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Supporting Information

Modulating the reactivity of polymer with pendant ester groups by Methylation Reaction for preparing functional polymers

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Experimental Section

Materials

All chemicals were commercially available and used as received unless otherwise stated. 2,2'-Azoisobutyronitrile (AIBN) was further purified by recrystallization from methanol. Prior to polymerization, the 1,4-dioxane is passed through base alumina to remove the polymerization inhibitor. CDTPA was prepared according to the literature.[1] Pentafluorophenyl acrylate (PFPA) was prepared according to the literature.[2]

Methods

Nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR spectra were recorded on a JNM-ECZ400S/L1 400MHz NMR spectrometer. Deuterated dimethyl sulfoxide (DMSO-d_6), deuterated chloroform ($CDCl_3$) and deuterium oxide (D_2O) were used as solvents.

Fourier Transform Infrared Spectrometer (FTIR Spectrometer). FTIR spectra were measured on Spectrum Two Li10014 spectrometer.

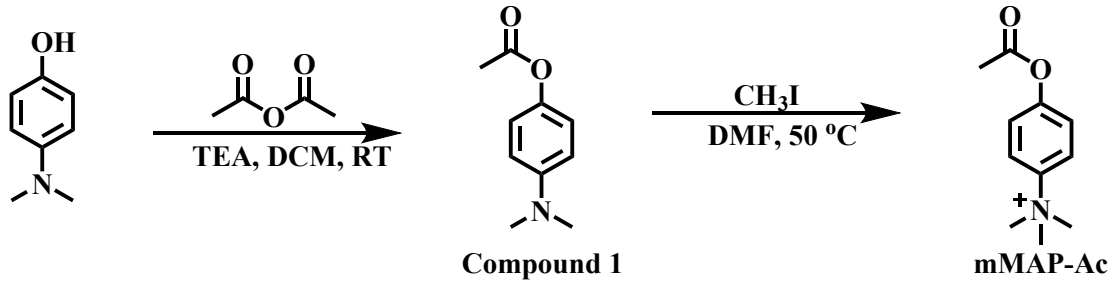
Gel permeation chromatography (GPC). Molecular weights and dispersities were determined by size exclusion chromatography (SEC), which was performed at 35 ^{o}C in DMF or THF at a flow rate of 1.0 mL/min (Shimadzu liquid chromatography infusion pump LC-20AD, autosampler SIL-20A, and detecter RID-10A). The number-average molecular weight (Mn) and molecular weight distribution ($Đ$) of the polymers were calculated using Labsolutions software.

Thermal gravimetric analysis (TGA). Thermal gravimetric measurements were performed by the Swiss METTLER TOLEDO TGA2 thermogravimetric analyzer under nitrogen atmosphere at 60 mL/min flow rate over a temperature range of 30-600 °C. The heating rate was 10 °C/min.

Liquid chromatography-mass spectrophotometry (LC-MS). LC-MS/MS analyses were performed on Waters k13QSM 178a triple quadrupole liquid mass spectrometer in positive ESI mode.

Procedures

Synthesis of 4-acetoxy-N,N,N-trimethylbenzenaminium iodide (mMAP-Ac).

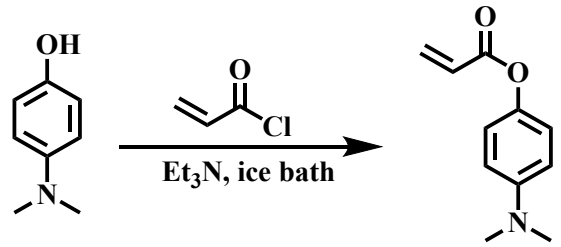


Compound 1 **mMAP-Ac**

Compound 1. 4-(dimethylamino)phenyl acetate was synthesized according to the following procedure. Acetic anhydride (10 g, 10 mmol) was added dropwise to a dichloromethane solution (DCM, 100 mL) of 4-(dimethylamino)phenol (8.8 g, 100 mmol) and 4-Dimethylaminopyridine (DMAP, 20.8 mL, 150 mmol) under ice cold condition for 0.5 h. And the solution was stirred for 12 h at room temperature (RT). Then, the mixture was washed with saturated sodium bicarbonate solution three times and saturated salt water one times, respectively. After drying with anhydrous sodium sulfate, the solvent was removed and the compound 1 was obtained as white solid (2.5 g, 90 % yield) by column chromatography (Petroleum ether / Ethyl acetate, 9 / 1). ^{1}H NMR (400 MHz, Chloroform-d): 6.94 (2 H, d, J 9.1), 6.70 (2 H, d, J 9.1), 2.92 (6 H, s), 2.25 (3 H, s).

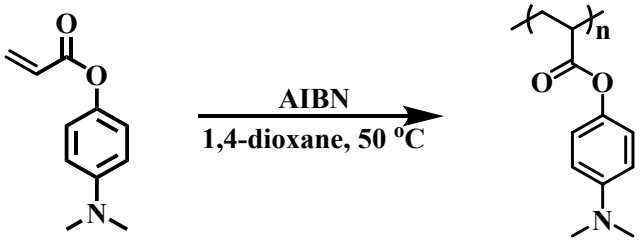
mMAP-Ac. In this step, compound 1 and Iodomethane (CH_3I,) were dissolved in 30 mL of N,N-Dimethylformamide (DMF). The solution was stirred at 50 °C for 12 h. And then, the solvent was removed by rotary evaporation and the crude product was washed with diethyl ether (100 mL). The pure product was obtained as a white solid (2 g, 90 % yeild).^{1}H NMR (400 MHz, DMSO-d_6): 8.00 (2 H, d, *J* 9.2), 7.38 (2 H, d, *J* 9.3), 3.59 (9 H, d, *J* 2.0), 2.27 (3 H, s). ^{13}C NMR (101 MHz, DMSO-d_6): 169.54, 151.56, 144.97, 123.85, 122.70, 57.12, 21.41.

Synthesis of MAPA.



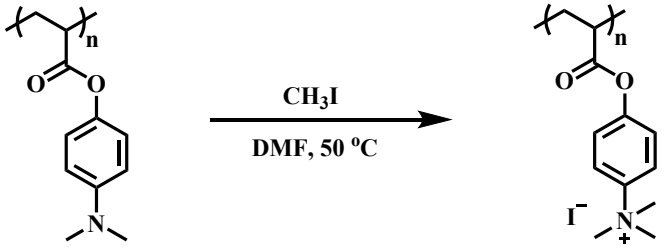
4-(dimethylamino)phenol (2 g, 14.6 mmol) and triethylamine (2.23 mL, 16 mmol) were dissolved in 20 mL of DCM and then acryloyl chloride (1.45 g, 16 mmol) was added dropwise the above solution at 0 °C for 30 min. After the reaction mixture was stirred for 12 h at RT, the mixture was washed with saturated sodium bicarbonate solution three times and saturated salt water one times, respectively. After drying with anhydrous sodium sulfate, the solvent was removed and the monomer was obtained as white solid (2.5 g, 91 % yield) by column chromatography (Petroleum ether / Ethyl acetate, 20 / 1). ^{1}H NMR (400 MHz, Chloroform-*d*): 6.99 (2 H, d, *J* 8.9), 6.71 (2 H, d, *J* 9.1), 6.65 – 6.48 (1 H, m), 6.40 – 6.20 (1 H, m), 6.06 – 5.87 (1 H, m), 2.93 (6 H, s). ^{13}C NMR (101 MHz, DMSO-d_6): 164.39, 151.31, 145.13, 134.93, 127.81, 123.81, 122.79, 57.13. ESI MS m/z: mass calculated for $C_{11}H_{13}NO_2$ $[M+H]^+$=191.0, found 191.99.

Radical polymerization of DMPA (PMAPA)



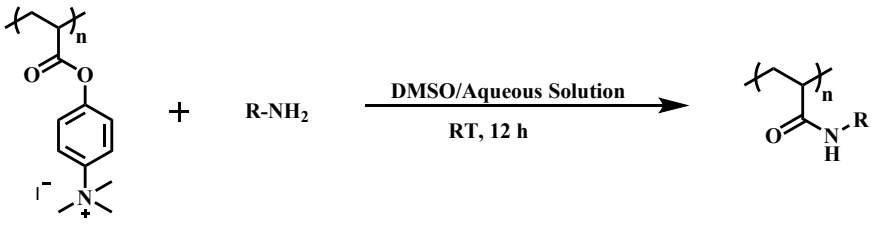
In a 10 mL of Schlenk flask, MAPA (0.5 g, 2.6 mmol) and AIBN (4.3 mg, 0.026 mmol) were dissolved in anhydrous dioxane (0.7 mL). The mixture was degassed with Ar at RT for 30 min. And then the reaction mixture was stirred at 70 °C for 12 h. And the polymerization reaction was terminated with ice water and by exposure to air. Subsequently, the polymer was purified by precipitation into n-hexane (200 mL) and dried as a white solid (0.45 g, 90 % yield). ^{1}H NMR (400 MHz, Chloroform-*d*): 6.92 (2 H, Ar-**H**), 6.52 (2 H, Ar-**H**), 2.82 (7 H, -CH_2C**H**- and -N(C**H$_3$)$_2$**), 2.25 – 1.50 (2 H, -C**H$_2$**CH-).

