5355	5391	1.007002	1.013691

Figure S35. The GPC result of PPA of entry 10 in Table 2.

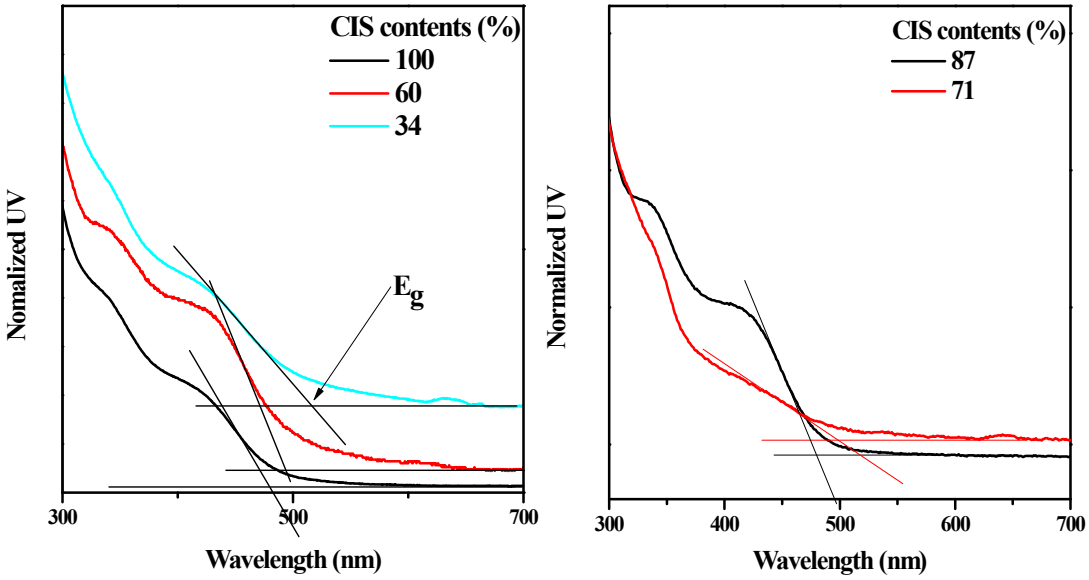


Figure S36. Calculation of Eg by the tangent of the max slope method.

