

Supporting Information

Engineering of Polystyrene-Supported Acid-Base Catalysts for Aldol Condensation in Water

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Table of Contents

1. Nomenclature and Abbreviations	S3
2. Organic Synthesis	S4
3. NMR Data	S7
4. DLS Data	S15
5. TEM Image	S19
6. FT-IR spectra	S20
7. Condensation reactions.....	S21
8. References	S22

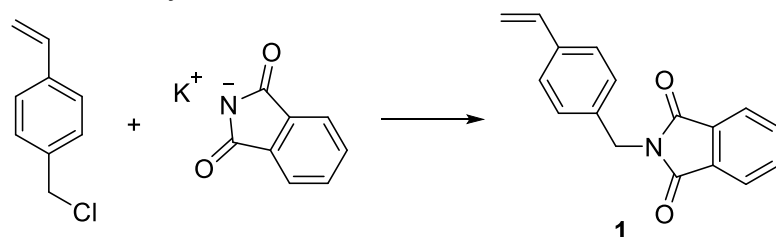
1. Nomenclature and Abbreviations

Table S1. Nomenclature and abbreviations

Abbreviation	Name/description
DCM	dichloromethane
DLS	dynamic light scattering
DMF	<i>N,N</i> -dimethylformamide
EtOAc	ethyl acetate
FT-IR	Fourier-transform infrared spectroscopy
GPC	gel permeation chromatography
M_n	number average molecular weight
M_w	weight average molecular weight
NMR	nuclear magnetic resonance
PDI	polydispersity index
PE	petroleum ether
TEM	transmission electron microscopy
THF	tetrahydrofuran
TLC	thin-layer chromatography

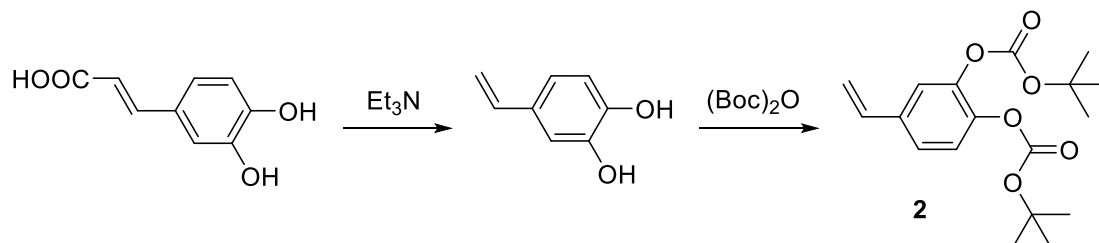
2. Organic Synthesis

Scheme S1. Synthesis of **1**.



Compound **1** was synthesized (Scheme S1) according to a previously reported procedure.¹ To a flask was added 4-vinylbenzyl chloride (10.77 g, 70.36 mmol), *N,N*-dimethylformamide (40 mL), and potassium phthalimide (13.02 g, 70.36 mmol). The reaction mixture was stirred at room temperature for 24 h. After which, the solution was added to an aqueous solution of NaOH (1 M, 1 L), and the formed precipitate was collected by filtration, and dissolved in ethyl acetate (100 mL). The solvent was removed under reduced pressure and the desired product was recrystallized from methanol three times to afford **1** as a white crystal (5.80 g, 22.04 mmol, 22 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.41 – 7.33 (m, 4H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 18.4 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.83 (s, 2H).

Scheme S2. Synthesis of **2**.



Compound **2** was synthesized (Scheme S2) according to a previously reported procedure.² To a two-neck flask was added caffeic acid (8.00 g, 44.4 mmol), *N,N*-dimethylformamide (60 mL), and triethylamine (13.48 g, 133.2 mmol). The solution was stirred at 100°C under a nitrogen atmosphere for 1 h. After cooling to room temperature, the solvent was removed under reduced pressure to give a viscous tan oil, which was purified by column chromatography to give 4-vinylbenzene-1,2-diol as a yellow oil (4.11 g, 68%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.99 (s, 2H), 6.86 (s, 1H), 6.69 (s, 2H), 6.52 (s, 1H), 5.52 (s, 1H), 5.02 (s, 1H). To a two-neck flask was added di-tert-butyl decarbonate (16.03 g, 73.45 mmol), 4-dimethylaminopyridine (225 mg, 1.84 mmol), and THF (15 mL). After stirring for 10 min, 4-vinylbenzene-1,2-diol (2.50 g, 18.4 mmol) was added. The reaction mixture was stirred for 12 h. After which, the solvent was removed under reduced pressure to give a yellow oil, which was washed with an aqueous solution of ammonium chloride (5 wt%) three times and extracted with ethyl acetate. The crude product was purified by column chromatography to afford **2** as a yellow oil (2.97 g, 48 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.19 (m, 5H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.69 (d, *J* = 17.5 Hz, 1H), 5.27 (d, *J* =

10.9 Hz, 1H), 1.55 (d, J = 2.8 Hz, 18H).

Scheme S3. Synthesis of **PPA1**, **PPA2**, **PPA3**, **PPA4**.

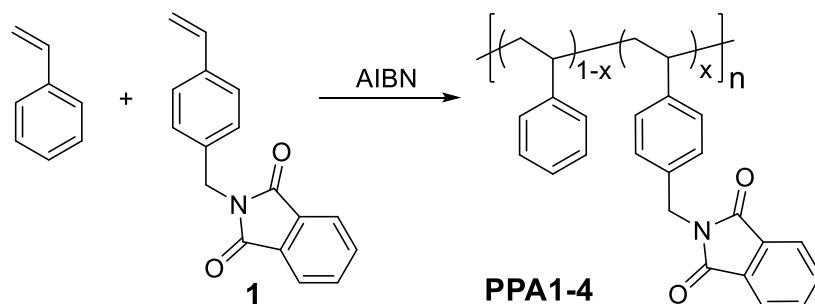


Table S2. Feed amount and yield of the synthesis of **PPA1**, **PPA2**, **PPA3**, and **PPA4**.

Polymer	Feed amount				Yield / %
	AIBN/mg	Styrene / g	1 / g	1,4-Dioxane / mL	
PPA1	40	1.56	0.44	30	40
PPA2	42	1.38	0.70	30	58
PPA3	40	1.07	0.90	30	56
PPA4	43	0.95	1.20	30	42

Scheme S4. Synthesis of **PA1**, **PA2**, **PA3**, and **PA4**.

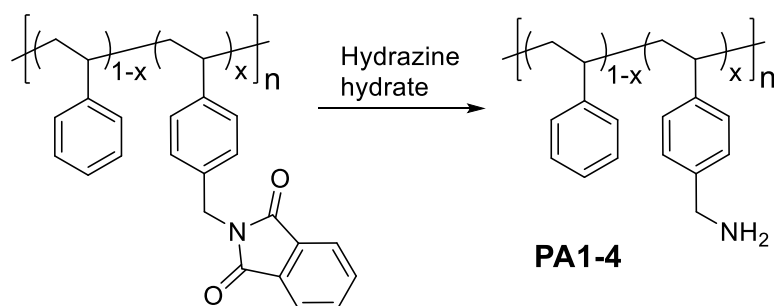


Table S3. Feed amount and yield of the synthesis of **PA1**, **PA2**, **PA3**, and **PA4**.

Polymer after deprotection	Feed amount		1,4-Dioxane/mL	Yield/%
	Polymer/g	N ₂ H ₄ ·H ₂ O/mL		
PA1	0.53	0.27	30mL	65
PA2	0.2	0.31	15mL	48
PA3	0.6	0.6	30mL	71
PA4	0.2	0.4	15mL	58

Scheme S5. Synthesis of **PPC1**, **PPC2**, and **PPC3**.

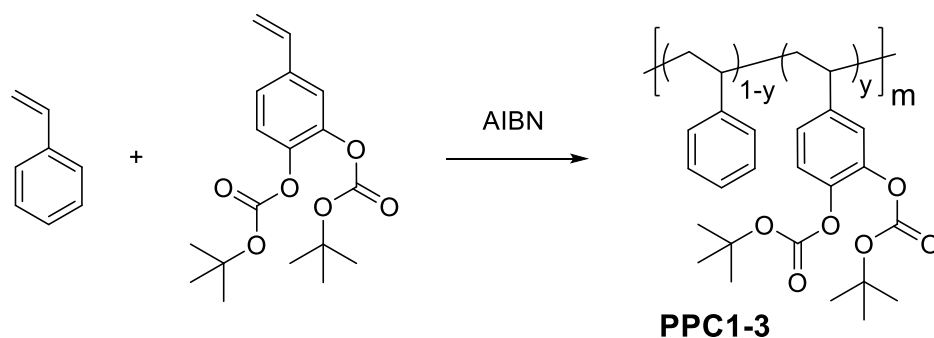


Table S4. Feed amount and yield of the synthesis of **PPC1**, **PPC2**, and **PPC3**.

Polymer	Feed amount				Yield / %
	AIBN / mg	Styrene / g	2 / g	1,4-Dioxane / mL	
PPC1	40	1.48	0.53	30	47
PPC2	41	1.05	0.98	30	42
PPC3	42	0.50	1.61	30	60

Scheme S6. Synthesis of **PC1**, **PC2**, and **PC3**.

