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Living radical polymerization of acrylates and acrylamides mediated by a versatile cobalt porphyrin complex

Yaguang Zhao[a], Huilong Dong[b], Youyong Li[b]*, Xuefeng Fu[a]*

Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China.

Institute of Functional Nano & Soft Materials (FUNSOM) and Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China

Experimental

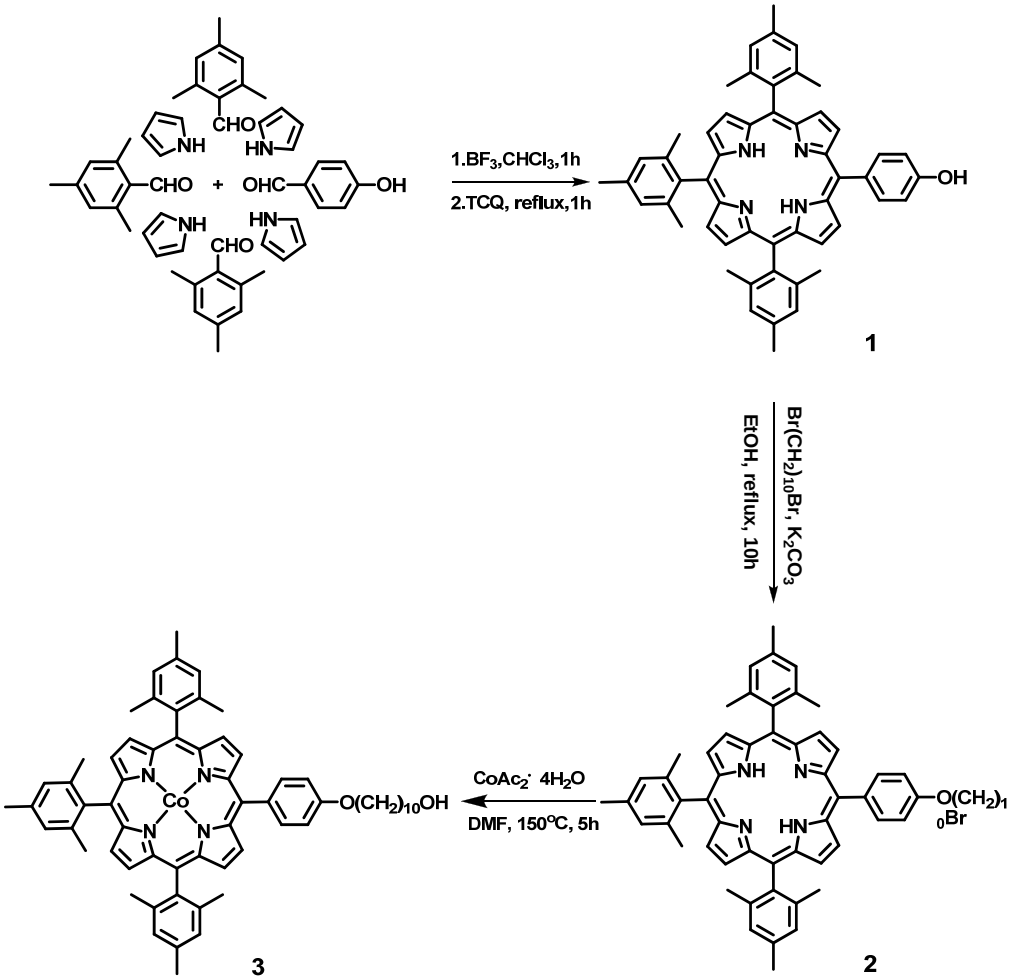
Materials. Methyl acrylate (MA, Alfa, 99%), *tert*-butyl acrylate (*t*BA, Alfa, 99%), and butyl acrylate (*n*BA, Alfa, 98+%) were filtered through neutral alumina, distilled under reduced pressure and stored in the refrigerator before use. 2-hydroxyethyl acrylate (HEA, Acros, 97%) were purified by passing through a basic alumina column and stored in the refrigerator. Acrylic acid (AA, Alfa, 99.5%) and N, N-dimethylacrylamide (DMA, Alfa, 99.5%) were distilled under reduced pressure. N-isopropylacrylamide (NIPAM, Aldrich, 97%) was recrystallized from hexane. The initiator, 2, 2'-azobissobutyronitrile (AIBN, $((CH_3)_2(CN)C)_2N_2$, Beijing Guoyao Co, 99%) was recrystallized from ethanol and stored in the refrigerator. N, N-dimethylformamide was distilled under reduced pressure. All other reagents were used as received if not mentioned.

Analytical Techniques. The determination of monomer conversions and identification of (TMP-OH)Co, organo-cobalt porphyrin complex were performed by ^{1}HNMR in $CDCl_3$, CD_3OD or C_6D_6, using a Bruker 400MHz FT spectrometer. Chemical shifts were calibrated relative to solvent chloroform peak at 7.26 ppm, solvent methanol peak at 3.31 ppm and solvent benzene peak at 7.16 ppm. The conversion of reaction monomer was determined by comparing the integrations of the resonances corresponding to the vinyl protons of the monomer and aliphatic protons of the polymer.