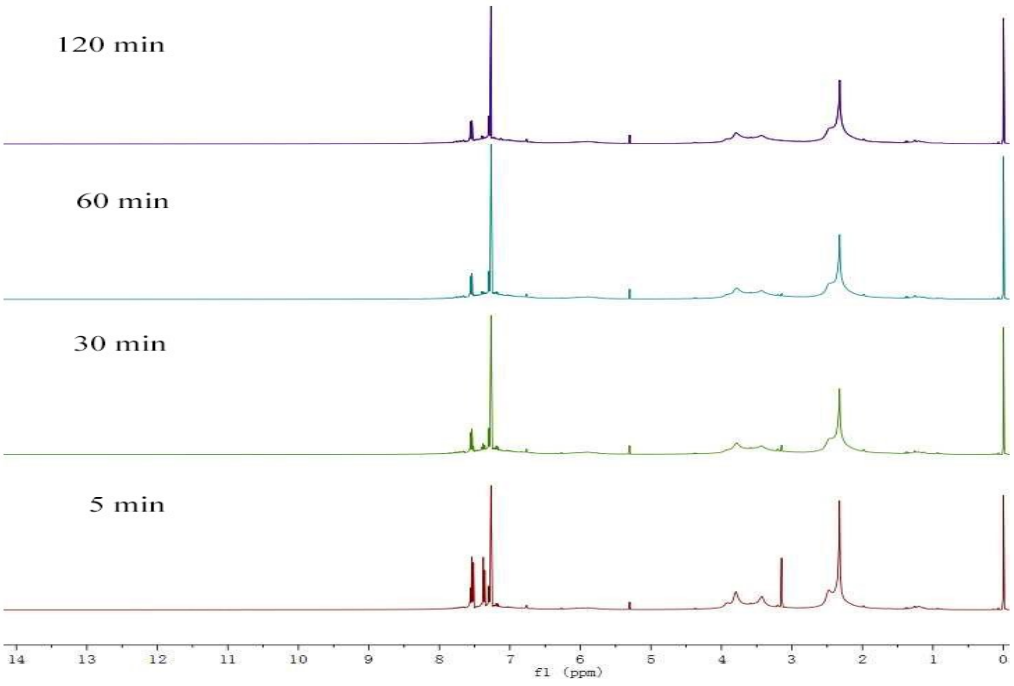


Figure S37. *In-situ* ^{1}H NMR spectra of polymerization of monomer **3** without cocatalyst at 40 ℃ in 5 min, 30 min, 60 min, 120min.

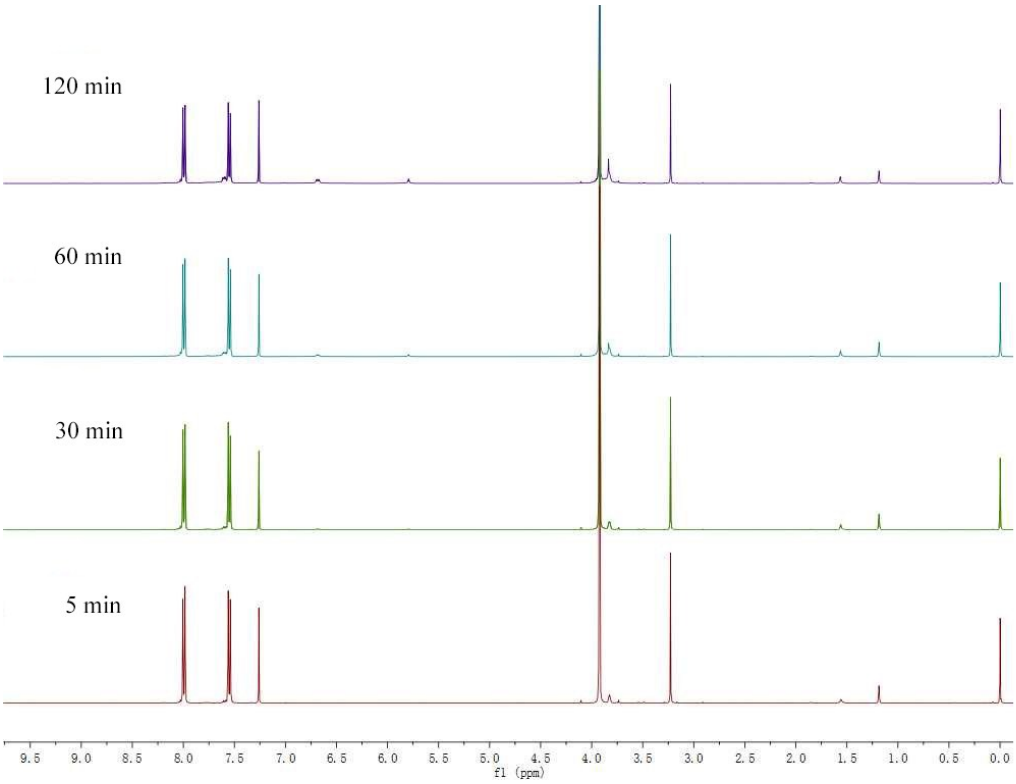


Figure S38. *In-situ* ^{1}H NMR spectra of polymerization of monomer **5** without cocatalysis at 40 ℃ in 5 min, 30 min, 60 min, 120min.