Typical Procedure for methylation reaction of PDMPA



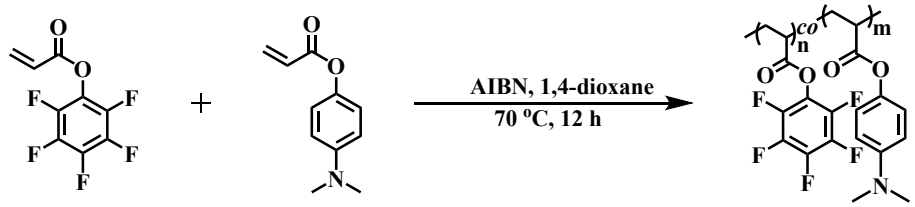
In a 50 mL of Schlenk flask, PMAPA (0.4 g, 2.6 mmol) and CH_3I (1.1 g, 7.8 mmol) were dissolved in anhydrous DMF (20 mL). The mixture was degassed with Ar at RT for 10 min. And then the reaction mixture was stirred at 50 °C for 24 h. Subsequently, the polymer was purified by precipitation into diethyl ether (200 mL) and dried as a pale-yellow solid (0.64 g, 91 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): 8.06 (2 H, Ar-**H**), 7.58 – 6.92 (2 H, Ar-**H**), 3.63 (10 H, -N(C**H$_3$)$_3$**), 3.02 (1 H, -CH_2C**H**-), 2.41 – 1.73 (2 H, -C**H$_2$**CH-).

Typical Procedure for post-polymerization modifications of PMAPA



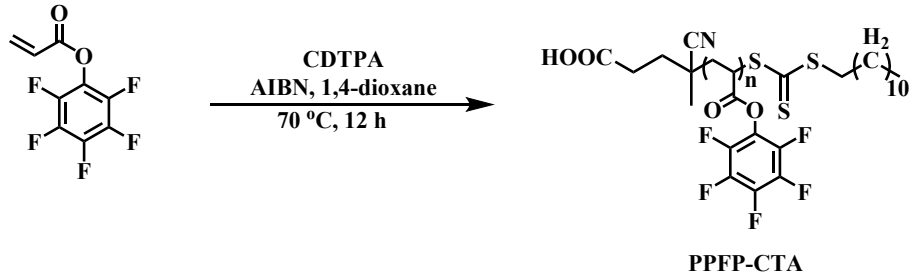
In a 5 mL Schlenk flask, PMAPA (20 mg, 0.06 mmol of monomer) and R-NH_2 (0.18 mmol) were dissolved in DMSO/water (1 mL). The mixture was stirred at rt for 12 h, then the functional polymer was purified by precipitation into methanol/water.

Radical polymerization of PPFPA-*co*-PMAPA



In a 10 mL of Schlenk flask, PFPA (0.43 g, 1.82 mmol), MAPA (0.15 g, 0.78 mmol) and AIBN (4.3 mg, 0.026 mmol) were dissolved in anhydrous dioxane (1 mL). The mixture was degassed with Ar at RT for 30 min. And then the reaction mixture was stirred at 70 °C for 12 h. And the polymerization reaction was terminated with ice water and by exposure to air. Subsequently, the polymer was purified by precipitation into n-hexane (200 mL) and dried as a white solid (0.54 g, 93 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): 6.75-7.01 (Ar-**H**), 6.30-6.70 (Ar-**H**), 2.98-3.20 (-CH_2C**H**- in PPFP), 2.78-2.95 (-CH_2C**H**- in PMAPA and -N(C**H$_3$**)$_2$), 1.65-2.55 (-C**H$_2$**CH-).

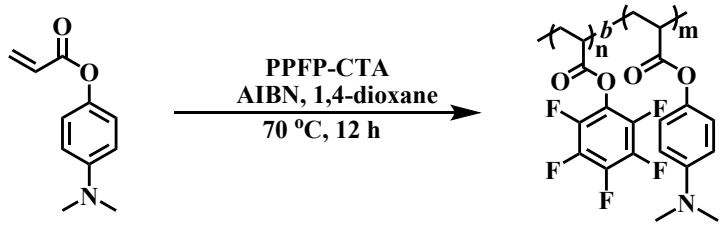
Raft polymerization of PPFPA-CTA



PPFP-CTA

In a 10 mL of Schlenk flask, PFPA (0.5 g, 2.1 mmol), AIBN (6.8 mg, 0.042 mmol) were dissolved in anhydrous dioxane (1 mL). The mixture was degassed with Ar at RT for 30 min. And then the reaction mixture was stirred at 70 °C for 12 h. And the polymerization reaction was terminated with ice water and by exposure to air. Subsequently, the polymer was purified by precipitation into n-hexane (200 mL) and dried as a white solid (0.47 g, 94 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): 3.0-3.2 (1 H, -CH_2C**H-**), 1.8-2.6 (2 H, -C**H$_2$**CH-);^{19}F NMR ($CDCl_3$): -153, -156, -162.

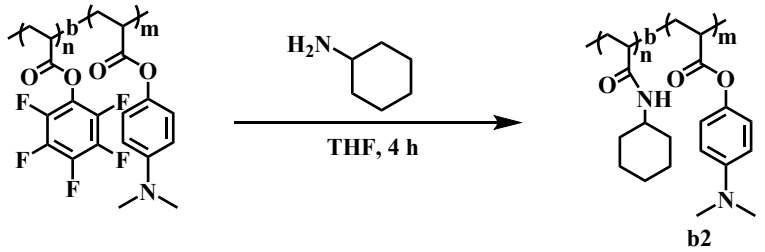
Raft polymerization of PPFPA-*b*-PMAPA



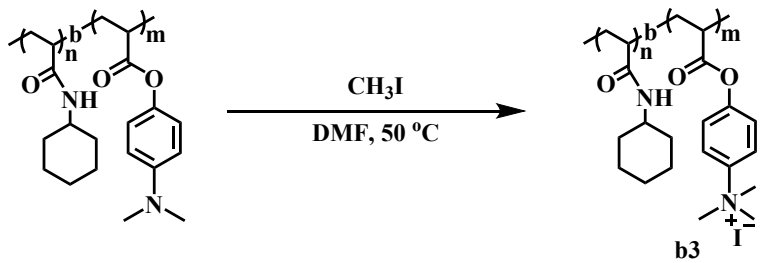
In a 10 mL of Schlenk flask, MAPA (0.5 g, 2.62 mmol), PFP-CTA (0.2 g, 0.0131 mmol), AIBN (0.715 mg, 0.0044 mmol) were dissolved in anhydrous dioxane (1 mL). The mixture was degassed with Ar at RT for 30 min. And then the reaction mixture was stirred at 70 °C for 12 h. And the polymerization reaction was terminated with ice water and by exposure to air. Subsequently, the polymer was purified by precipitation into n-hexane (200 mL) and dried as a white solid (0.266 g, 38 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): 6.75-7.01 (Ar-**H**), 6.30-6.70 (Ar-**H**), 2.98-3.20 (-CH_2C**H**-), 2.78-2.95 (-CH_2C**H**- and -N(C**H$_3$**)$_2$), 1.65-2.55 (-C**H$_2$**CH-).

Typical Procedure for post-polymerization modifications of PPFPA-*b*-PMAPA

The block copolymer b4 can be prepared according to the following procedure. The same general procedure was employed for all other PPM of copolymers.



In a 50 mL of Schlenk flask, PPFPA-*b*-PMAPA (0.2 g, 0.6 mmol PFP) and cyclohexylamine (75 mg, 0.76 mmol) were dissolved in anhydrous THF (5 mL). The mixture was degassed with Ar at RT for 10 min. And then the reaction mixture was stirred at rt for 4 h. Subsequently, the polymer was purified by precipitation into n-hexane (200 mL) and dried as a white solid (0.14 g, 94 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): 6.76-7.05 (Ar-**H**), 6.40-6.70 (Ar-**H**), 3.35-3.65 (-C**H**-),2.70-2.90 (-CH_2C**H**-, N(C**H$_3$**)$_2$), 1.34-2.00 (-C**H$_2$**C**H**-), 0.85-1.30 (-C**H$_2$**-).



In a 50 mL of Schlenk flask, b2 (0.1 g, 0.2 mmol MAPA) and CH_3I (86 mg, 0.6 mmol) were dissolved in anhydrous DMF (2 mL). The mixture was degassed with Ar at RT for 10 min. And then the reaction mixture was stirred at 50 °C for 24 h. Subsequently, the polymer was purified by precipitation into diethyl ether (50 mL) and dried as a pale-yellow solid (0.12 g, 98 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): 7.92-8.15 (Ar-**H**), 7.15-7.55 (Ar-**H**), 3.65-3.80 (-C**H**-), 3.55-3.65 (N(C**H$_3$**)$_3$), 1.35-1.85 (-C**H$_2$**C**H**-), 0.85-1.30 (-C**H$_2$**-).