Analytical gel permeation chromatography (GPC) was performed in an Agilent 1200 series system, equipped with a VARIAN PolarGel-M column (300×7.5mm), an Iso Pump (G1310A), a UV detector at 254nm, and a differential refractive index detector (RI). Except for special mentioned, we report the number average molecular weight (M_n), weight average molecular weight (M_w), and the polydispersity (PDI) from the RI detector. N, N-Dimethylformamide (DMF) was used as the eluent at 50^{o}C with a flow rate of 1mL/min. Nine narrowly distributed poly (MMA) samples (molecular weight range of 690-1944000 g/mol, from Polymer Laboratories) were used as the calibration standards for the system.

DFT computational methods: All the simulations and calculations were carried out by DMol3. We selected the BLYP functional, the basic set was DNP, the convergence tolerance of energy, maximum force and maximum placement were respectively $1*10^{-5}$ hartree, 0.002 hartree/A and 0.005 A.

Synthesis of [(TMP-OH)Co]



Scheme S1 Synthetic procedures of modified cobalt porphyrin complex [(TMP-OH)Co].

5-(4-hydroxyphenyl)-10, 15, 20-tris-(2, 4, 6-trimethylphenyl) porphyrin (1).

2, 4, 6-trimethylbenzaldhyde (1104uL, 7.5mmol), pyrrole (692uL, 10mmol, purified by vacuum distillation), 4-hydroxy benzaldehyde (305.3mg, 2.5mmol, purified by recrystallization in ethanol) were dissolved in 1L chloroform in a two-round flask. Then $BF_3 \cdot Et_2O$ (416uL, 3.3mmol) was added and the solution was stirred at room temperature for 1 h. The straw yellow mixture turned brown gradually. Finally, the oxidation reagent chloranil (TCQ) (1844mg, 7.5mmol) was added and the solution was refluxed for 1 h. After the mixture was cooled to room temperature, it was filtered and chloroform was pumped out. The remaining purple black solid was purified by column chromatography (silica gel, 200-300 mesh, $CHCl_3$ as eluent), gave a purple powder (180mg, 10% yield). ^{1}HNMR ($CDCl_3$, 400MHz) δ (ppm) -2.56(s, 2H, N*H*), 1.84(s, 12H, *o*-Ph-CH_3), 1.85(s, 6H, *o'*-Ph-CH_3), 2.61(s, 3H, *p'*-Ph-CH_3), 2.62(s, 6H, *p*-Ph-CH_3), 7.18(d, 2H, $^3J_{H\text{-}H}$= 8.5 Hz, *m'*-phenyl), 7.27(s, 6H, *m*-phenyl), 8.04(d, 2H, $^3J_{H\text{-}H}$= 8.5 Hz, *o*-phenyl), 8.62(s, 4H, pyrrole), 8.67(d, 2H, $^3J_{H\text{-}H}$= 4.8 Hz, pyrrole), 8.80(d, 2H, $^3J_{H\text{-}H}$= 4.8 Hz, pyrrole). MALDI-TOF MS m/z calcd for $[C_{53}H_{48}N_4O]H^+$: 757.39; found 757.38

5-(4-(10-bromo-1-decyloxy) phenyl)-10, 15, 20-tris-(2, 4, 6-trimethylphenyl) porphyrin (2).

1(200mg, 0.27mmol), 1, 10-dibromodecane (480mg, 1.60mmol) and potassium carbonate (184mg, 1.33mmol) were dispersed in 10mL ethanol in a 25-mL round bottom flask. The purple mixture was refluxed under stirring for 10 hours. The solvent was pumped out, and the residue

was dissolved in $CHCl_3$ and purified by column chromatography (silica gel, 200-300mesh, PE: $CHCl_3$= 4:3 as eluent), gave the desired product 2 as purple powder (197mg, 76% yield). ^{1}HNMR ($CDCl_3$, 400MHz) δ (ppm) -2.56(s, 2H, N*H*), 1.21-1.45(m, 12H, $ArOCH_2CH_2$ (CH_2)$_6CH_2CH_2Br$), 1.65(m, 2H, $-CH_2CH_2CH_2Br$), 1.84(s, 12H, *o*-Ph-CH_3), 1.85(s, 6H, *o'*-Ph-CH_3), 2.00(m, 2H, $ArOCH_2CH_2CH_2$-), 2.61(s, 3H, *p'*-Ph-CH_3), 2.62(s, 6H, *p*-Ph-CH_3), 3.44(t, 2H, $^3J_{H\text{-}H}$= 6.8 Hz, $-CH_2CH_2Br$), 4.24(t, 2H, $^3J_{H\text{-}H}$= 6.5 Hz, $ArOCH_2CH_2$-), 7.24(d, 2H, *m'*-phenyl), 7.27(s, 6H, *m*-phenyl), 8.08(d, 2H, $^3J_{H\text{-}H}$= 8.4 Hz, *o*-phenyl), 8.61(s, 4H, pyrrole), 8.66(d, 2H, $^3J_{H\text{-}H}$= 4.8 Hz, pyrrole), 8.80(d, 2H, $^3J_{H\text{-}H}$= 4.8 Hz, pyrrole). MALDI-TOF MS m/z calcd for $[(C_{63}H_{67}BrN_4O]H^+$: 975.46; found 975.47

(5-(4-(10-hydroxyl-1-decyloxy) phenyl)-10, 15, 20-tris-(2, 4, 6-trimethylphenyl) porphyrin) cobalt (3, (TMP-OH)Co).