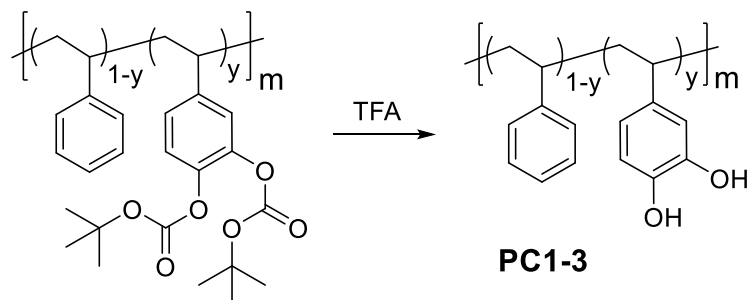
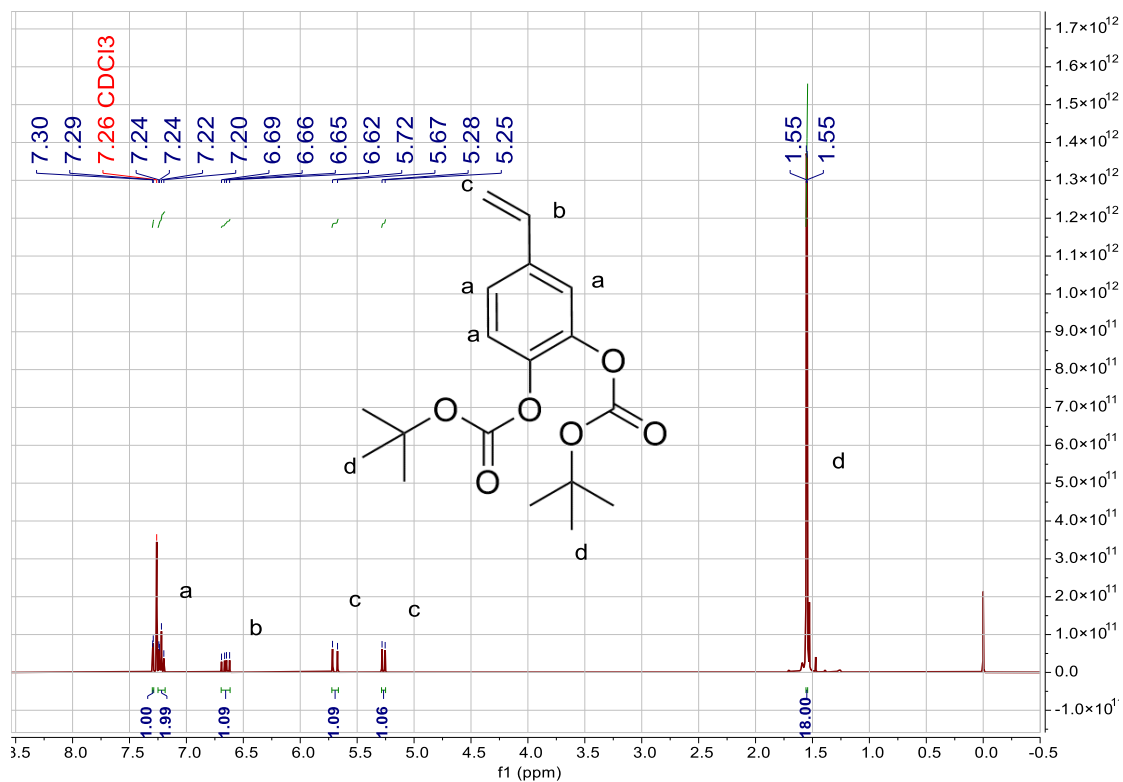
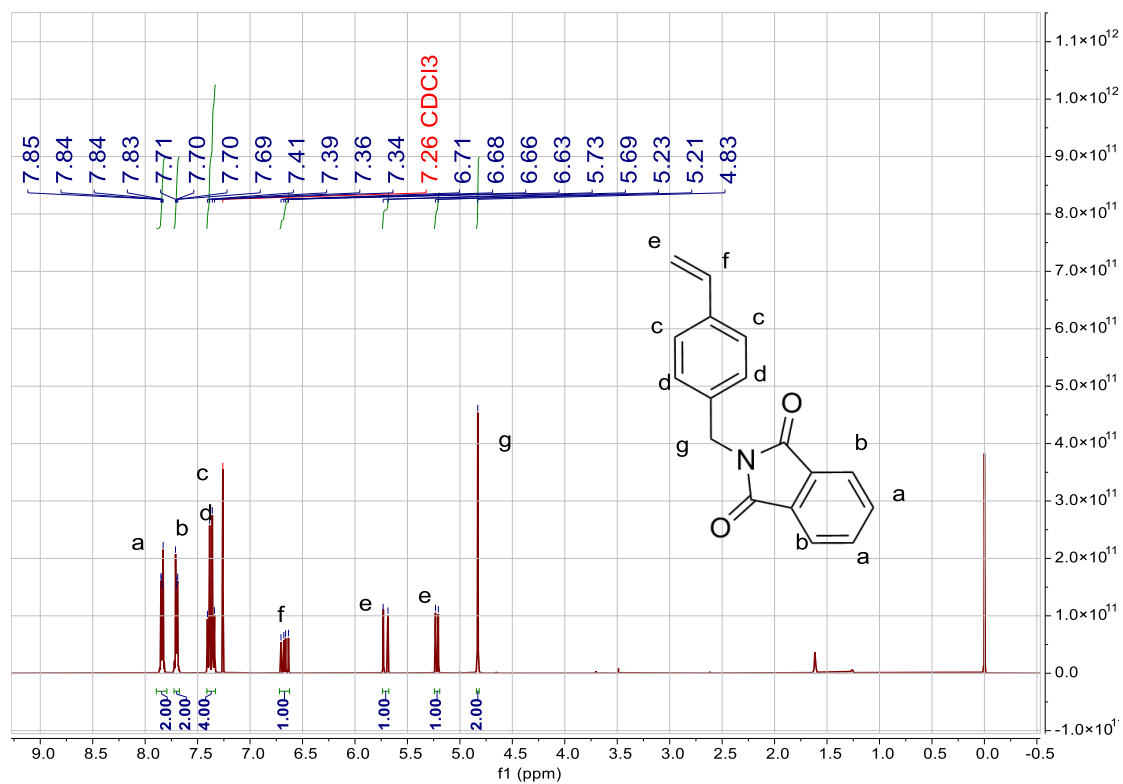


Table S5. Feed amount and yield of the synthesis of **PC1**, **PC2**, and **PC3**.

Polymer after deprotection	Feed amount		DCM/mL	Yield/%
	Polymer/g	TFA/mL		
PC1	0.4	0.26	25mL	65
PC2	0.38	0.26	25mL	46
PC3	0.5	0.85	25mL	39

3. NMR Data



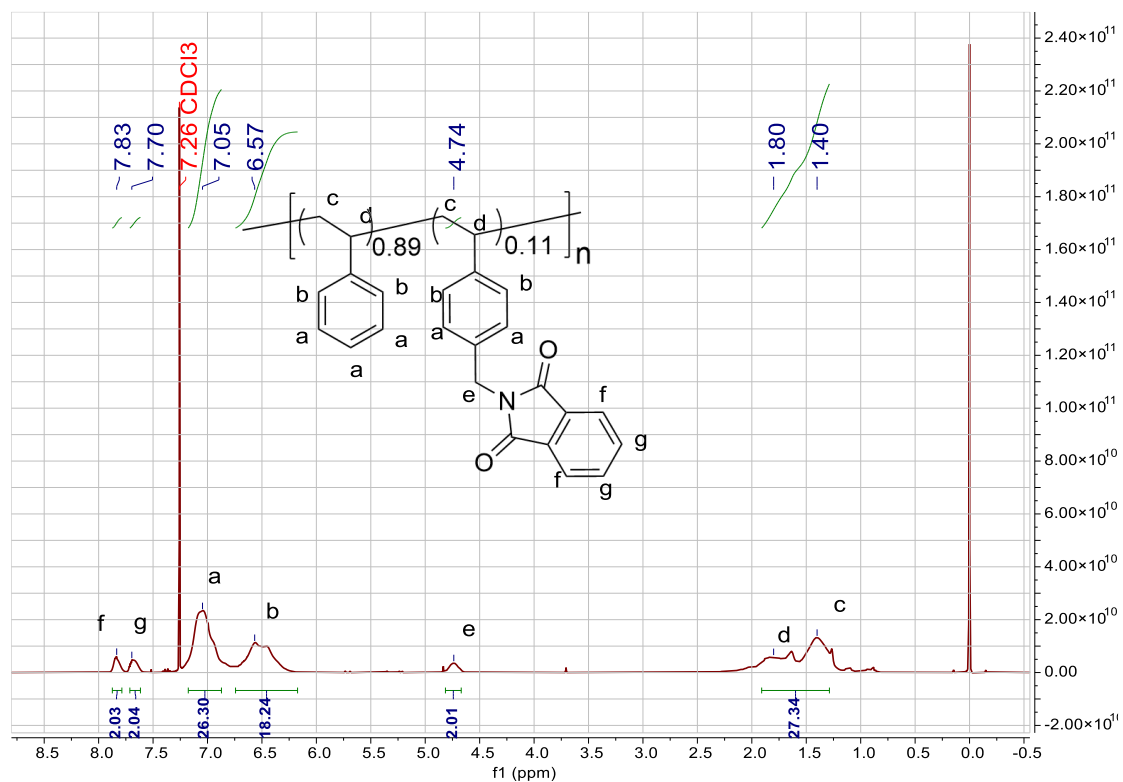


Figure S3. ¹H NMR spectrum in CDCl₃ of PPA1.