In a 5 mL Schlenk flask, b3 (20 mg, 0.03 mmol of monomer) and n-butylamine (0.09 mmol) were dissolved in DMSO (1 mL). The mixture was stirred at RT for 12 h, then the functional polymer was purified by precipitation into methanol and dried as a white solid (13 mg, 97 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): 3.55-3.78 (-C**H**-), 3.07-3.27 (-NHC**H$_2$**-), 1.53-1.96 (-C**H$_2$**C**H**-), 1.40-1.52 (-CH_2C**H$_2$**C**H**-), 1.04-1.36 (-CH_2C**H$_2$**CH_3, -CH_2C**H$_2$**CH_2-), 0.85-0.97 (-C**H$_3$**).

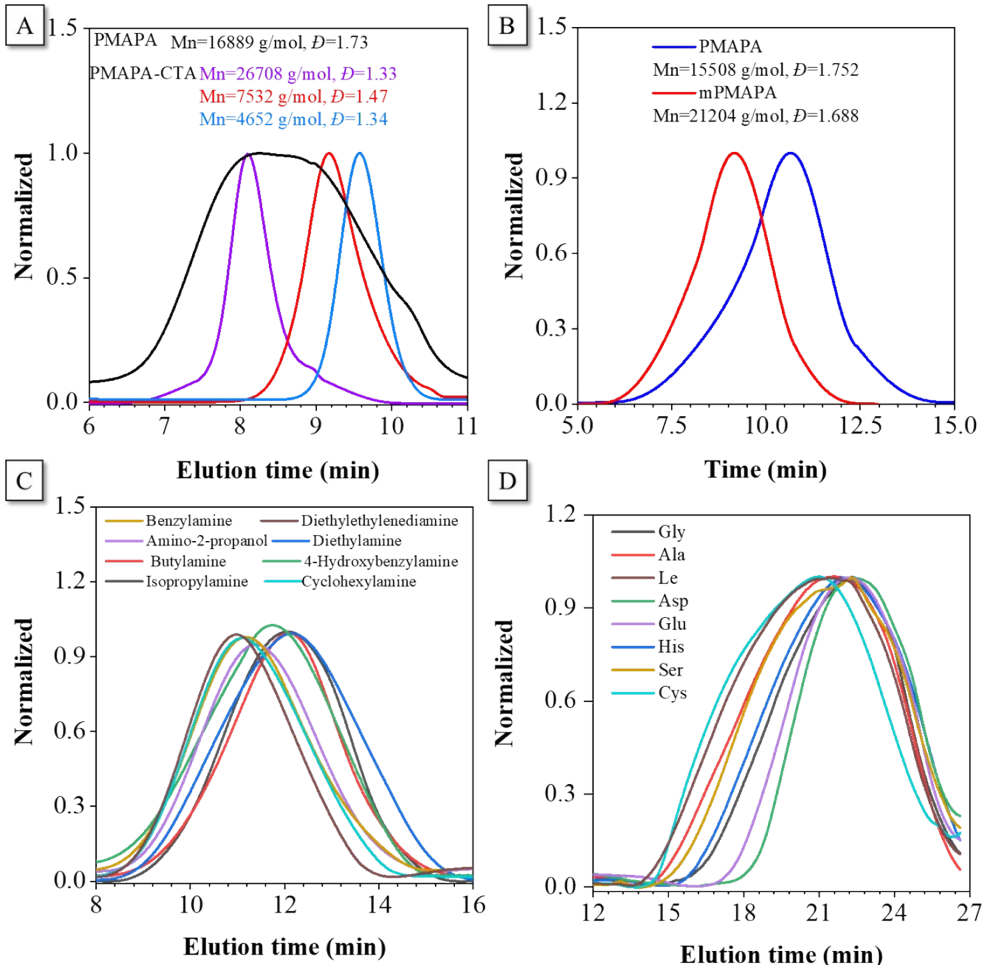


Fig.S1 (A) GPC trace for PMAPA and PMAPA-CTA (THF as mobile phase). (B) GPC trace for PMAPA and mPMAPA (DMF as mobile phase). (C) GPC trace of different amines for PPM of mPMAPA (DMF). (D) GPC trace of different amino acids for PPM of mPMAPA (Water as mobile phase).

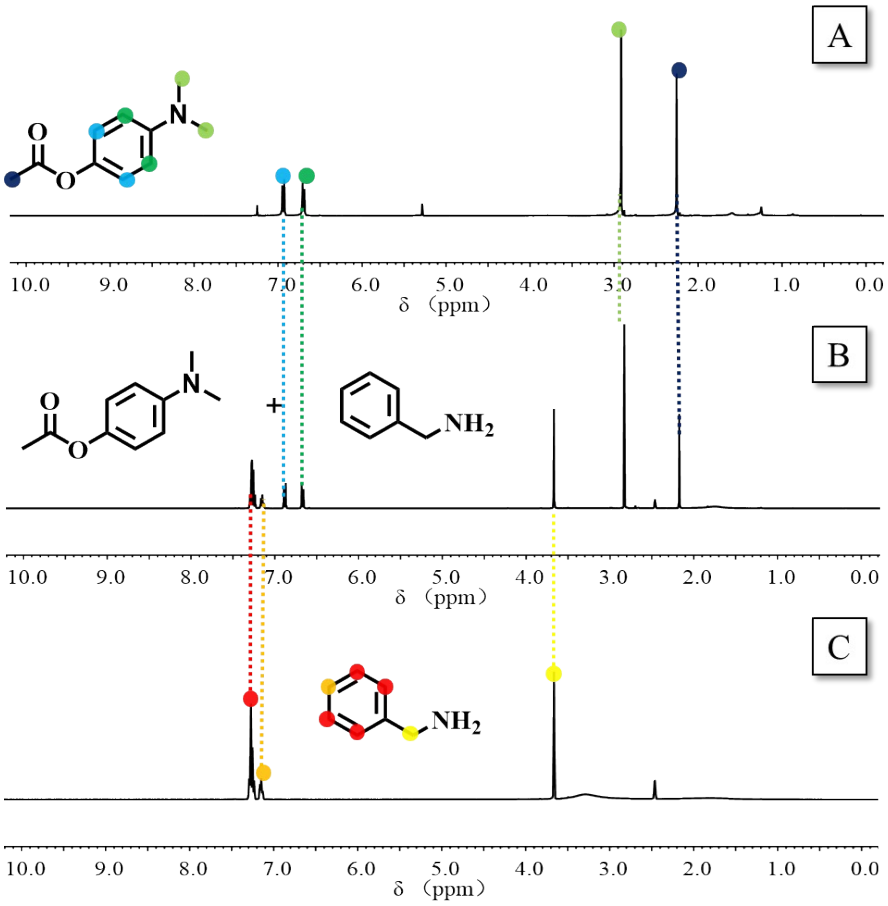


Fig.S2 (A) ^{1}H NMR spectra of mMAP-Ac in $CDCl_3$. (B) ^{1}H NMR spectra of mMAP-Ac and BZA (2 eq) in DMSO-d_6 for 12 h. (C) ^{1}H NMR spectra of BZA in DMSO-d_6.

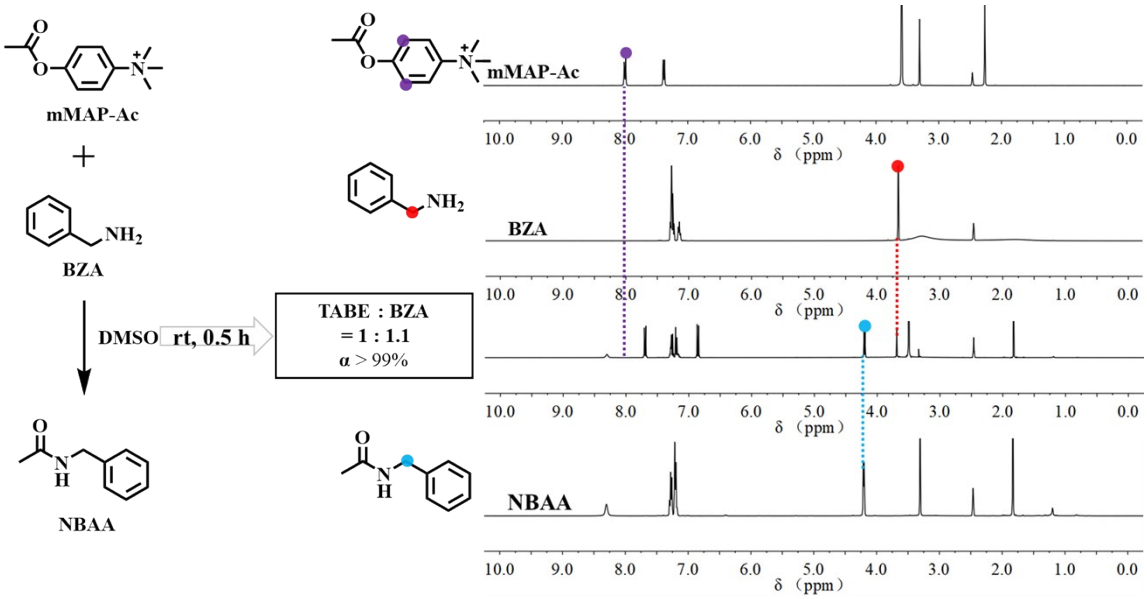
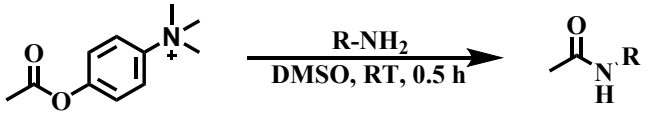
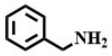
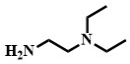
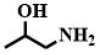
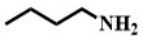
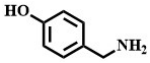
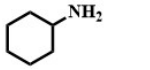
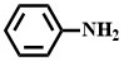