2(80mg, 0.082mmol), cobalt acetate tetrahydrate ($CoAc_2 \cdot 4H_2O$, 62mg, 0.082×3mmol) were dispersed in 5mL DMF under an inert atmosphere. The resultant purple mixture was degassed and allowed to stir at 150^{o}C for 5 hours and then cooled to room temperature. DMF was pumped out and the residue was purified by column chromatography (silica gel, 200-300mesh, $CHCl_3$ as eluent), gave the title compound (3) as orange-red solid (more than 30% yield). ^{1}HNMR ($CDCl_3$, 400MHz) δ (ppm) 1.64-1.85(m, 10H, $ArOCH_2CH_2(CH_2)_5CH_2CH_2CH_2OH$), 1.99(m, 2H, $ArOCH_2CH_2(CH_2)_5CH_2CH_2CH_2OH$), 2.28(m, 2H, $-CH_2CH_2CH_2OH$), 2.74(m, 2H, $ArOCH_2CH_2$-), 3.25(bs, 6H, *o'*-Ph-CH_3), 3.56(bs, 12H, *o*-Ph-CH_3), 3.80(t, 2H, $^3J_{H\text{-}H}$= 5.8 Hz, $-CH_2CH_2CH_2OH$), 3.88(s, 3H, *p'*-Ph-CH_3), 3.97(s, 6H, *p*-Ph-CH_3), 5.36(t, 2H, $^3J_{H\text{-}H}$= 5.6 Hz, $ArOCH_2CH_2$-), 9.13(s, 2H, *m'*-phenyl), 9.19(s, 2H, *m"*-phenyl), 9.26(s, 4H, *m*-phenyl), 12.43(bs, 2H, *o*-phenyl), 15.21-15.40(bd, 8H, pyrrole). ^{13}CNMR ($CDCl_3$, 100MHz) δ (ppm) 23.1, 23.3, 24.8, 25.0, 26.3, 27.1, 29.9, 30.0, 30.1, 30.2, 30.5, 33.4, 63.3, 69.7, 115.9, 130.6, 130.8, 140.3, 140.4, 142.2, 146.0, 146.9, 150.3, 151.9, 161.5. MALDI-TOF MS m/z calcd for $[C_{63}H_{66}CoN_4O_2]^+$: 969.45; found 969.35

Typical polymerization procedure with (TMP-OH)Co

A certain amount of [(TMP-OH)Co] in benzene and AIBN in methanol were mixed in a J. Young Valve NMR tube. The solvents were removed by vacuum evacuation. Certain amount of monomers in C_6D_6/CD_3OD was injected into the tube and thoroughly mixed which is subjected to three freeze-pump-thaw cycles. The sample was sealed in the inert atmosphere glove box and placed in a thermostated water bath (326K or 323K) and the progress of polymerization was followed by ^{1}HNMR detection. When the desired conversion was reached, the reaction was stopped by cooling in ice water and exposed to air. Solvent and excess monomers were removed under vacuum. For PHEA, the polymer was precipitated in ethyl acetate and dried. The resulting polymer products were dissolved in DMF for GPC analysis without further purification.

Table S1 Molecular weight and conversion data for poly (methyl acrylate) at 326K in C_6D_6

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	1500	9.5	23	30600	1.22
2	2000	9.5	30	54800	1.21

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

Table S2 Molecular weight and conversion data for poly (butyl acrylate) at 326K in C_6D_6

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	1000	7.5	30	48100	1.21
2	1000	8	40	59700	1.20
3	1000	9	57	84900	1.18
4	1500	9	34	64200	1.27

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

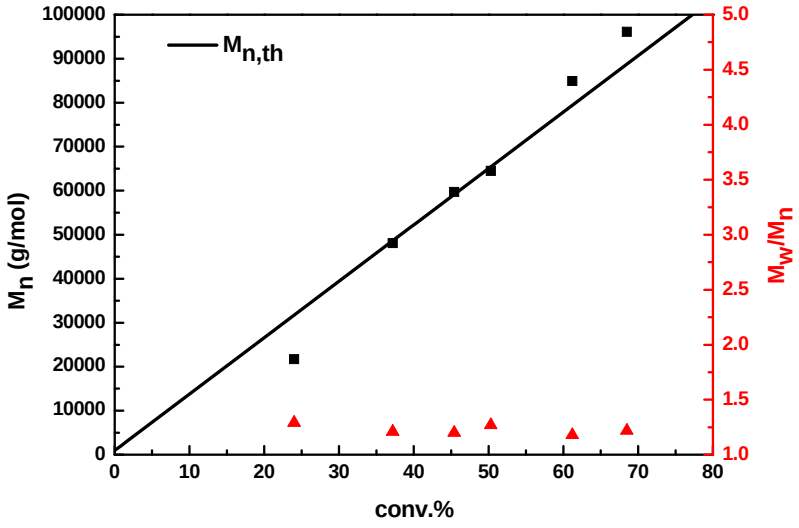


Fig. S1 Changes in number average molecular weight of P*n*BA and polydispersity dependence with conversion of *n*BA to P*n*BA in C_6D_6. $[nBA]_0$=1.0M, $[AIBN]_0=1.0 \times 10^{-2}$M, $[(TMP\text{-}OH)Co]_0=1.0 \times 10^{-3}$M, and T=326 K.