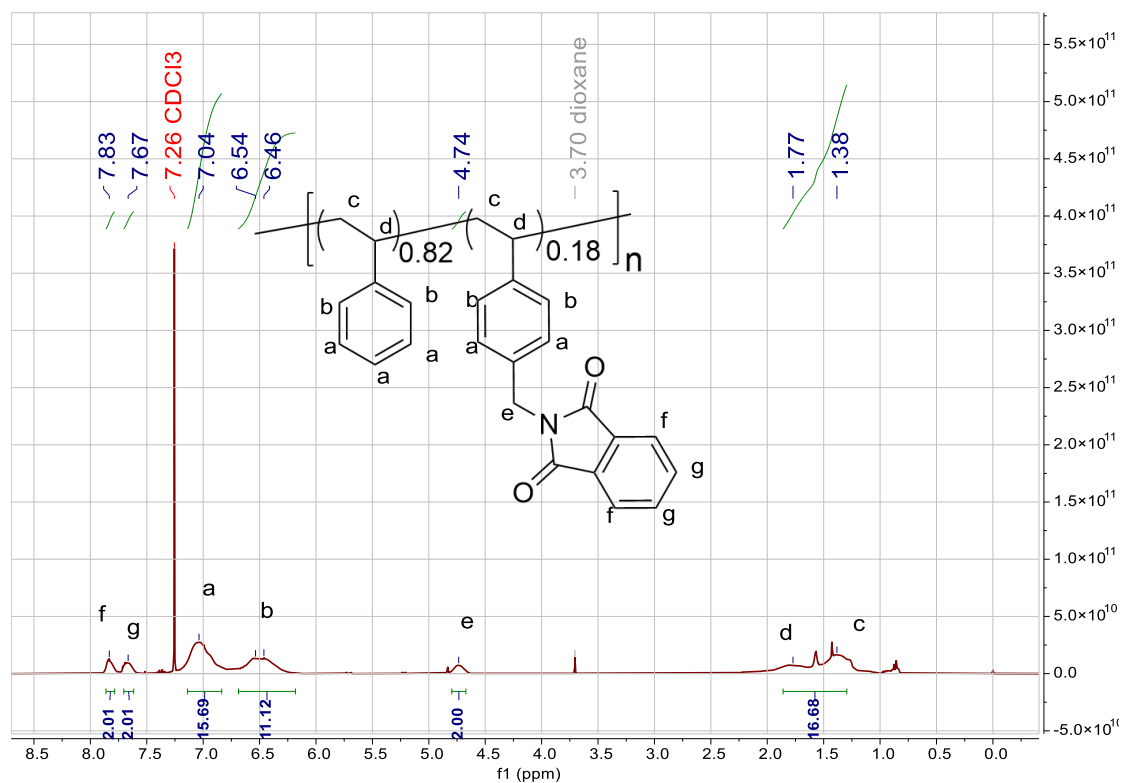


Figure S4. ¹H NMR spectrum in CDCl₃ of PPA2. The signal at 3.70 ppm arises from 1,4-dioxane.

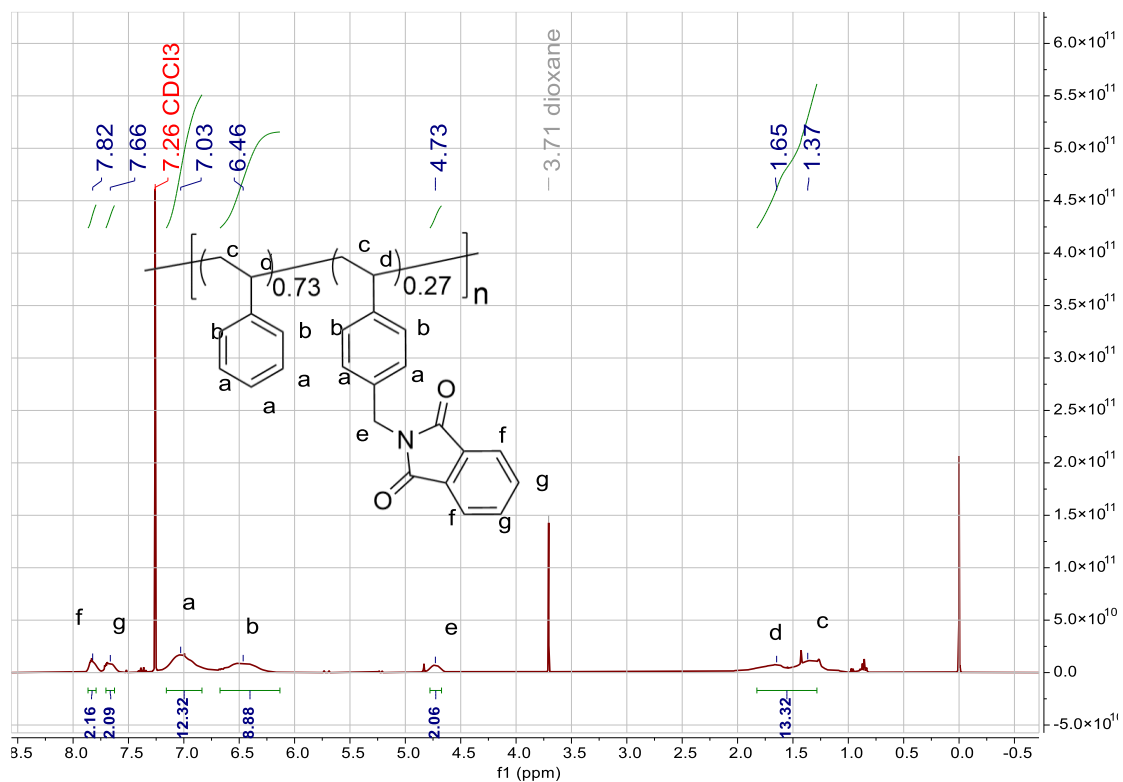


Figure S5. ^1H NMR spectrum in CDCl_3 of PPA3. The signal at 3.71 ppm arises from 1,4-dioxane.

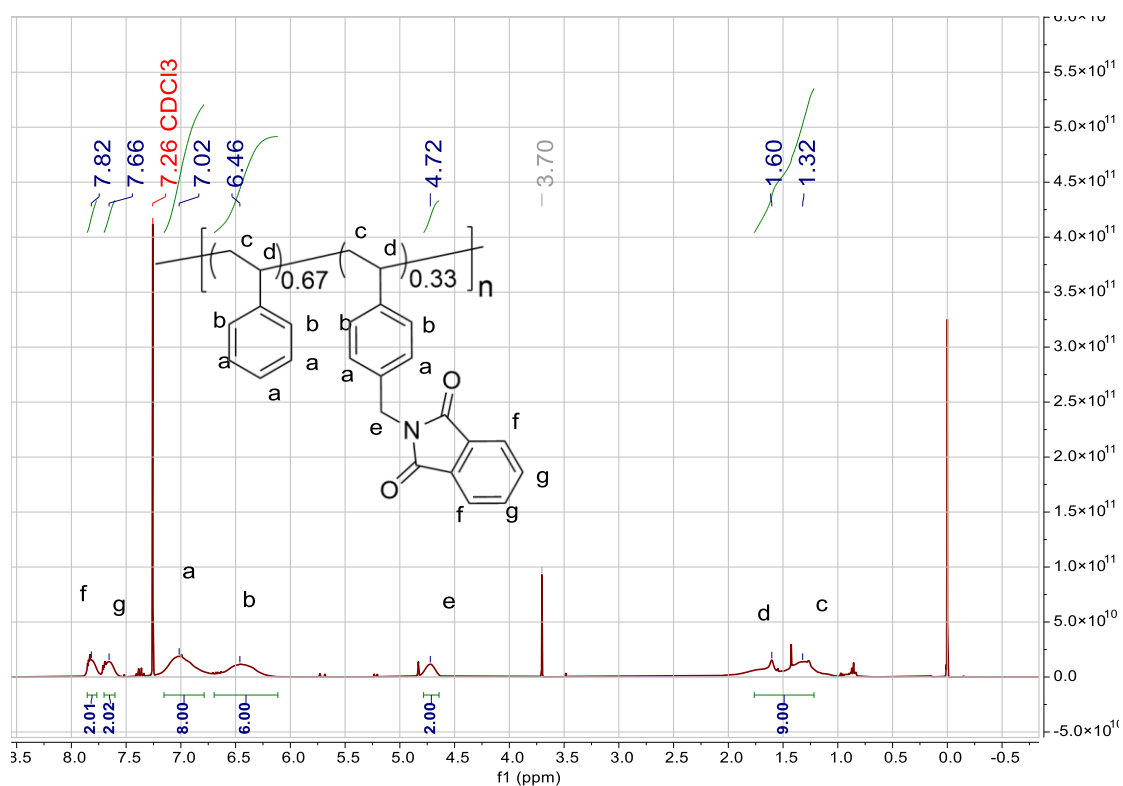


Figure S6. ^1H NMR spectrum in CDCl_3 of PPA4. The signal at 3.70 ppm arises from 1,4-dioxane.

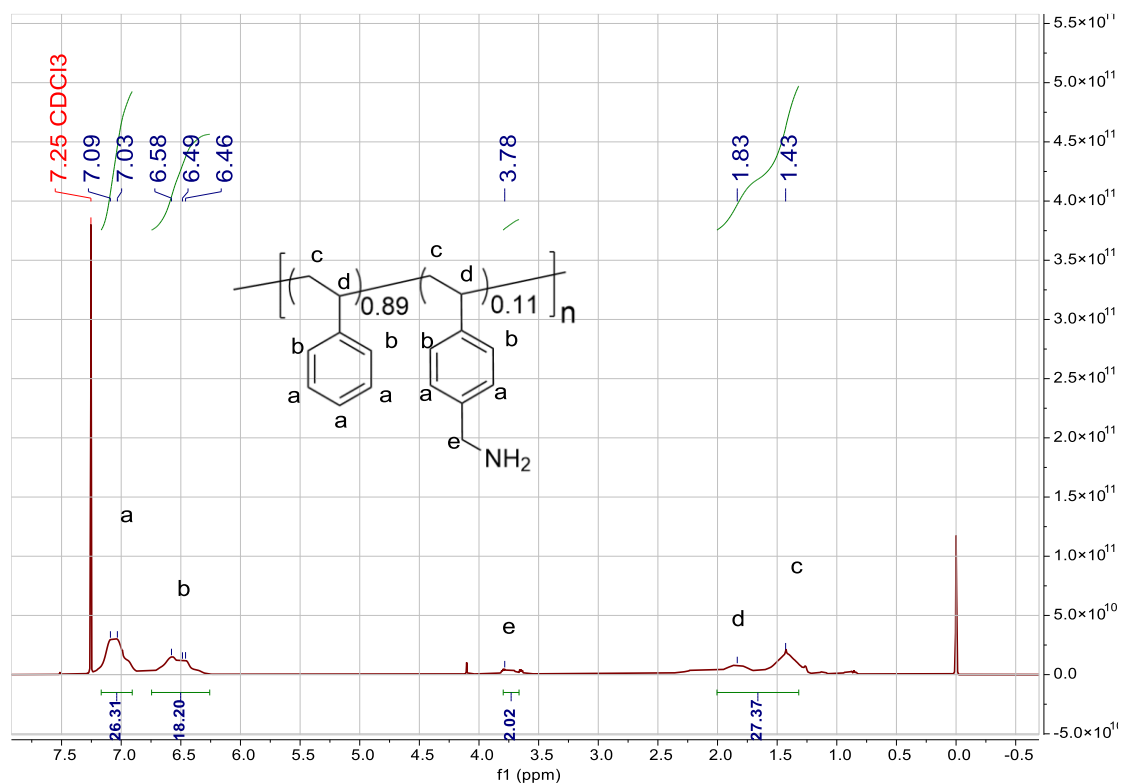


Figure S7. ^1H NMR spectrum in CDCl_3 of PA1.