Fig.S3 The reactions between mMAP-Ac and BZA in DMSO-d_6.

Table S1 Small molecule model studies of mMAP-Ac and different Amines in DMSO. [a]

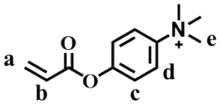


R-NH2	α[b]	R-NH2	α[b]
	>99%[c]		>99%
	>99%		>99%
	>99%		>99%
	>99%		>99%
	0%		

[a]Initial amine concentration was adjusted to be 0.5 mol/L; $[amine]_0/[mMAP\text{-}Ac]_0$ was adjusted to be 1.2/1; the reaction was conducted for 0.5 h at RT. [b]The chemical compositions of the obtained polymers were determined by *in situ* ^{1}H NMR measurements in DMSO-d_6.

Table S2 Summary of the PPM of mPMAPA in DMSO.

R-NH_2	Mn (g/mol)	*Đ*	R-NH_2	Mn (g/mol)	*Đ*
	12718	1.89		14876	1.57
	11315	1.82		6862	1.96
	9352	1.48		10029	1.79
	7273	1.61		13700	1.68



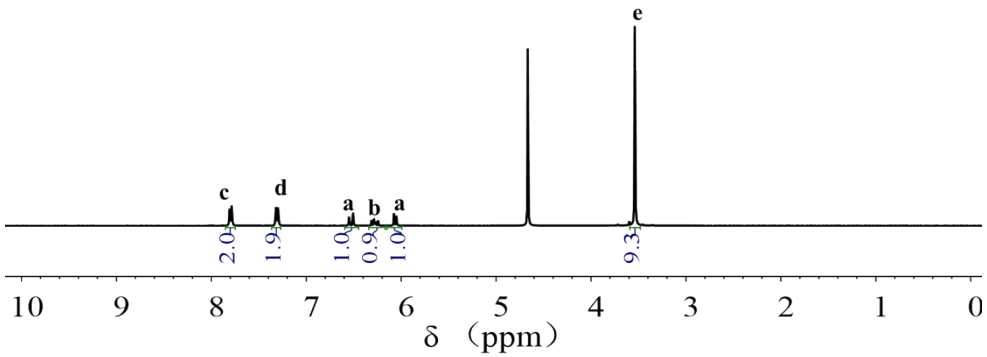


Fig. S4 ^{1}H NMR spectra of m-MAPA in D_2O for 12 h.

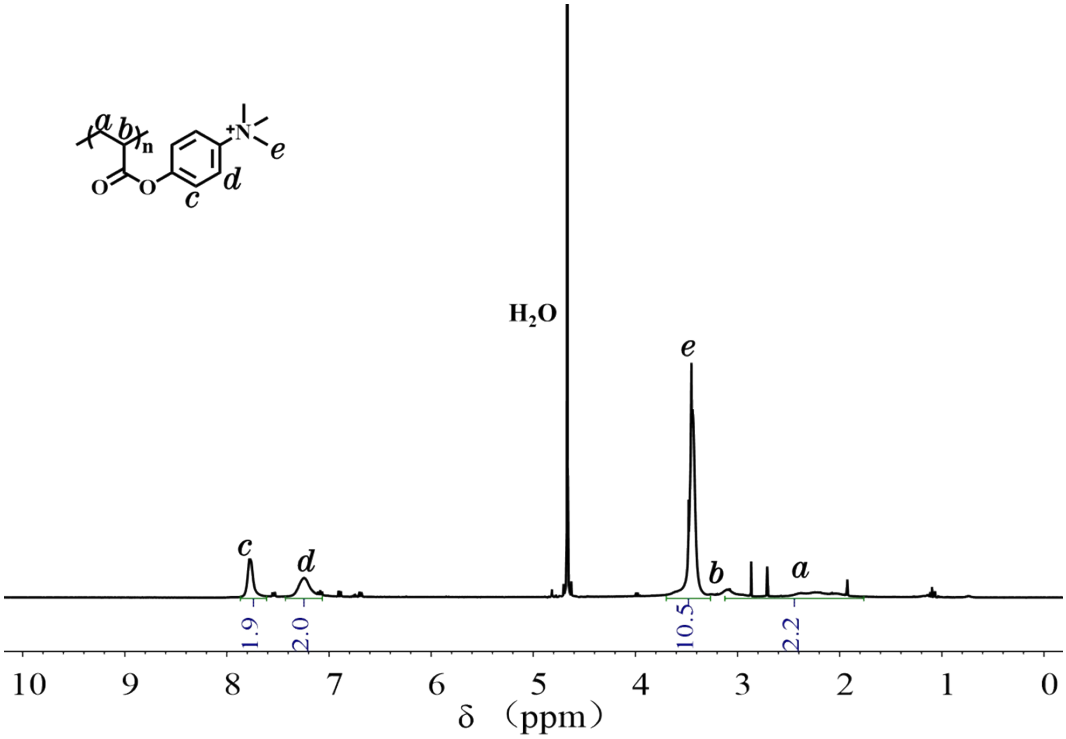
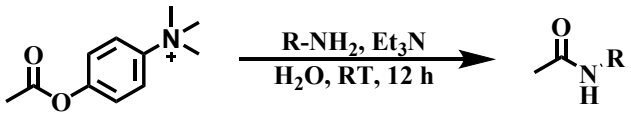
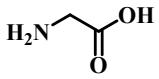
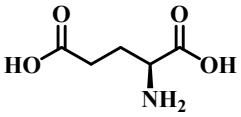
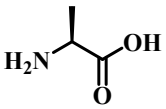
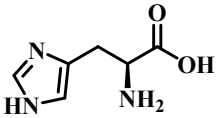
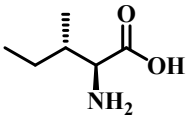
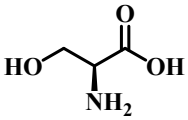
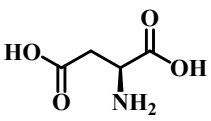
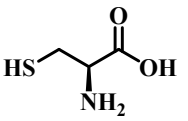


Fig. S5 ^{1}H NMR spectra of m-PMAPA in D_2O for 12 h.

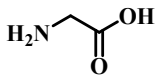
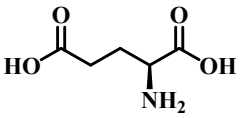
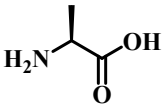
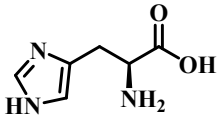
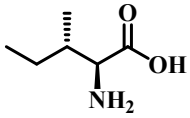
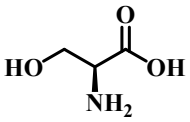
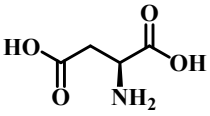
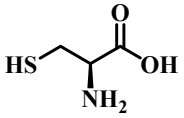
Table S3 Small molecule model studies of mMAP-Ac and different Amines in water. [a]



R-NH_2	α[b]	R-NH_2	α[b]
	80%		14%
	70%		40%
	50%		60%
	50%		70%

[a]Initial amino acid concentration was adjusted to be 1.5 mol/L; $[Amino\ acid]_0/[mMAP\text{-}Ac]_0/[Et_3N]$ was adjusted to be 1.2/1/1.2; the reaction was conducted for 12 h at RT. [b]The chemical compositions of the obtained compounds were determined by in situ ^{1}H NMR measurements in D_2O.

Table S4 Summary of the PPM of mPMAPA in water.