Table S3 Molecular weight and conversion data for poly (*tert*-butyl acrylate) at 326K in C_6D_6

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	1000	5	17	36500	1.29
2	1000	6	32	47900	1.30

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

Table S4 Molecular weight and conversion data for poly (*tert*-butyl acrylate) at 326K in CD_3OD

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	1000	9	40	40900	1.28
2	2000	7	34	64100	1.29

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

Table S5 Molecular weight and conversion data for poly (2-hydroxyethyl acrylate) prepared by CMRP at 326K in CD_3OD

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	2000	9	28	79500	1.32
2	2000	9.5	41	140000	1.25

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

Table S6 Molecular weight and conversion data for poly (N-isopropylacrylamide) at 326K in

CD_3OD

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	1500	5	23	68800	1.29
2	2000	5	18	82400	1.34

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

Table S7 Molecular weight and conversion data for poly (N, N-dimethylacrylamide) prepared by CMRP at 323K in CD_3OD

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	700	14	38	23900	1.27
2	700	18.5	94	60000	1.21

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

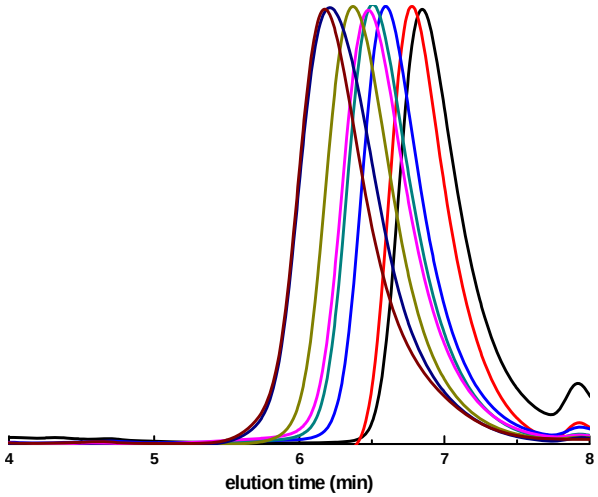


Fig. S2 Gel permeation chromatography (GPC) traces illustrate the molecular weight (M_n) of PDMA increase with DMA conversion for DMA polymerization in CD_3OD at 323K. $[DMA]_0$=1.0M, $[AIBN]_0=1.0\times10^{-2}$M and $[(TMP\text{-}OH)Co]_0=1.43\times10^{-3}$M..

Table S8 Molecular weight and conversion data for poly (N, N-dimethylacrylamide) at 323K in C_6D_6

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	700	17.5	17	13600	1.26
2	700	19.5	44	24400	1.23

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

Method for methylation of PAA

The acrylic acid polymers were methylated using trimethylsilyldiazomethane according to the reported method.[1, 2] The methylated PAA products PMA were dissolved in DMF for GPC analysis without further purification. The GPC result of PMA with different conversion was shown below.

Table S9 Molecular weight and conversion data for poly (acrylic acid) at 323K in CD_3OD

Entry	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n

1	700	21	28	21400	1.28
2	700	25.5	42	26500	1.33

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

Typical polymerization procedure with (TMP)Co

(TMP)Co was synthesized according to the literature.[3] A certain amount of (TMP)Co in chloroform and AIBN in methanol were mixed in a J. Young Valve NMR tube. The solvents were removed by vacuum evacuation. Certain amount of monomers (AA, DMA) in CD_3OD was injected into the tube and thoroughly mixed which is subjected to three freeze-pump-thaw cycles. The concentration of substrates was the same as that for (TMP-OH)Co ($[M]_0$=1.0M, $[AIBN]_0$=1.0 $\times 10^{-2}$M, $[TMPCo]_0$=1.43 $\times 10^{-3}$M) The sample was sealed in the inert atmosphere glove box and placed in a thermostated water bath (323K) and the progress of polymerization was followed by ^{1}HNMR detection. For both of the polymerizations mediated by (TMP)Co, due to the poor solubility of (TMP)Co in methanol, most of the complex aggregated on the bottom of reaction tube. According to the ^{1}HNMR detection, polymerizations of AA and DMA mediated by (TMP)Co were much faster than that by (TMP-OH)Co. Monomer conversion and GPC results were summarized in table S10 below. These results gave indubitable conclusion that compared with (TMP-OH)Co, (TMP)Co was not suitable for polymerization of hydrophilic monomers.

Table S10 Molecular weight and conversion data for poly (acrylic acid) and poly (N, N-dimethylacrylamide) at 323K in CD_3OD mediated by TMPCo

Entry	M	[M]/[Co]	Time/h	conv%	M_n[a]	M_w/M_n
1	AA	700	9	34	41900[b]	1.46[b]
2	AA	700	12	53	47800[b]	1.60[b]
3	DMA	700	7.5	68	77500	1.59

[a] Number average molecular weight in poly (methyl methacrylate) equivalents.

[b] Molecular weight (M_n) and polydispersity (PDI) were obtained after methylation.

Typical procedures for the synthesis of diblock copolymers.

Macroinitiators (PDMA, PAA, and P*t*BA) were prepared according to the procedure described above. A solution (benzene or methanol) of macroinitiator and fresh monomer were mixed in the glove box. The substrate was immerged in a preheated water bath (323K) and the conversion of second monomer was followed by ^{1}HNMR detection. After a period of reaction time, the reaction was stopped by cooling at ice water and exposed to air. Solvent and unreacted monomer was pumped out. For block copolymer PAA-b-PDMA, it was methylated to be PMA-b-PDMA before GPC detection. All the other block copolymers PDMA-b-PHEA, PDMA-b-P*t*BA, PDMA-b-P*n*BA and P*t*BA-b-PDMA were dissolved in DMF for GPC analysis without further purification. GPC results for these block copolymers were shown below.