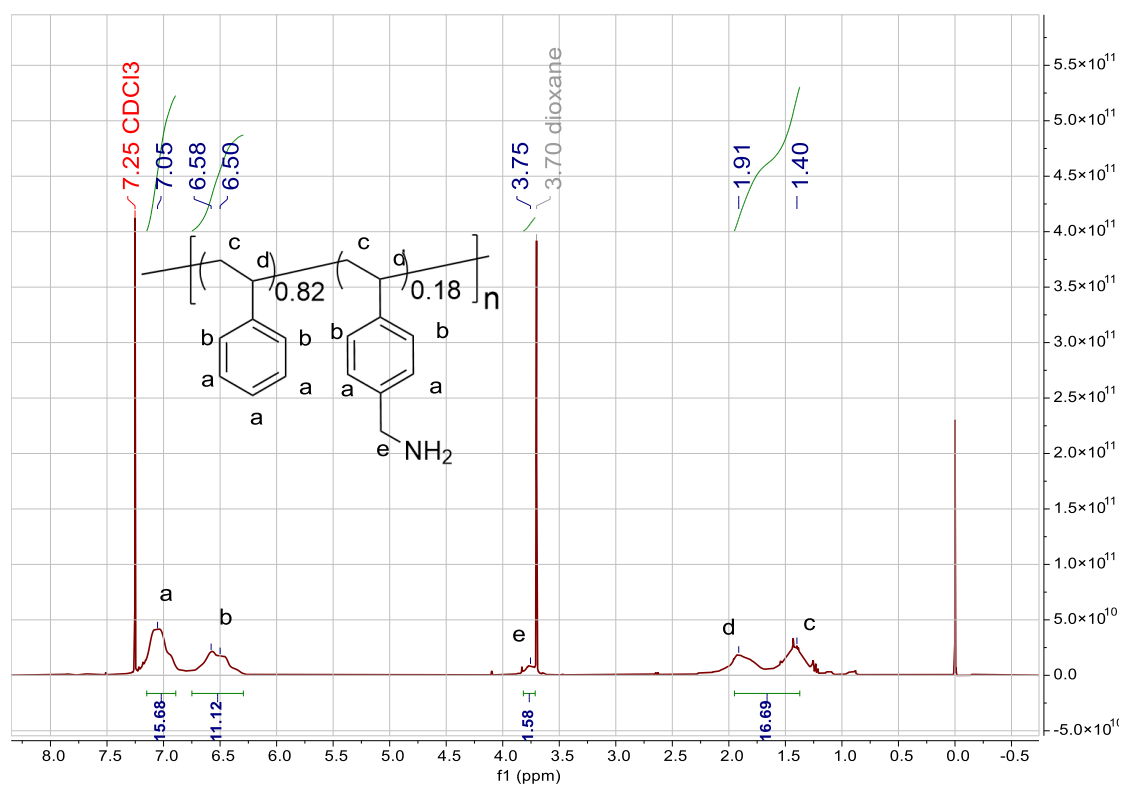


Figure S8. ^1H NMR spectrum in CDCl_3 of PA2. The signal at 3.70 ppm arises from 1,4-dioxane.

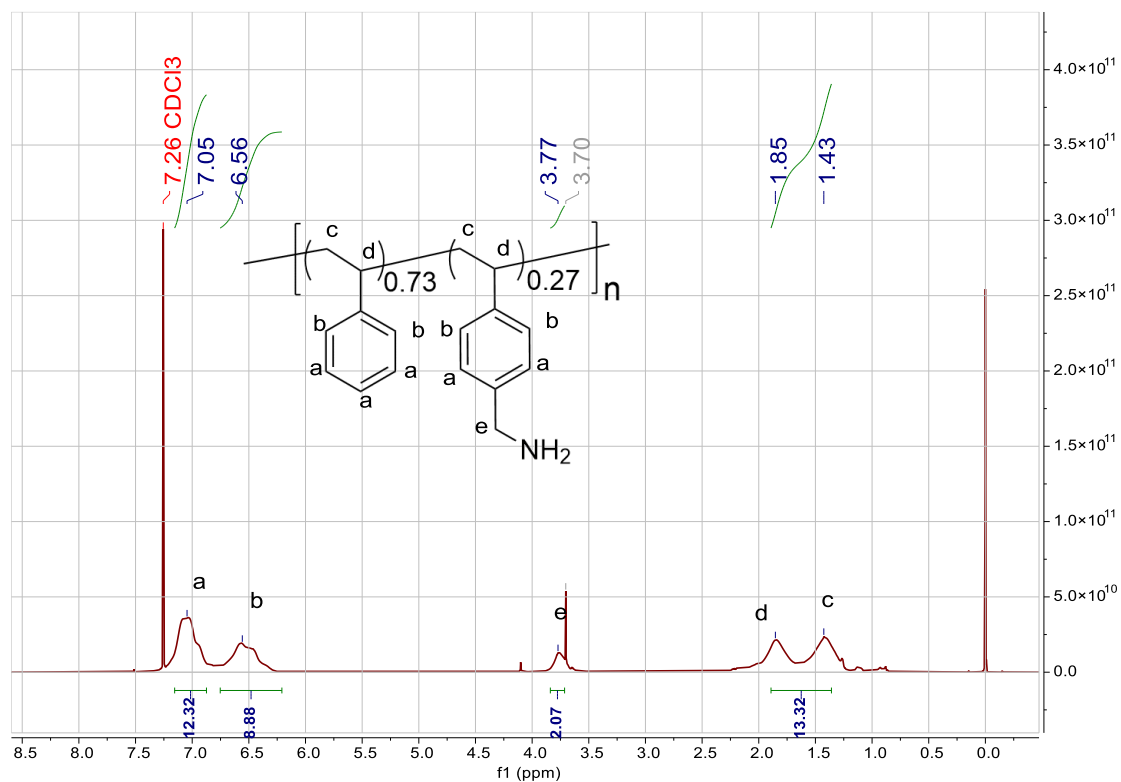


Figure S9. ^1H NMR spectrum in CDCl_3 of PA3. The signal at 3.70 ppm arises from 1,4-dioxane.

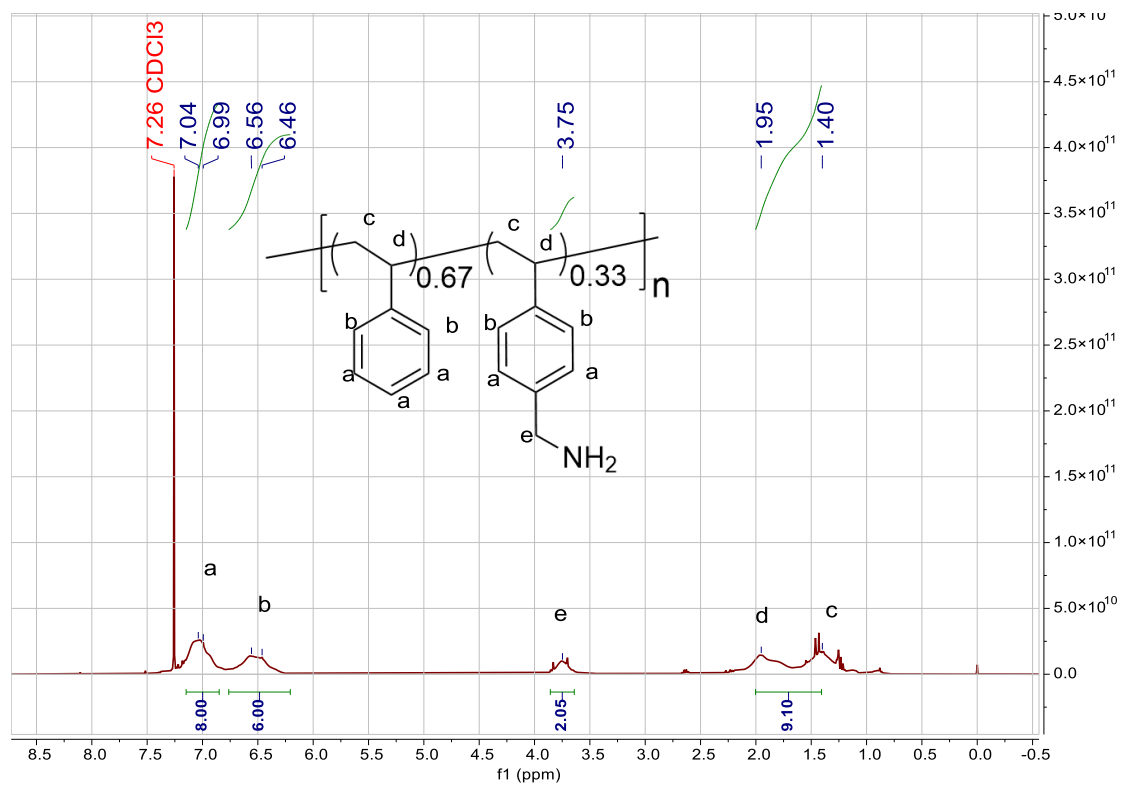


Figure S10. ^1H NMR spectrum in CDCl_3 of PA4. The signal at 3.70 ppm arises from 1,4-dioxane.