R-NH_2	Mn (g/mol)	*Đ*	R-NH_2	Mn (g/mol)	*Đ*
	10670	1.56		11295	1.37
	11490	1.71		12754	1.47
	12016	1.58		9854	1.67
	9628	1.54		14623	1.52

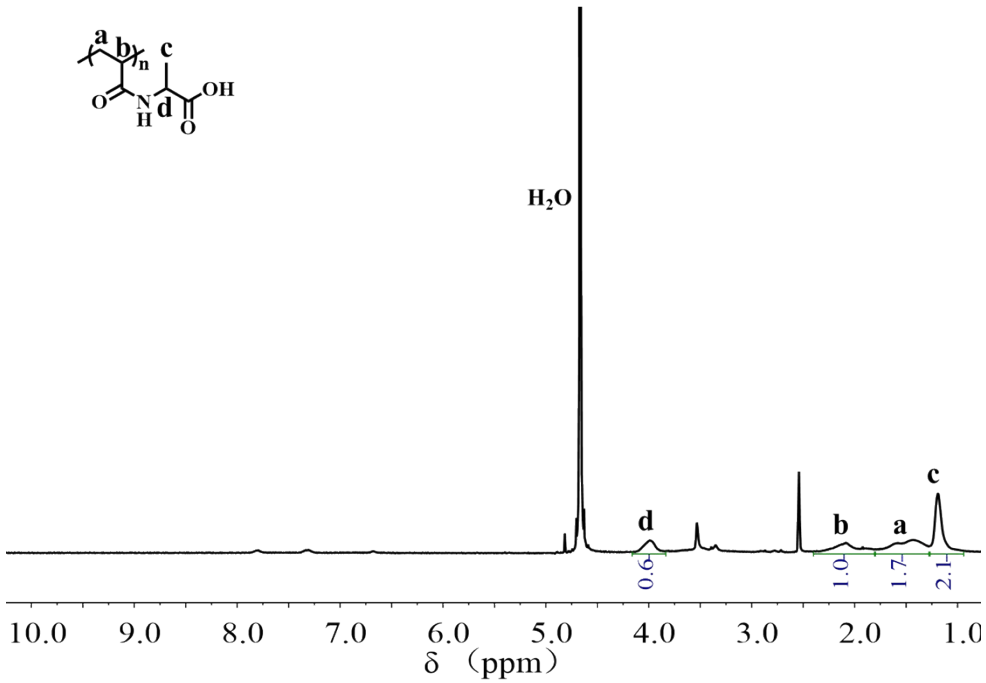


Fig.S6 ^{1}H NMR spectra of m-PMAPA after PPM with *L*-alanine in D_2O.

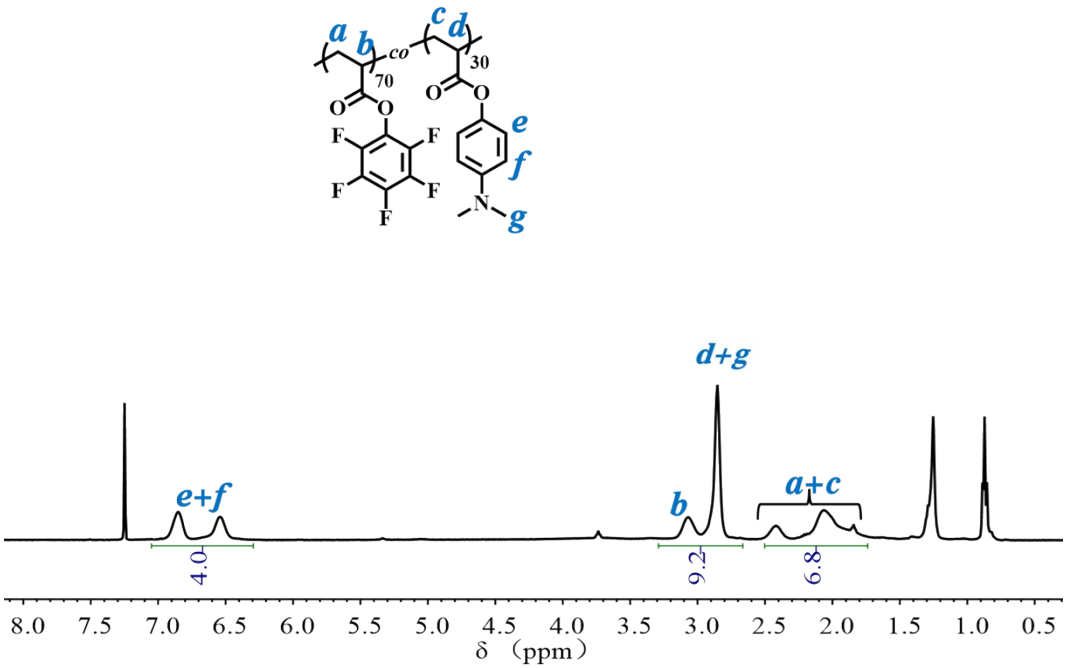


Fig.S7 ^{1}H NMR spectra in $CDCl_3$ of PFPA-*co*-PMAPA.

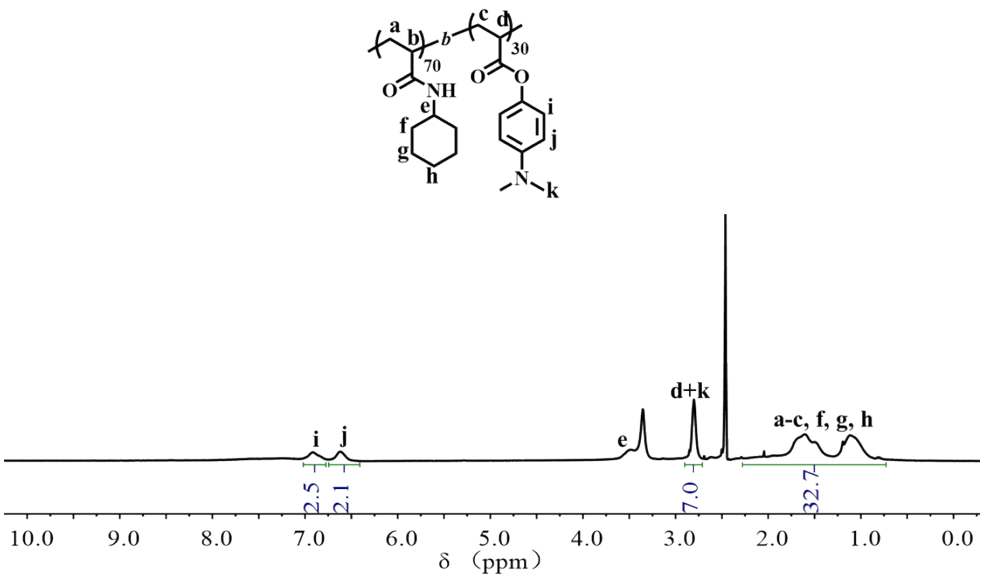


Fig.S8 ^{1}H NMR spectra in DMSO-d_6 of PFPA-*b*-PMAPA after PPM with cyclohexylamine.

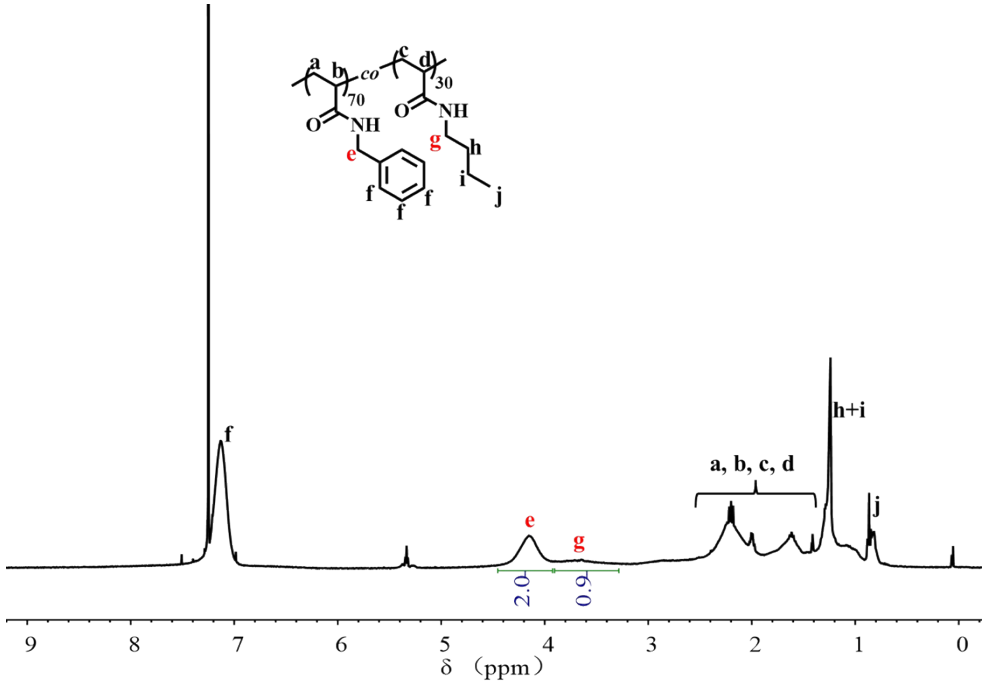


Fig.S9 ^{1}H NMR spectra in $CDCl_3$ of PFPA-*co*-PMAPA after PPM with BZA and n-butylamine sequentially.