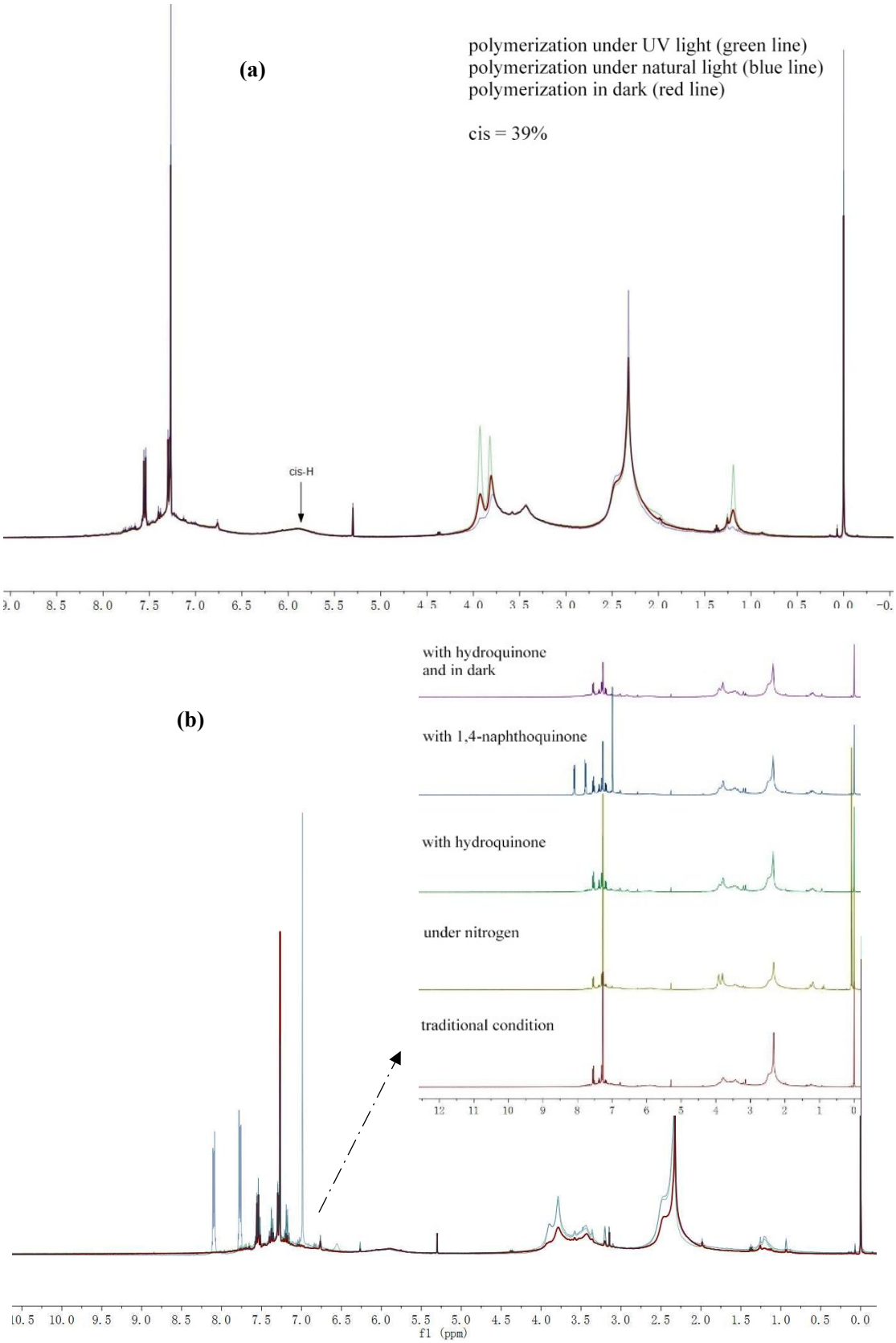