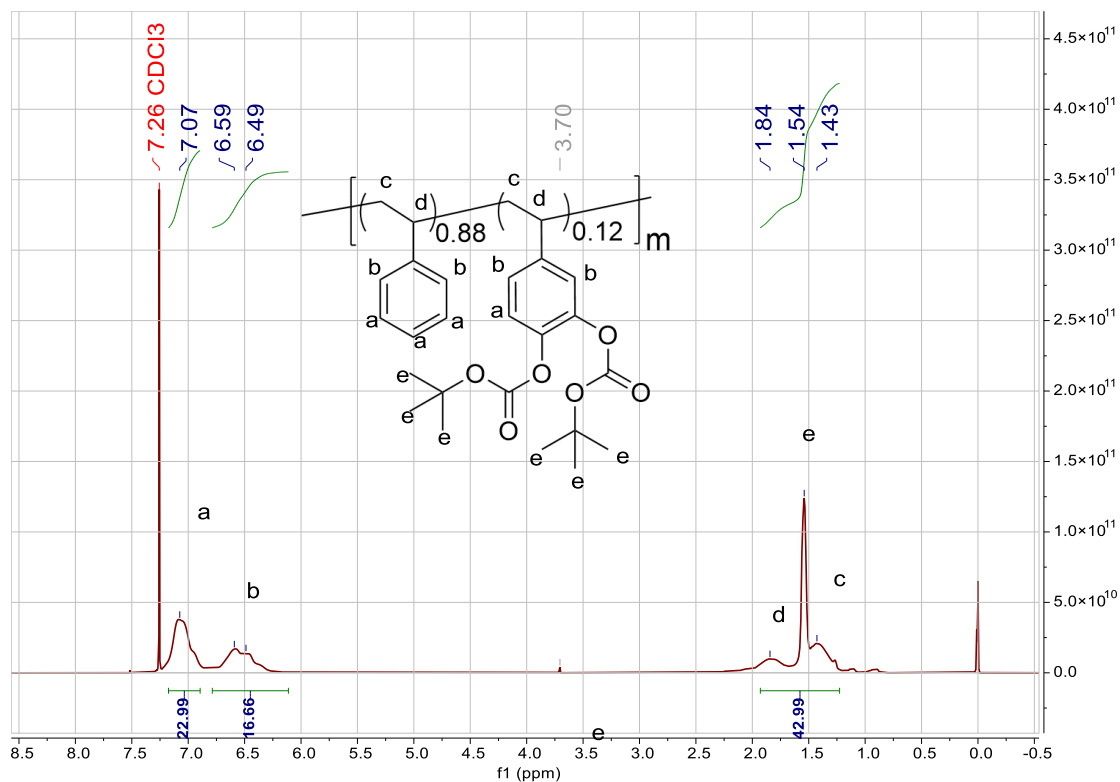


Figure S11. ^1H NMR spectrum in CDCl_3 of **PPC1**. The signal at 3.70 ppm arises from 1,4-dioxane.

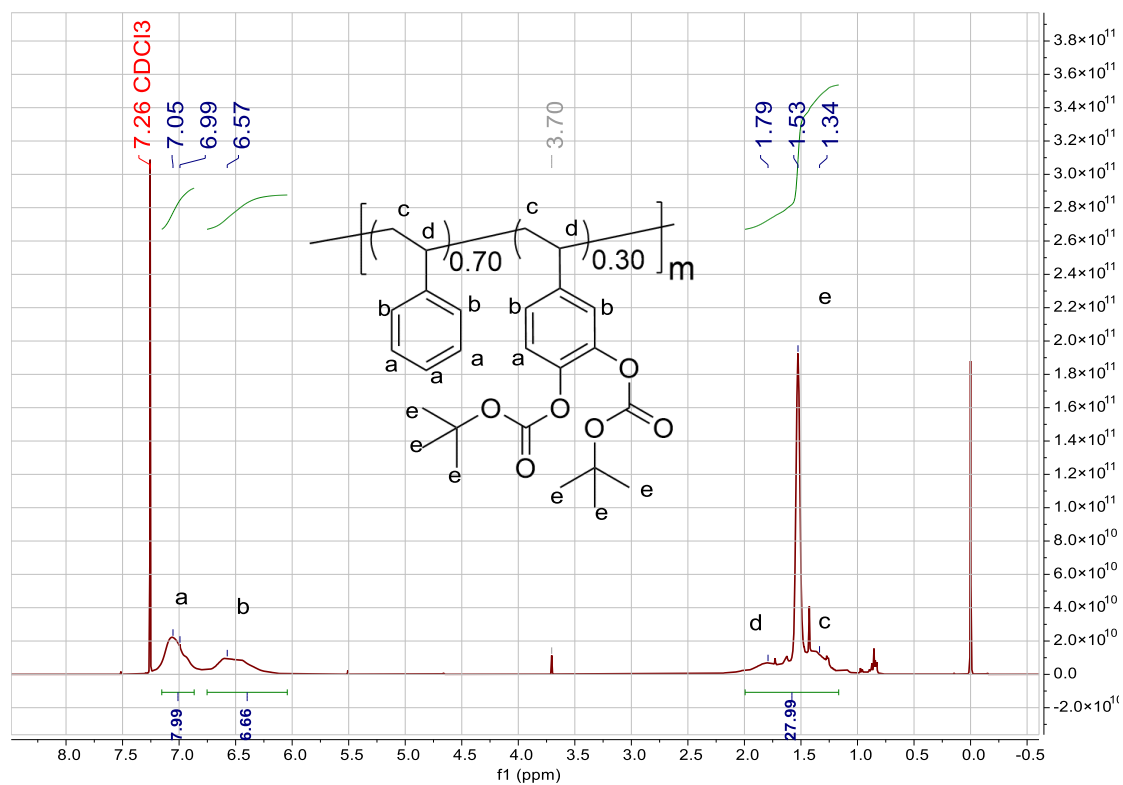


Figure S12. ^1H NMR spectrum in CDCl_3 of **PPC2**. The signal at 3.70 ppm arises from 1,4-dioxane.

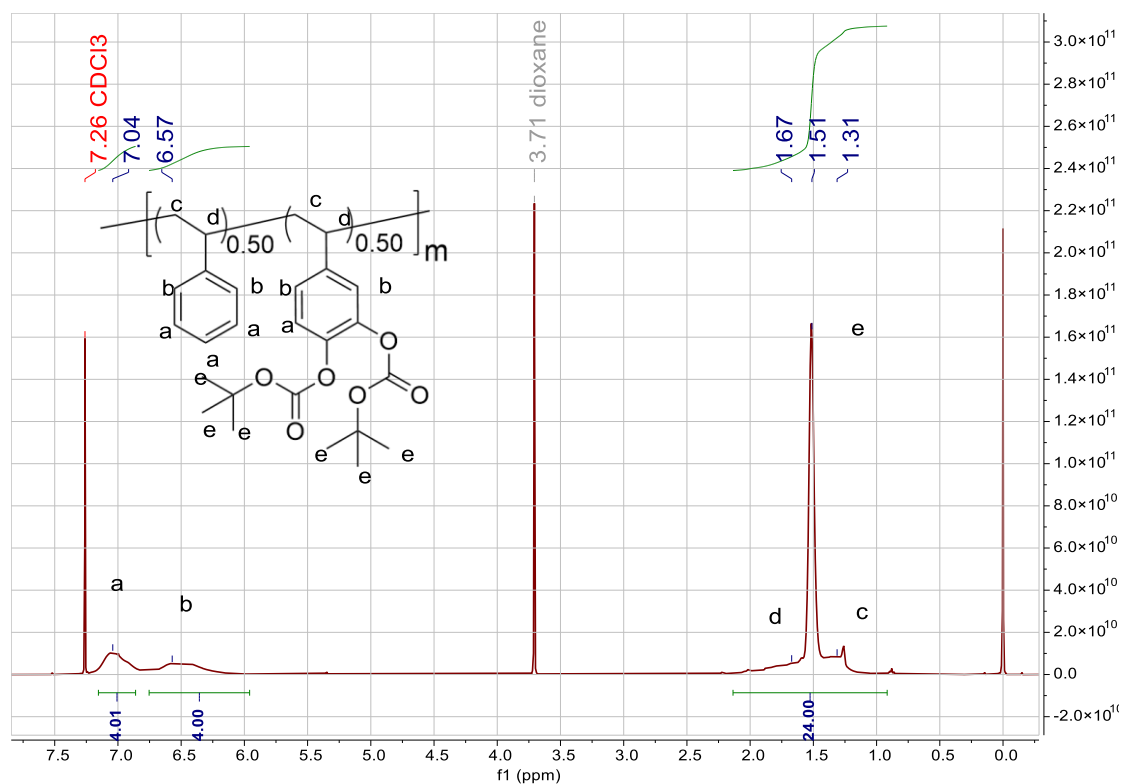


Figure S13. ^1H NMR spectrum in CDCl_3 of PPC3. The signal at 3.71 ppm arises from 1,4-dioxane.