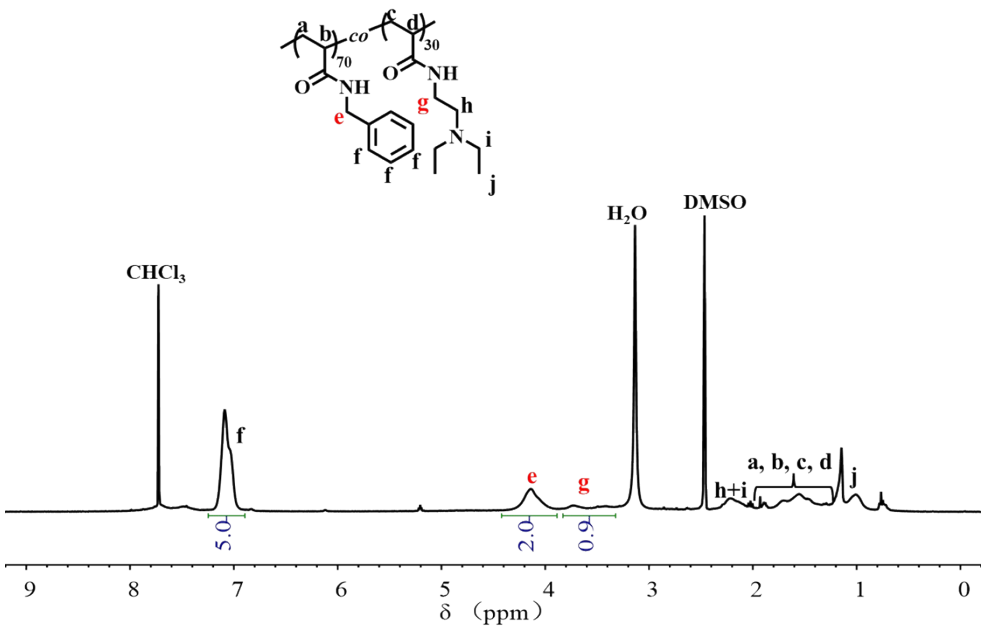


Fig.S10 ^{1}H NMR spectra in DMSO-d_6 of PFPA-*co*-PMAPA after PPM with BZA and N,N-diethylethylenediamine sequentially.

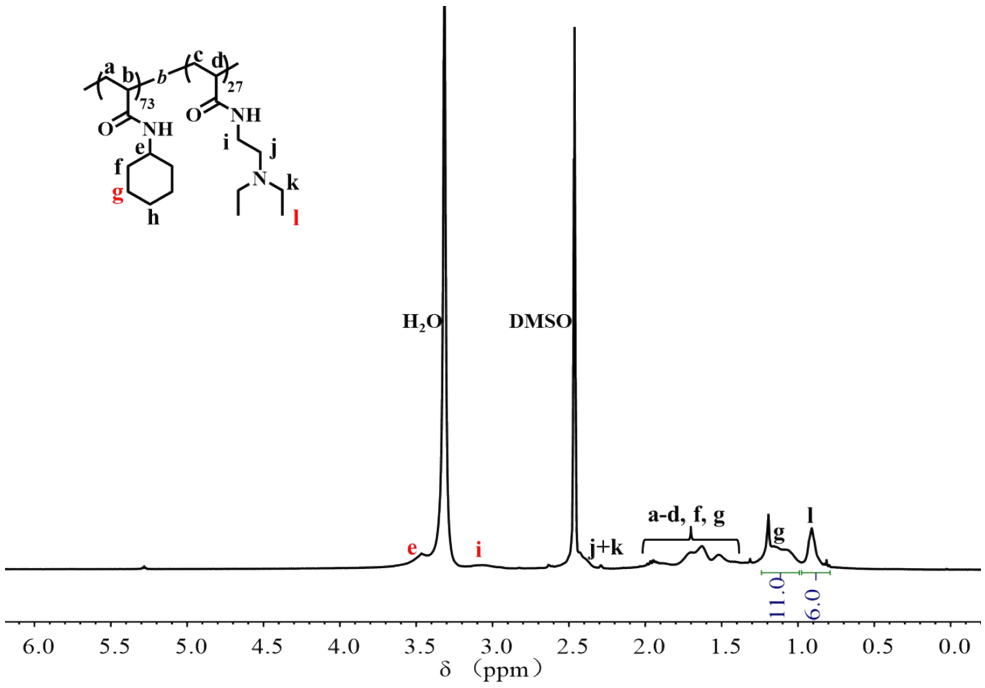
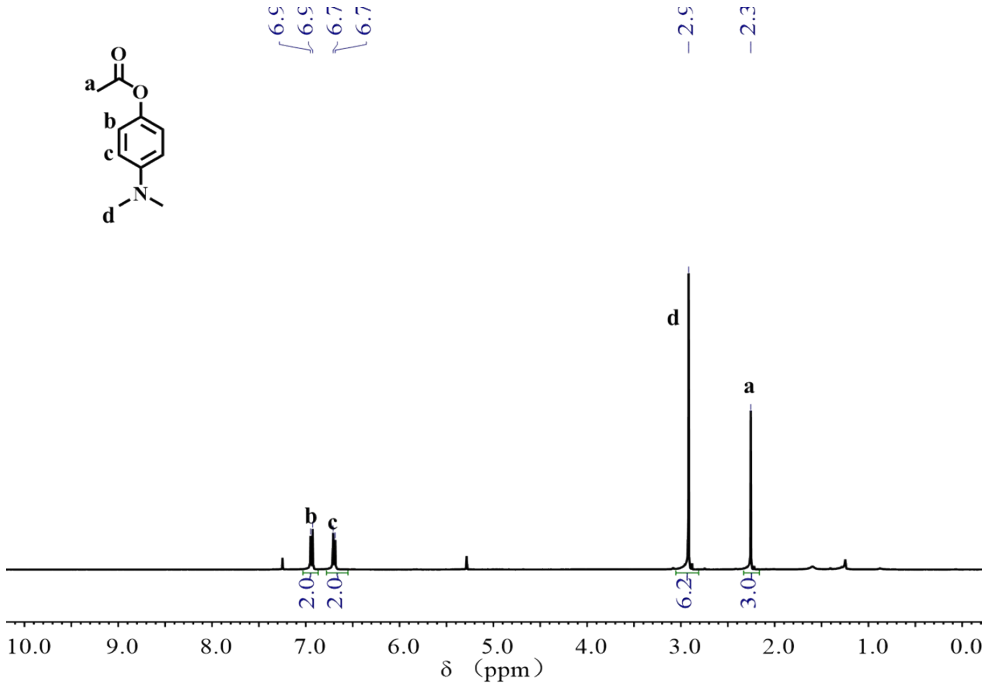
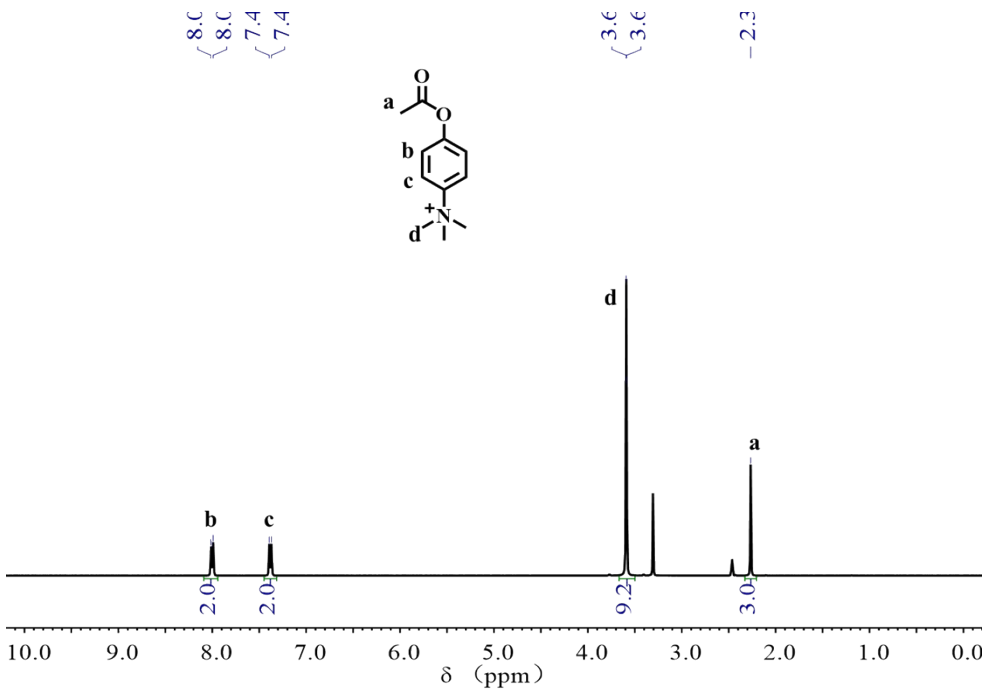


Fig.S11 ^{1}H NMR spectra in DMSO-d_6 of PFPA-*b*-PMAPA after PPM with cyclohexylamine and N,N-diethylethylenediamine sequentially.