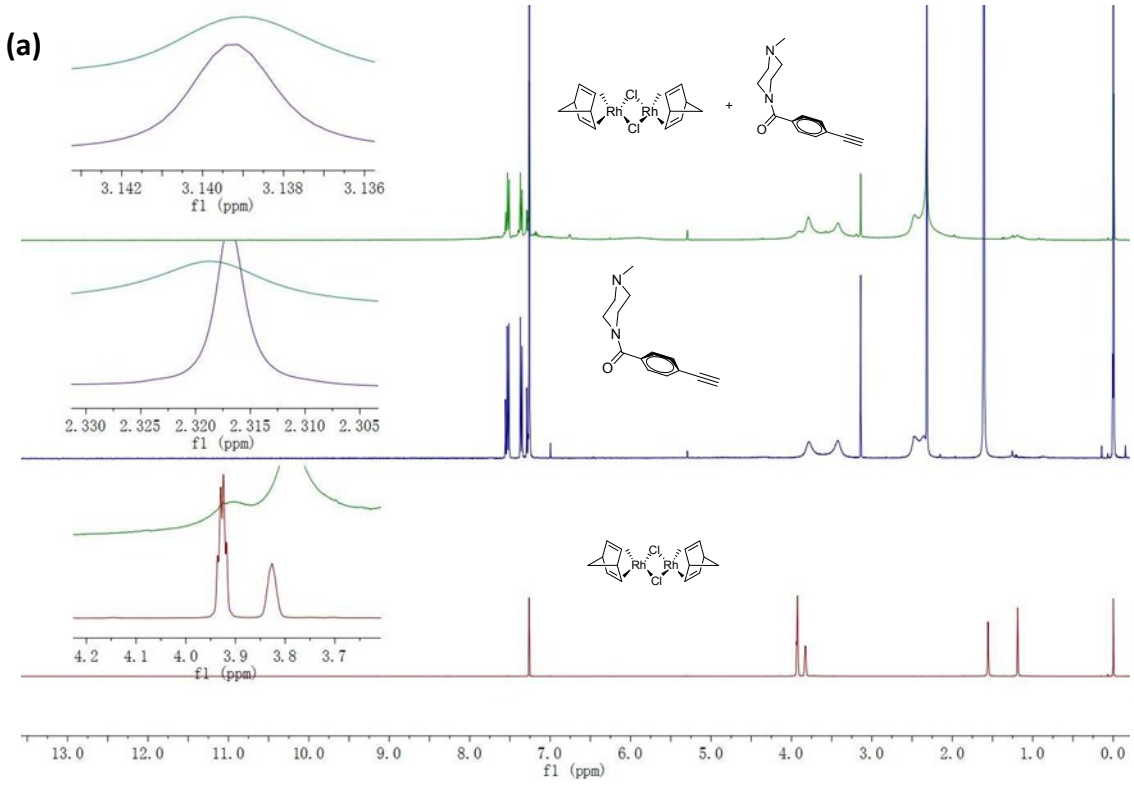