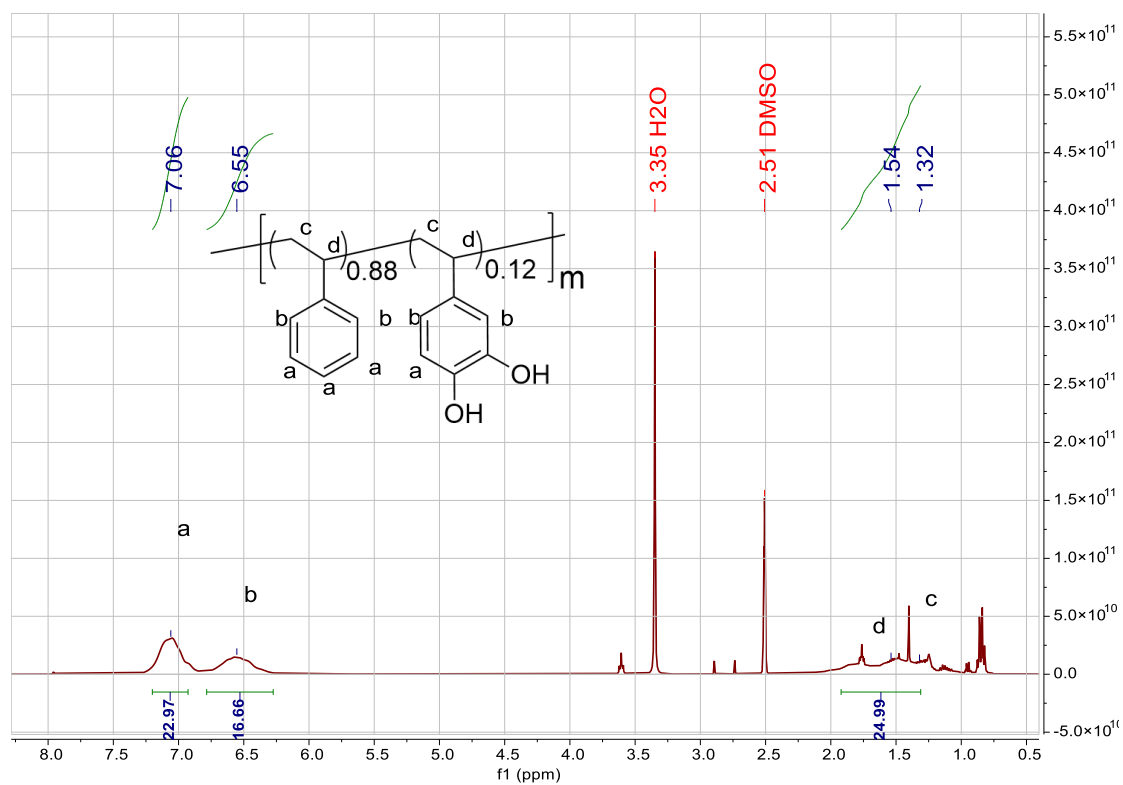


Figure S14. ^1H NMR spectrum in DMSO of PC1. The signal at 3.35 ppm arises from water.

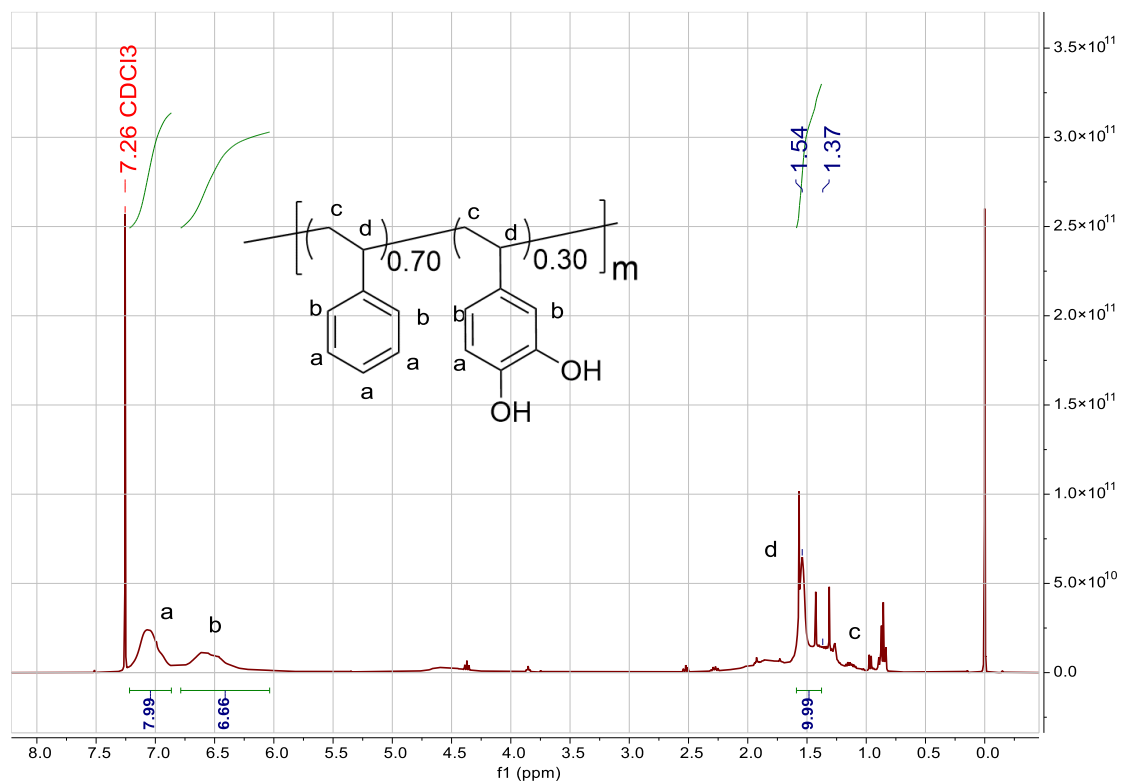


Figure S15. ^1H NMR spectrum in CDCl_3 of **PC2**.

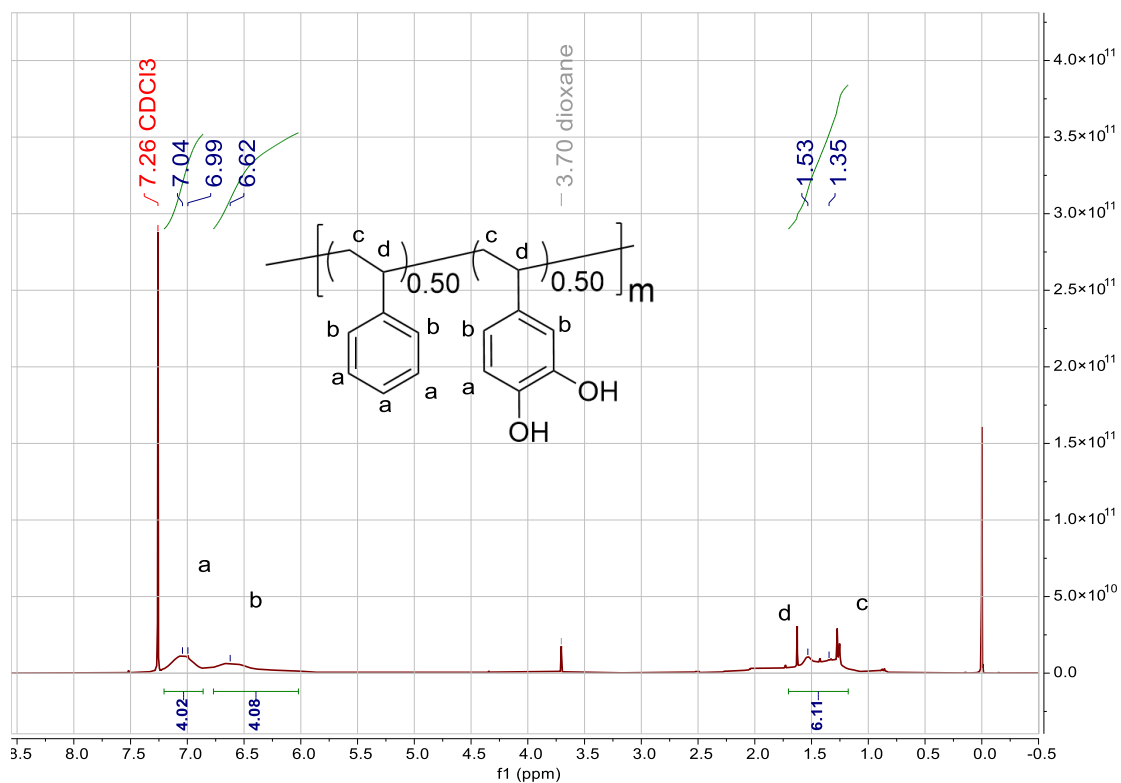


Figure S16. ^1H NMR spectrum in CDCl_3 of **PC3**. The signal at 3.70 ppm arises from 1,4-dioxane.