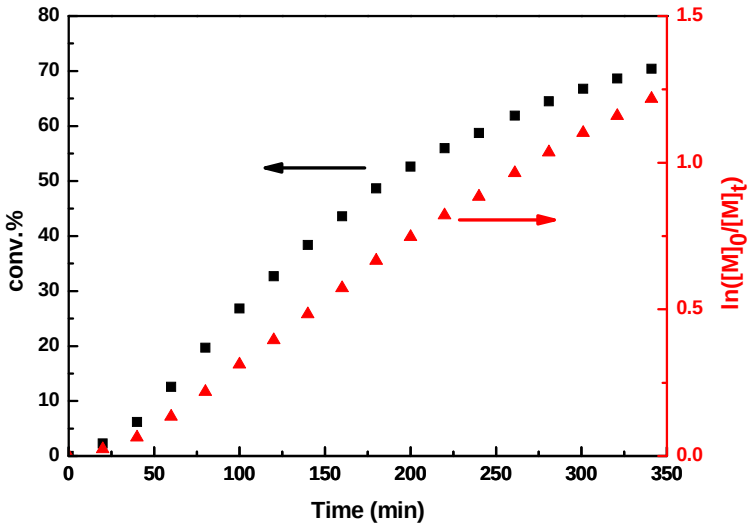
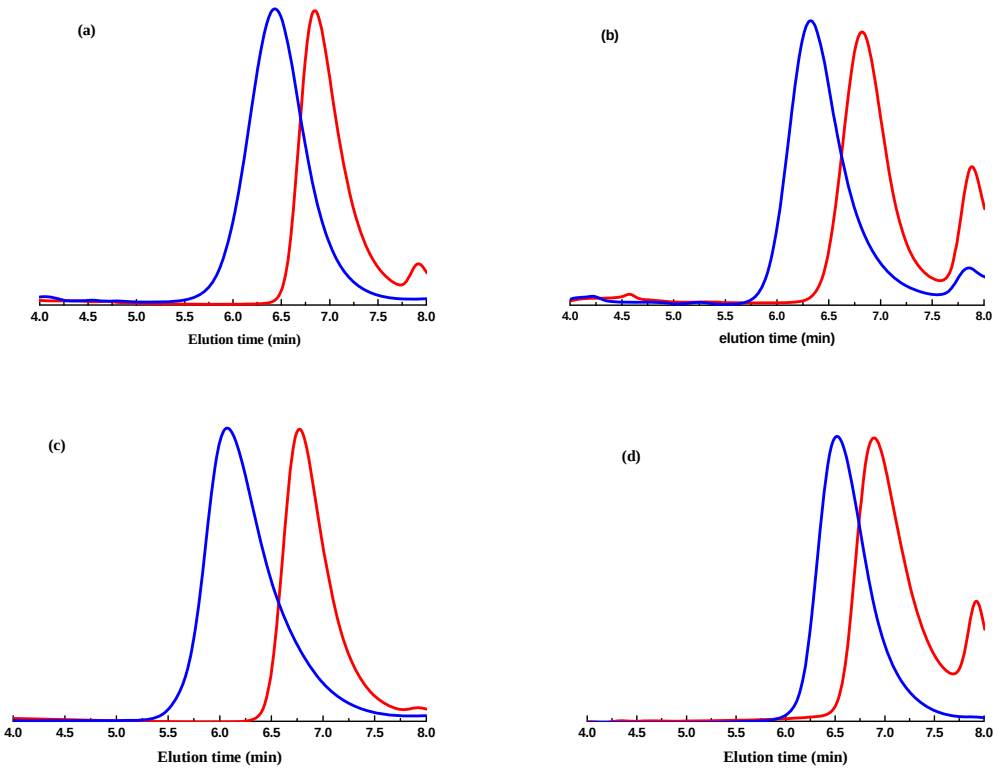


Fig. S3 Kinetic plot for the block copolymerization of DMA with *n*BA starting from PDMA macroinitiator (M_n=18000, M_w/M_n=1.28) at 323 K in C_6D_6. $[n\text{BA}]_0$=1.0M and $[(\text{TMP-OH})\text{Co-PDMA}]_0=1.43\times10^{-3}$M.



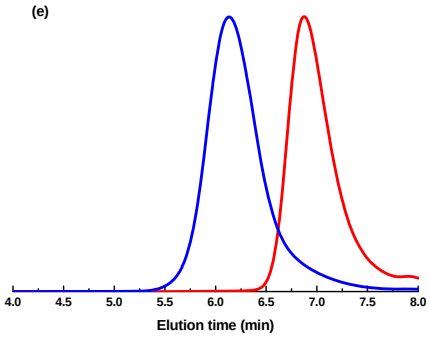


Fig. S4 GPC chromatograms of (a) Table 2, entry 1, PDMA macroinitiator (red curve, M_n=13100, PDI=1.30) and PDMA-b-PHEA (blue curve, M_n=37400, PDI=1.34), (b) Table 2, entry 2, PAA macroinitiator (red curve, M_n=16100, PDI=1.26) and PAA-b-P*t*BA (blue curve, M_n=41700, PDI=1.30), (c) Table 2, entry 3, PDMA macroinitiator (red curve, M_n=15800, PDI=1.30) and PDMA-b-P*t*BA (blue curve, M_n=59700, PDI=1.36), (d) Table 2, entry 4, P*t*BA macroinitiator (red curve, M_n=11500, PDI=1.34) and P*t*BA-b-PDMA (blue curve, M_n=27100, PDI=1.33), and (e) Table 2, entry 5, PDMA macroinitiator (red curve, M_n=12700, PDI=1.28) and PDMA-b-P*n*BA (blue curve, M_n=64900, PDI=1.24).