Figure S39. *In-situ* ^{1}H NMR spectra of polymerization of monomer **3** (a) under UV

light, under natural light and in dark. (b) in the presence of radical inhibitors such as hydroquinone and 1,4-naphthoquinone and under nitrogen

In the Figure S39, spectra under UV light, under natural light and in dark are almost overlapped, suggesting cis-content of polymers is approximately equal. Therefore, the light had not any influence on the polymerization. Moreover, spectra with the addition of radical inhibitors such as hydroquinone and 1,4-naphthoquinone and under nitrogen are almost overlapped, suggesting cis-content of polymers is approximately equal. the addition of radical inhibitors and oxygen could not restrain the polymerization, indeed ruling out the possibility of the thermal *cis-trans* isomerization and degradation via the radical mechanism. These results demonstrated that the cis-trans transformation and the decrease of molecular weight of the resulting PPAs occurred prior to double bond formation.


(a)
3.142 3.140 3.138 3.136
f1 (ppm)
2.330 2.325 2.320 2.315 2.310 2.305
f1 (ppm)
4.2 4.1 4.0 3.9 3.8 3.7
f1 (ppm)
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

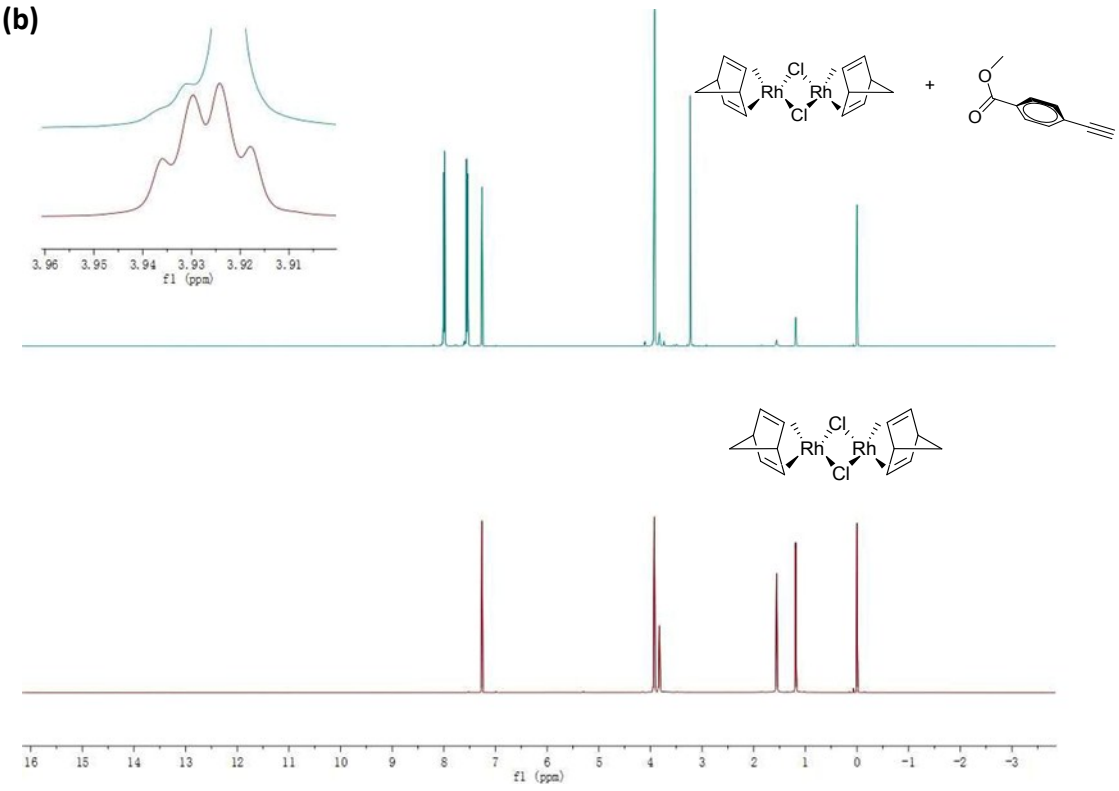

(b)
3.96 3.95 3.94 3.93 3.92 3.91
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

Figure S40. In situ ^{1}H NMR spectra of polymerization of phenylacetylenes: (a) comparison of NMR spectrum between $[Rh(nbd)Cl]_2$, monomer **3** and mixture. (b) comparison of NMR spectrum between mixture and monomer **5**.

NMR spectrums of $[Rh(nbd)Cl]_2$ and monomer **3** were shown in Figure S40 respectively. After mixed $[Rh(nbd)Cl]_2$ and monomer **3** together 5 min, the resonances of protons of double bond in nbd have changed from 3.925 ppm to 3.905 ppm (Figure S40 (a)). Similarly, the resonances of protons of methylene nearby tertiary nitrogen atom in piperazine and protons of acetenyl have changed from 2.317 ppm and 3.1393 ppm to 2.319 ppm and 3.1390 ppm respectively (Figure S40 (a)). It is indicated that rhodium was coordinative with tertiary nitrogen atom and acetenyl before insertion of monomer. Comparison of NMR spectrum between mixture and monomer **1** was shown in Figure S40. Without bifunctional monomer, the resonances of protons of double bond in nbd, methylene in piperazine and acetenyl have not changed (Figure S40 (b)). It was indicated that $[Rh(nbd)Cl]_2$ hardly translated into active species. Such results agreed with the truth that the monomer **5** can't polymerized without cocatalyst.

References

1 C. I. Simionescu, V. Percec, *J. Polym. Sci., Part A: Polym. Chem*., 1980, **18**, 147–155.

2 T. Masayoshi, Y. Wu, Y. Kazuaki, *J. Polym. Sci., Part A: Polym. Chem*., 1994, **32**, 1113–1120.

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