4. DLS Data

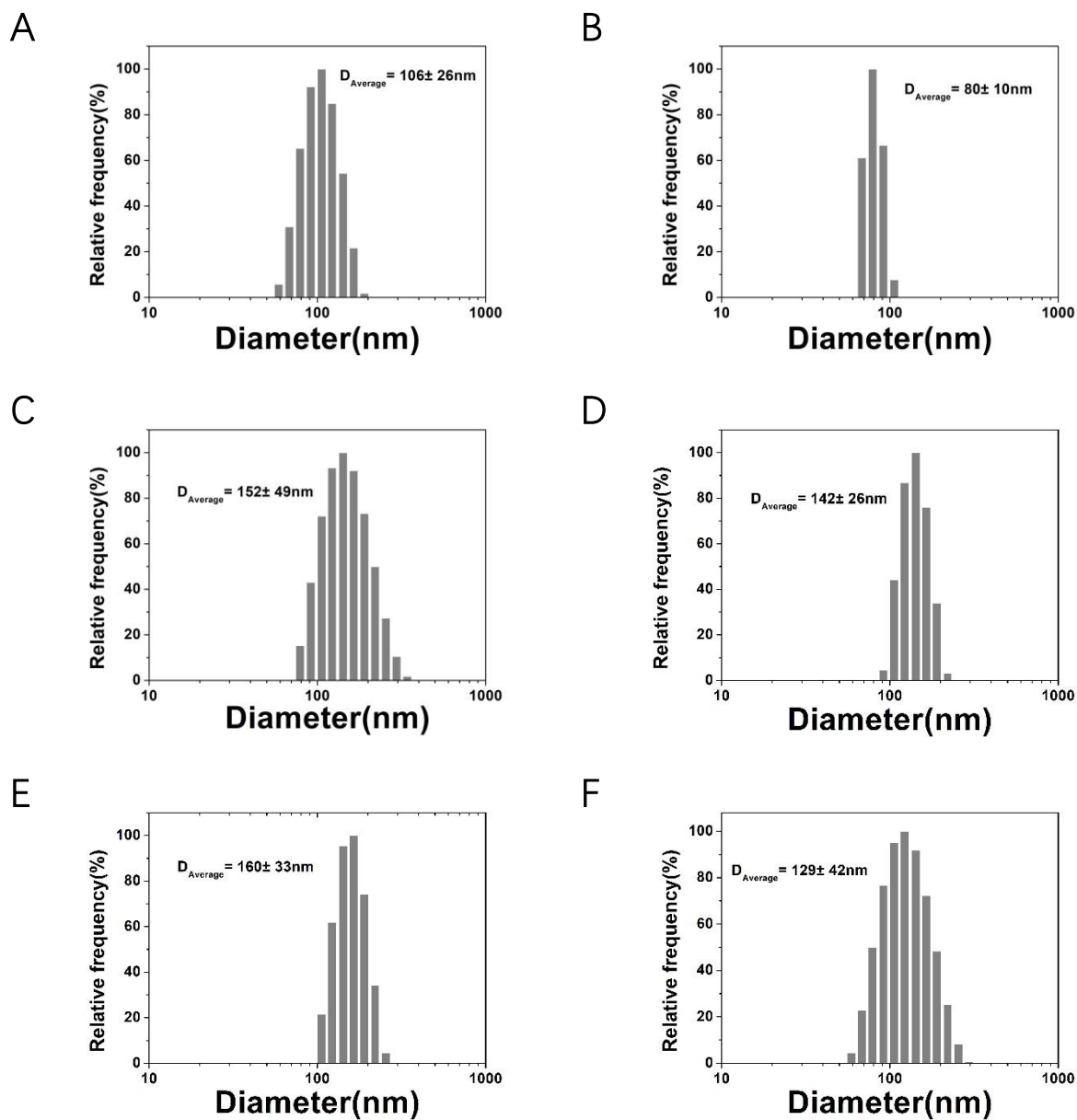


Figure S17. Size distributions of nanoparticles prepared by using (A) **PC1** (5 mol%), (B) **PA3** (5 mol%), (C) **PC1/PA3** (5/5 mol%), and (D) **PC1/PA3** (10/10 mol%), (E) **PC1/PA3** (15/15 mol%), (F) **PC1/PA3** (20/20 mol%).

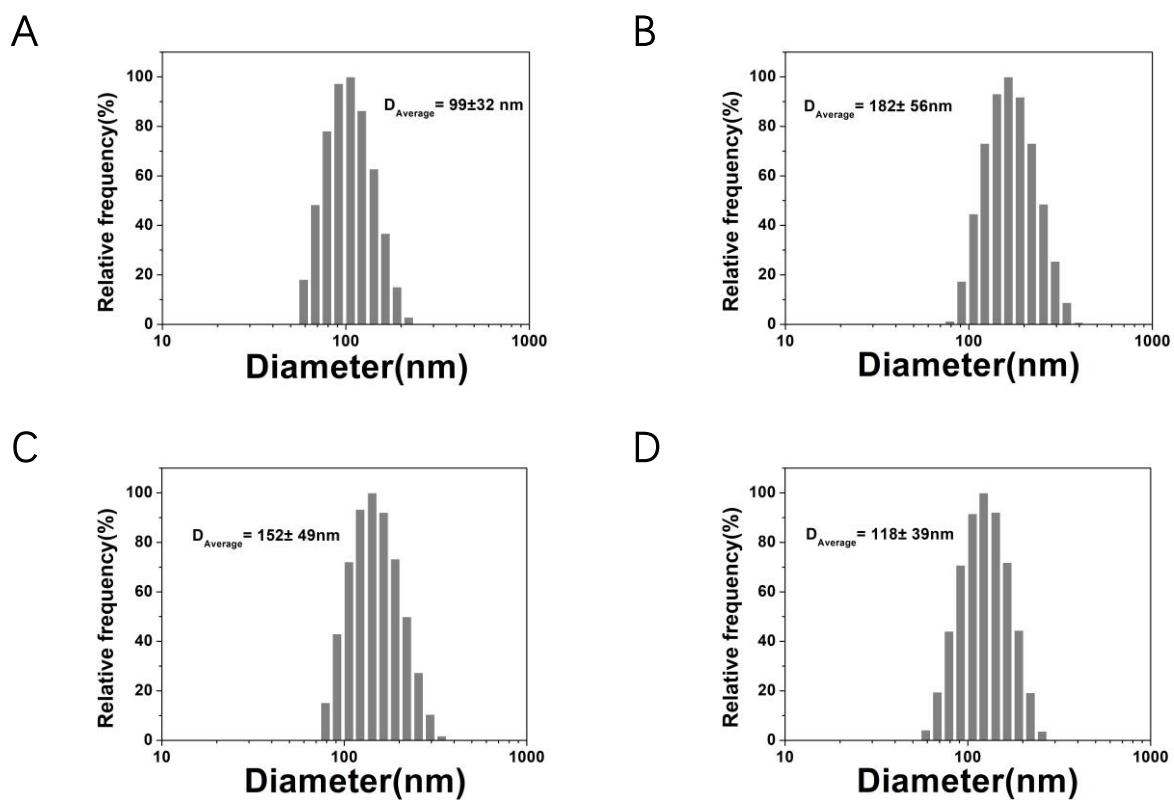


Figure S18. Size distributions of nanoparticles prepared by using (A) **PC1/PA1** (5/5 mol%), (B) **PC1/PA2** (5/5 mol%), (C) **PC1/PA3** (5/5 mol%), and (D) **PC1/PA4** (5/5 mol%).

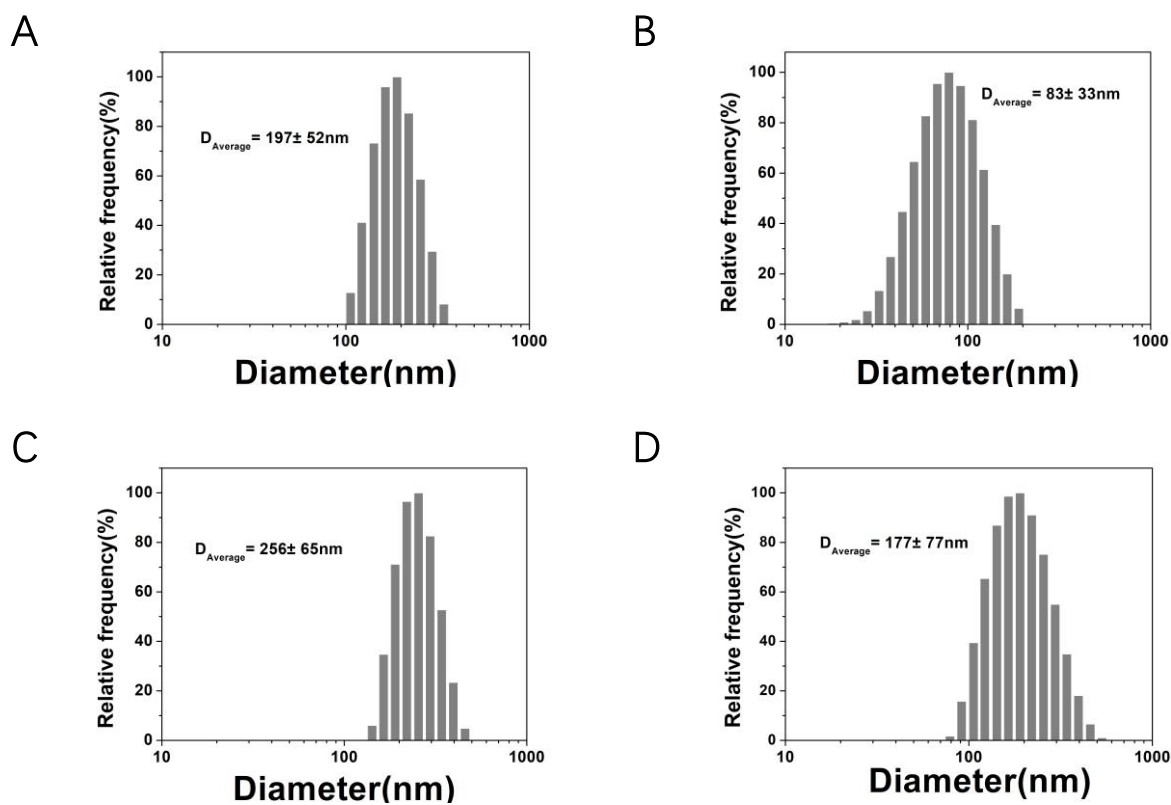


Figure S19. Size distributions of nanoparticles prepared by using (A) **PC2/PA1** (5/5 mol%), (B) **PC2/PA2** (5/5 mol%), (C) **PC2/PA3** (5/5 mol%), and (D) **PC2/PA4** (5/5 mol%).