^{1}HNMR and ^{13}CNMR of polymers

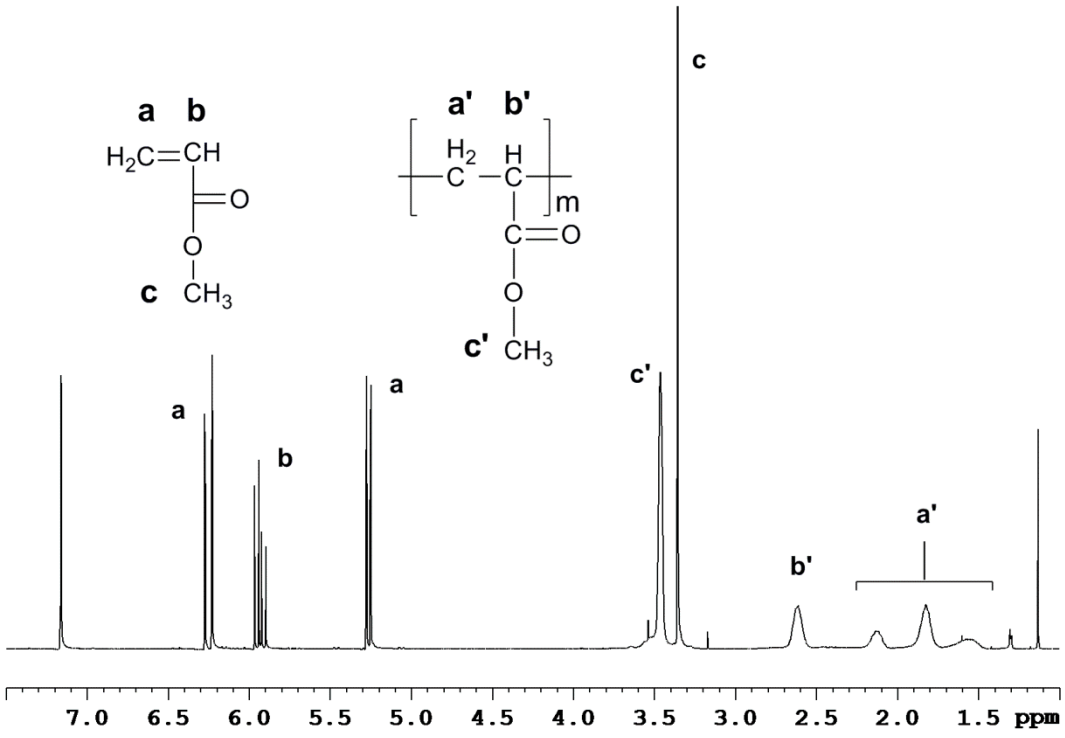


Fig. S5 ^{1}HNMR spectrogram of methyl acrylate and poly(methyl acrylate) in C_6D_6

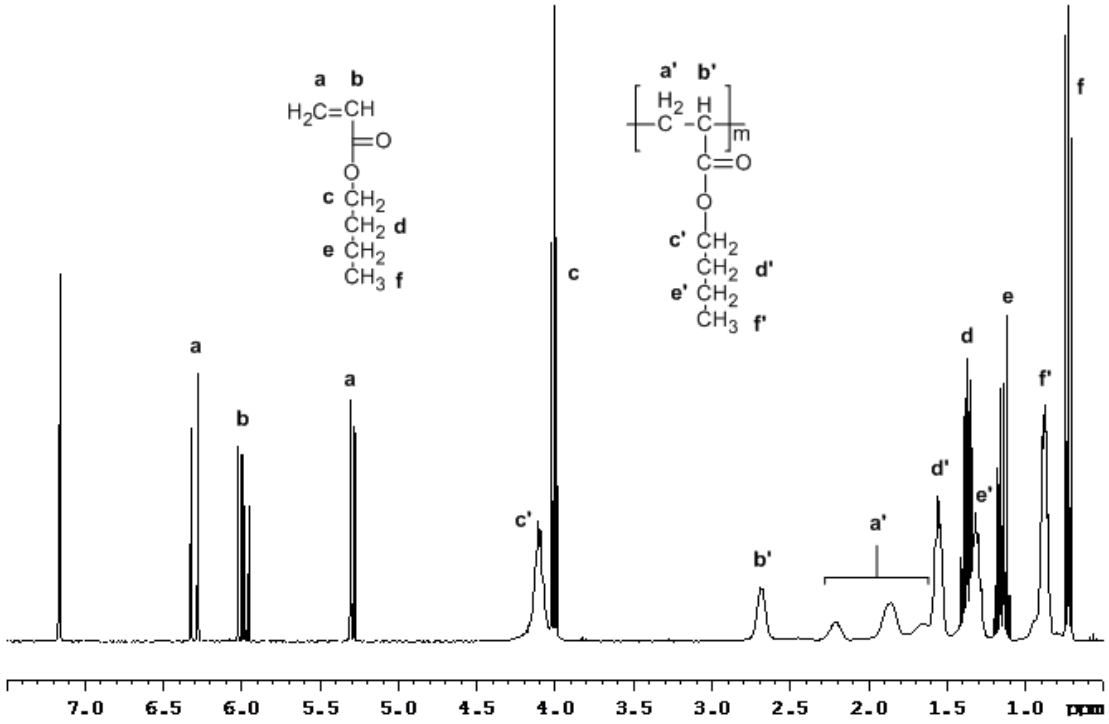


Fig. S6 ^{1}HNMR spectrogram of *n*-butyl acrylate and poly(*n*-butyl acrylate) in C_6D_6.