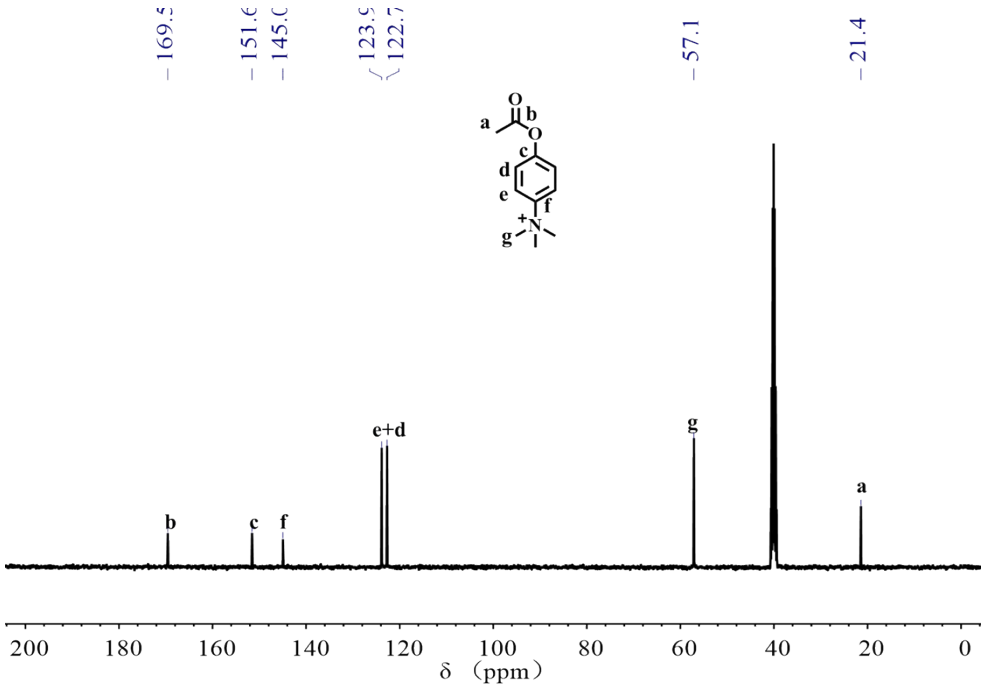
Characterization.



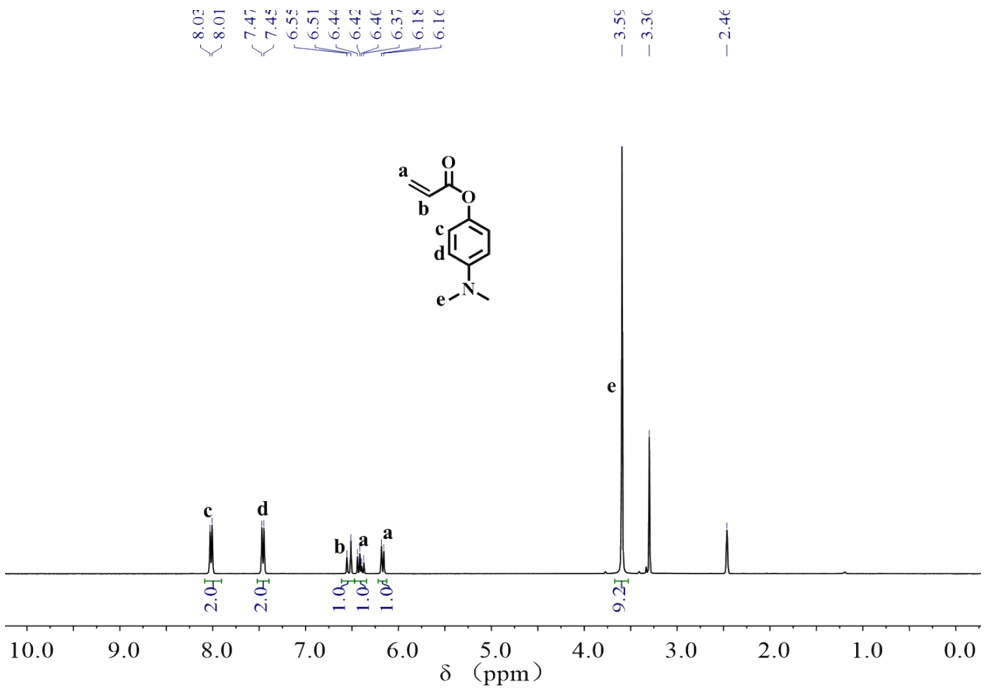
^{1}H NMR spectrum of compound 1.



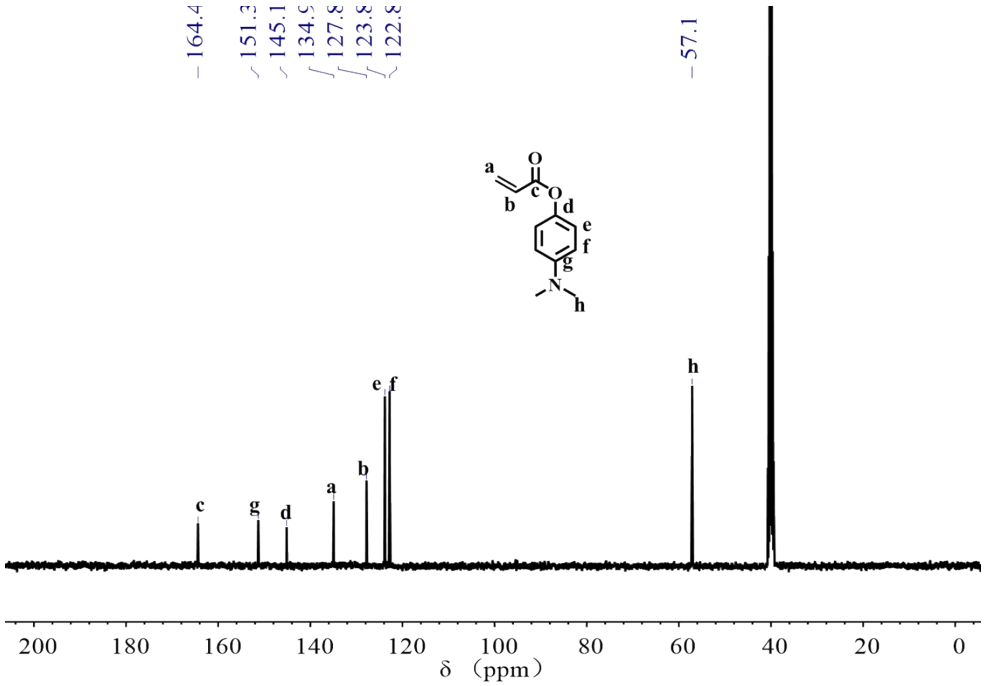
^{1}H NMR spectrum of MAP-Ac.



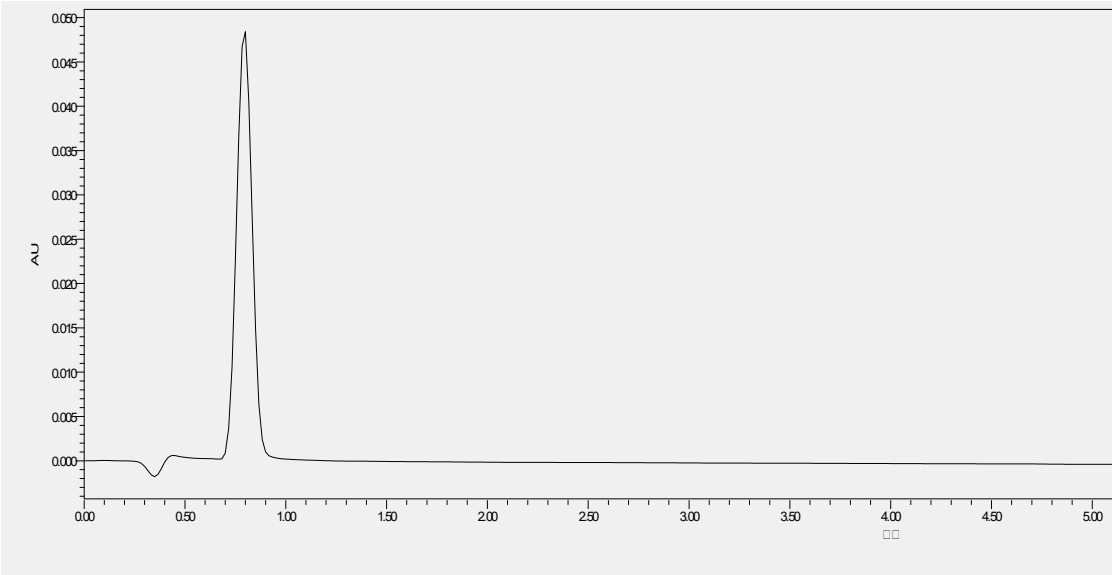
^{13}C NMR spectrum of MAP-Ac.