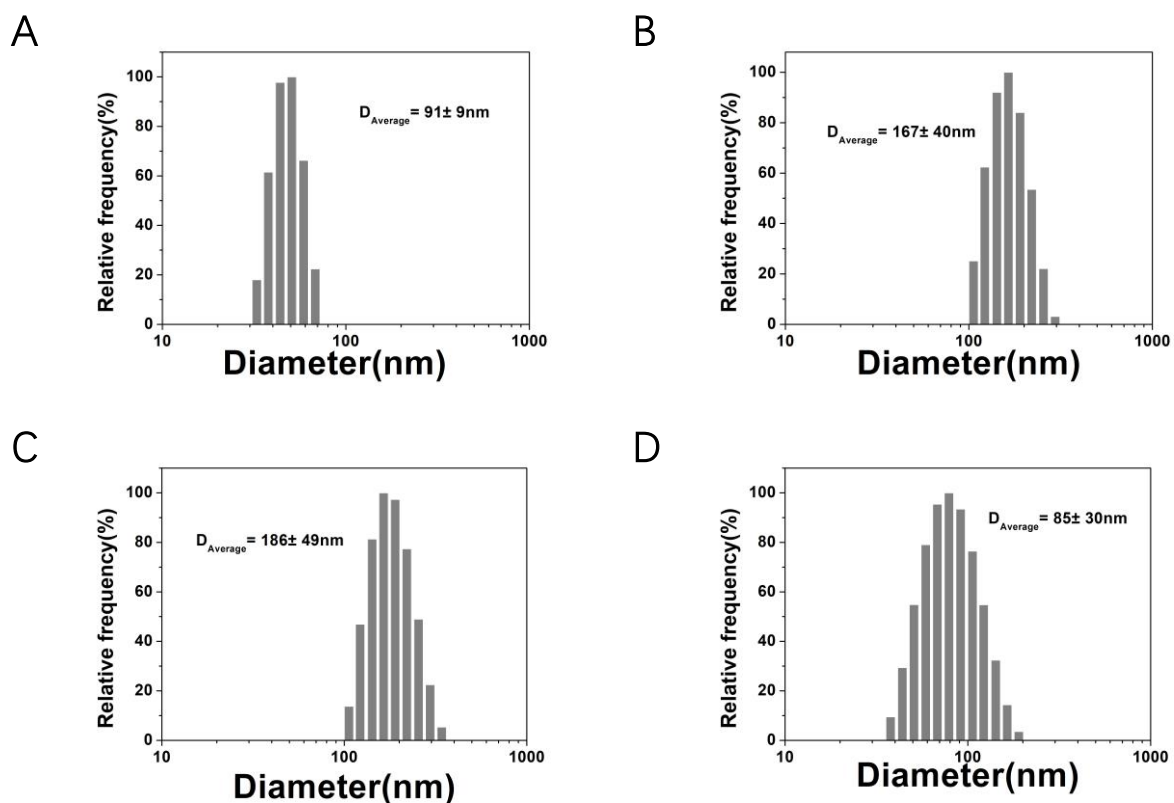


Figure S20. Size distributions of nanoparticles prepared by using (A) PC3/PA1 (5/5 mol%), (B) PC3/PA2 (5/5 mol%), (C) PC3/PA3 (5/5 mol%), and (D) PC3/PA4 (5/5 mol%).

5. TEM Image

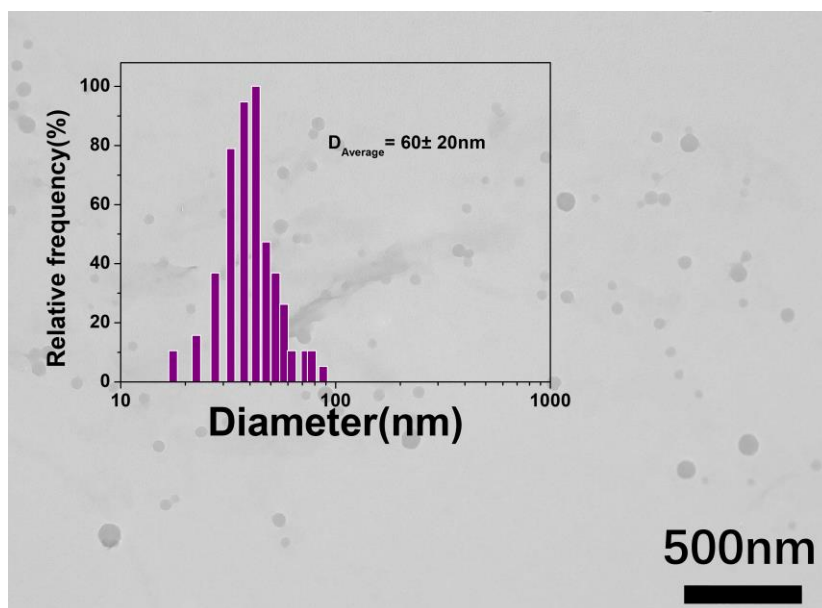


Figure S21. Typical TEM image and the corresponding size distribution determined by TEM of the reused nanoparticle catalysts prepared using **PA3** and **PC3**.

6. FT-IR spectra

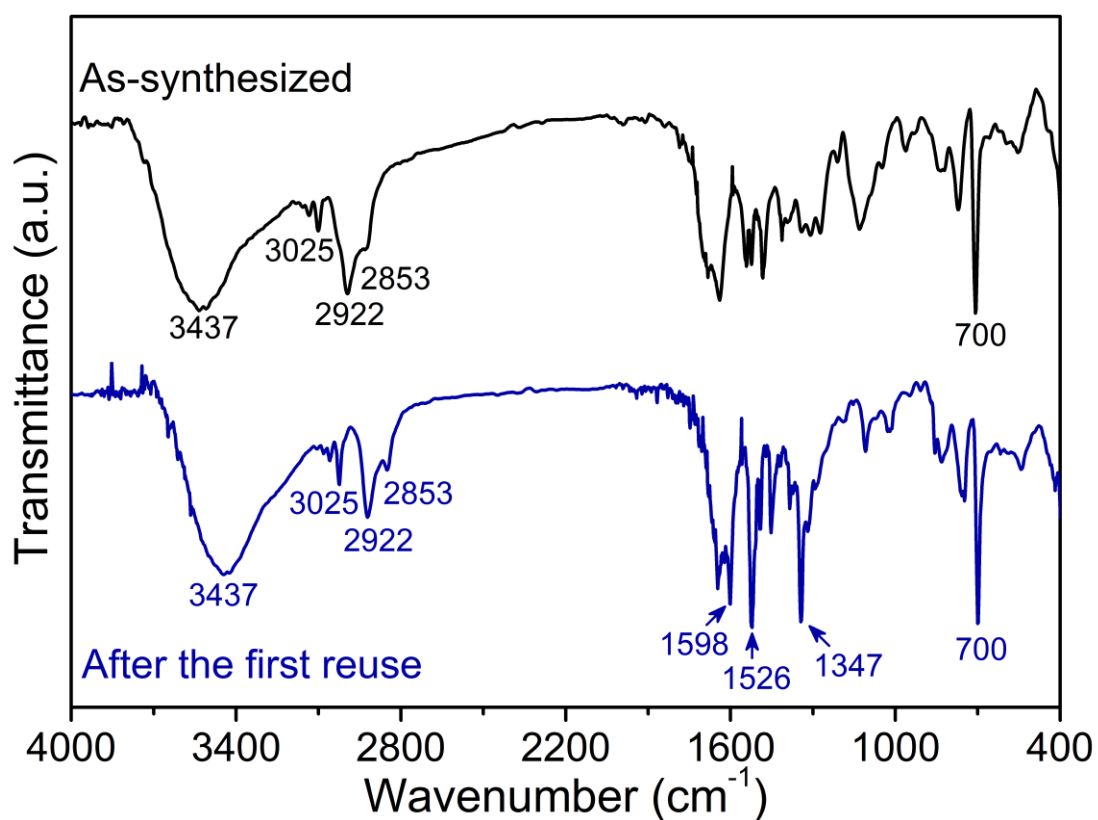
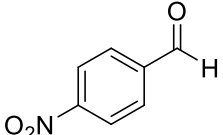
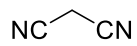
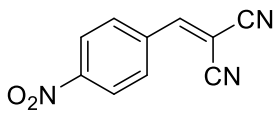
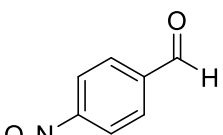
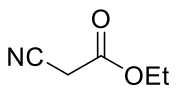
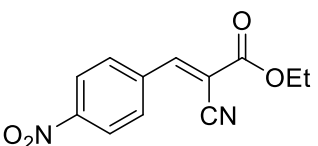


Figure S22. FT-IR spectra of the as-synthesized and after the first reused nanoparticle catalysts prepared using **PA3** and **PC3**. The characteristic bands of benzene groups were found at 3025 cm⁻¹ and 700 cm⁻¹. The characteristic bands of -CH₂-groups were observed at 2922 cm⁻¹ and 2853 cm⁻¹. A broad band at 3437 cm⁻¹ was assigned to -OH and -NH₂ groups. The characteristic band of -C=N- groups was detected at 1598 cm⁻¹. The formation of -C=N- was ascribed to the reaction between benzylamine groups of catalysts and 4NBA. The characteristic bands of -NO₂ groups were observed at 1526 cm⁻¹ and 1347 cm⁻¹.

7. Condensation reactions

Table S6. Condensation reactions catalyzed by **PA3/PC3**.^a

Entry	Substrate	Product	Conversion	Selectivity	
1	 <chem>O=Cc1ccc([N+](=O)[O-])cc1</chem>	 <chem>NC#CC#N</chem>	 <chem>O=C=C(C#N)C#Nc1ccc([N+](=O)[O-])cc1</chem>	> 99%	> 99%
2	 <chem>O=Cc1ccc([N+](=O)[O-])cc1</chem>	 <chem>CCOC(=O)CC#N</chem>	 <chem>CCOC(=O)C=C(C#N)C#Nc1ccc([N+](=O)[O-])cc1</chem>	> 99%	> 99%

^a Reaction condition: **PA3/PC3** (5/5 mol%, effective constituent ratio, relative to 4-NBA), kept at 60 °C under nitrogen atmosphere for 5 h.

8. References

1. Thielbeer, F.; Johansson, E. M.; Chankeshwara, S. V.; Bradley, M., Influence of spacer length on the cellular uptake of polymeric nanoparticles. *Macromol Biosci* **2013**, *13* (6), 682-6.
2. Takeshima, H.; Satoh, K.; Kamigaito, M., Scalable Synthesis of Bio-Based Functional Styrene: Protected Vinyl Catechol from Caffeic Acid and Controlled Radical and Anionic Polymerizations Thereof. *ACS Sustain. Chem. Eng.* **2018**, *6* (11), 13681-13686.