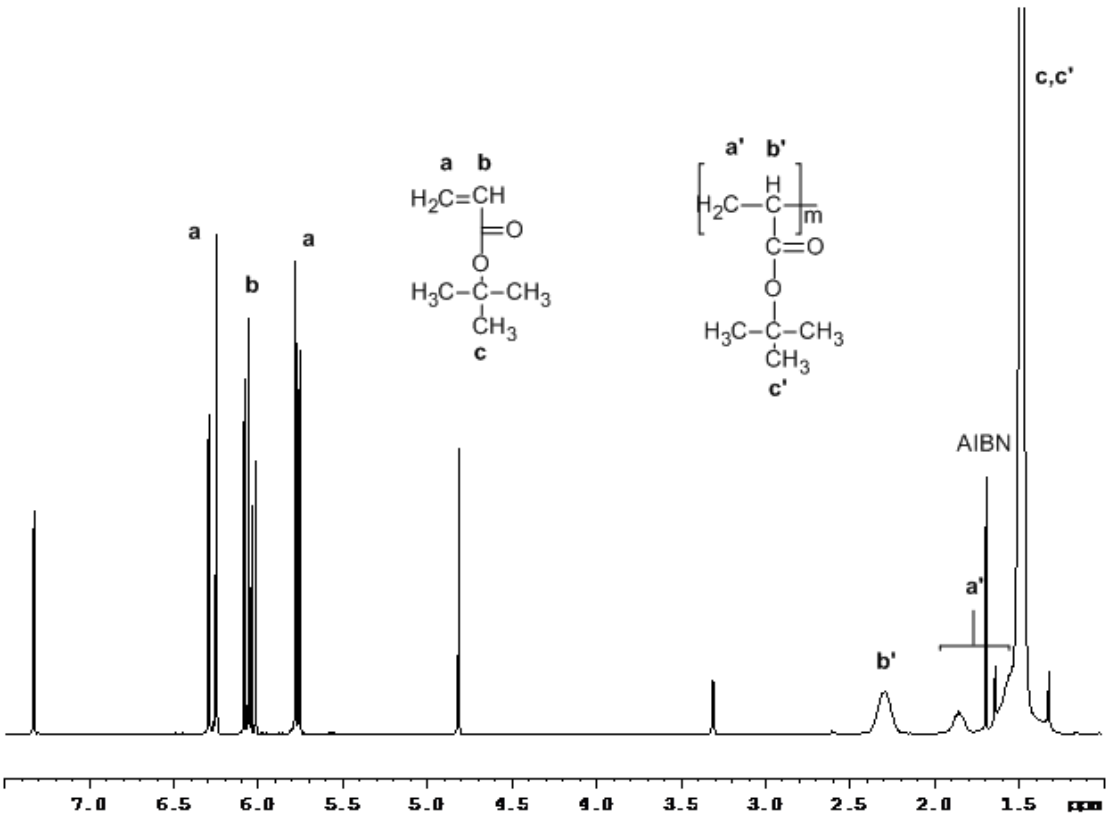


Fig. S7 ^{1}HNMR spectrogram of *tert*-butyl acrylate and poly(*tert*-butyl acrylate) in CD_3OD.

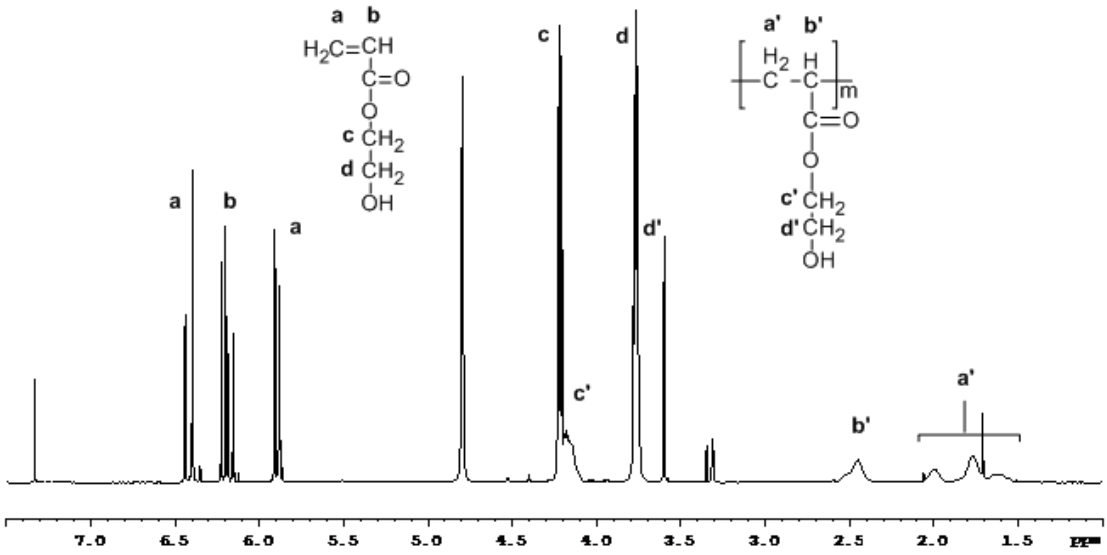


Fig. S8 [1]HNMR spectrogram of 2-hydroxyethyl acrylate and poly(2-hydroxyethyl acrylate) in CD_3OD.