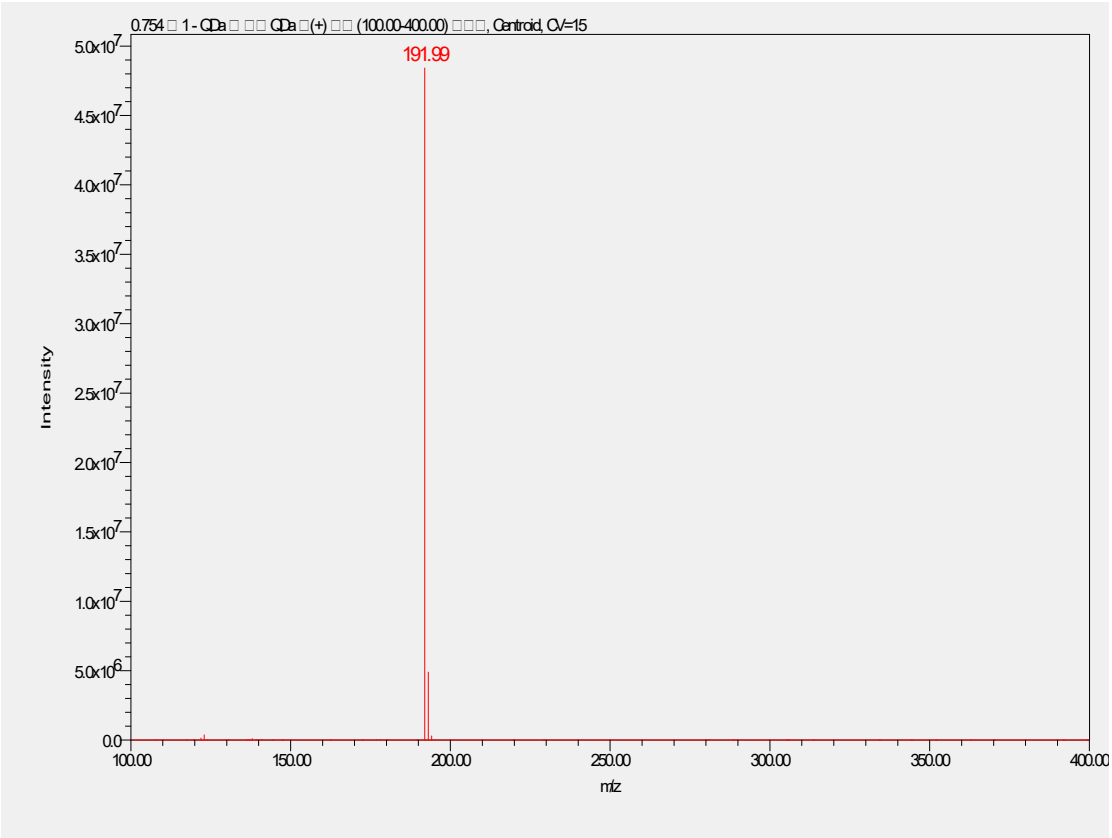
^{1}H NMR spectrum of MAPA.



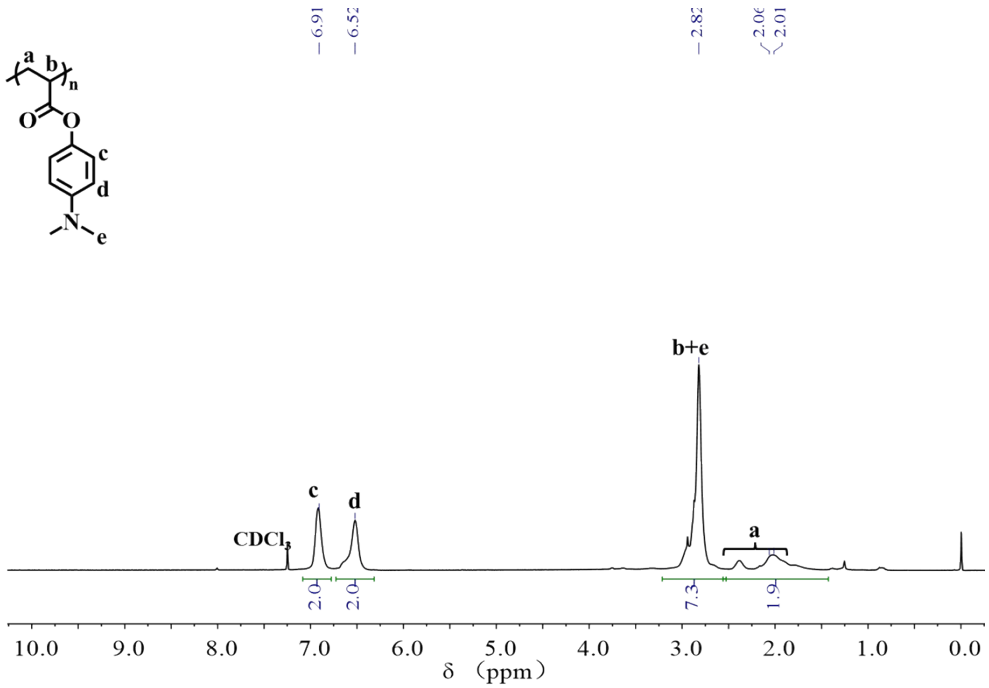
^{13}C NMR spectrum of MAP-Ac.



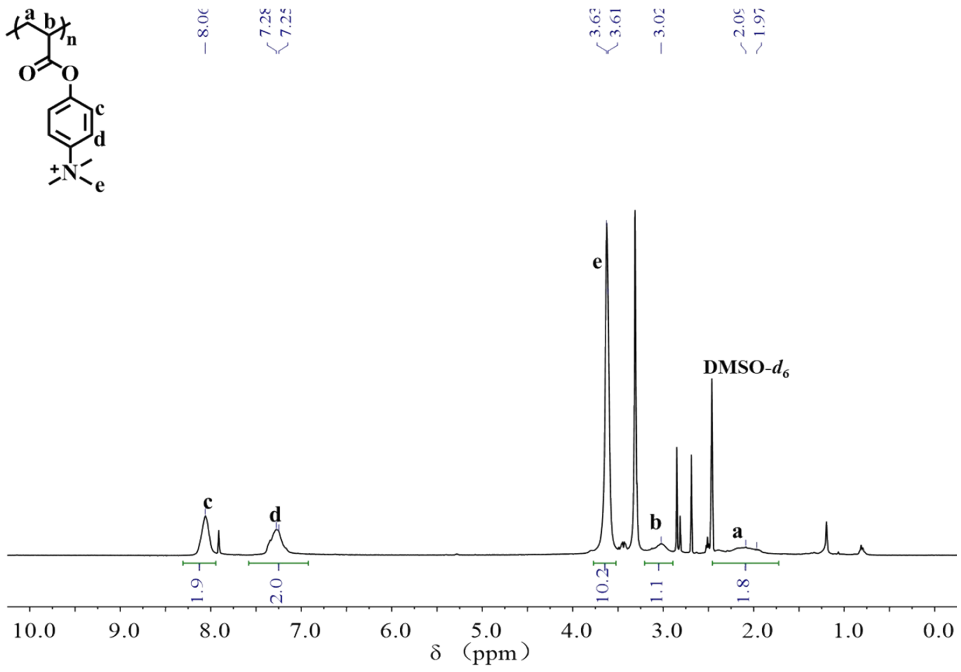
UPLC trace for MAPA, detector (254 nm), Isocratic 20% (MeCN in 0.1% Formic acid of water), 0-5 min.



ESI-MS analysis of MAPA, positive charge mode.



^{1}H NMR spectrum of m-PMAPA.



^{1}H NMR spectrum of m-PMAPA.

References

1. L. Yuan, L. He, Y. Wang, X. Lang, F. Yang, Y. Zhao and H. Zhao, *Macromolecules*, 2020, **53**, 3175-3181.

2. D. N. F. Bajj, M. V. Tran, H.-Y. Tsai, H. Kim, N. R. Paisley, W. R. Algar and Z. M. Hudson, *ACS Applied Nano Materials*, 2019, **2**, 898-909.