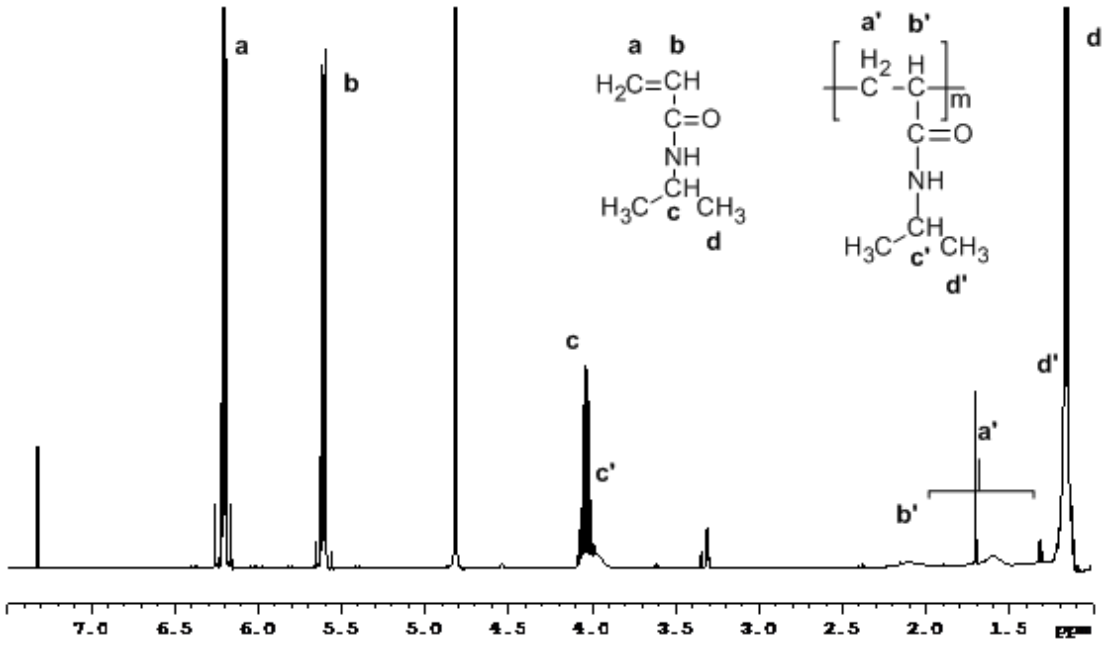


Fig. S9 [1]HNMR spectrogram of N-isopropyl acrylamide and poly(N-isopropyl acrylamide) in CD_3OD.

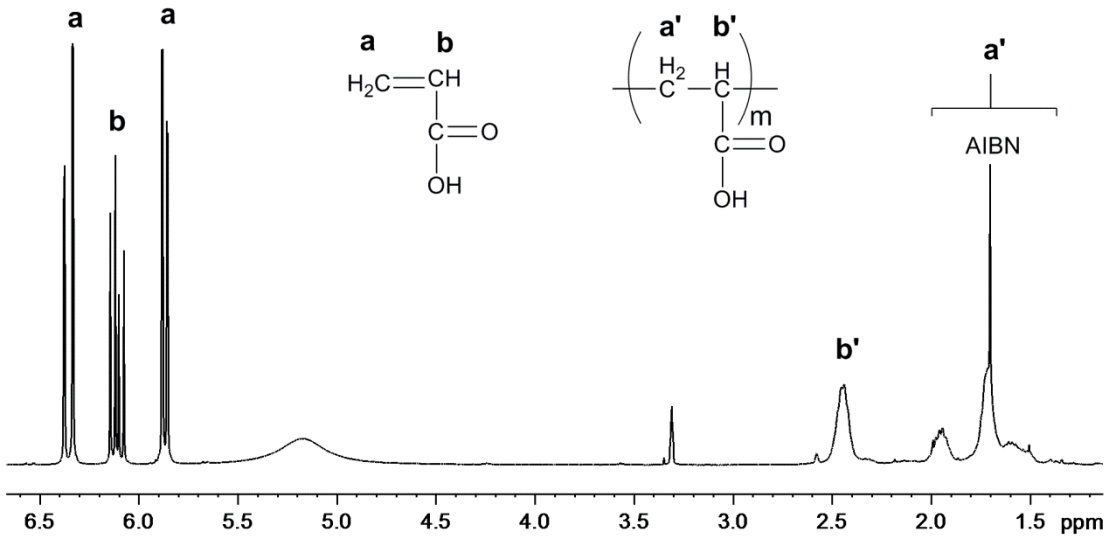


Fig. S10 ^{1}HNMR spectrogram of acrylic acid and poly(acrylic acid) in CD_3OD.

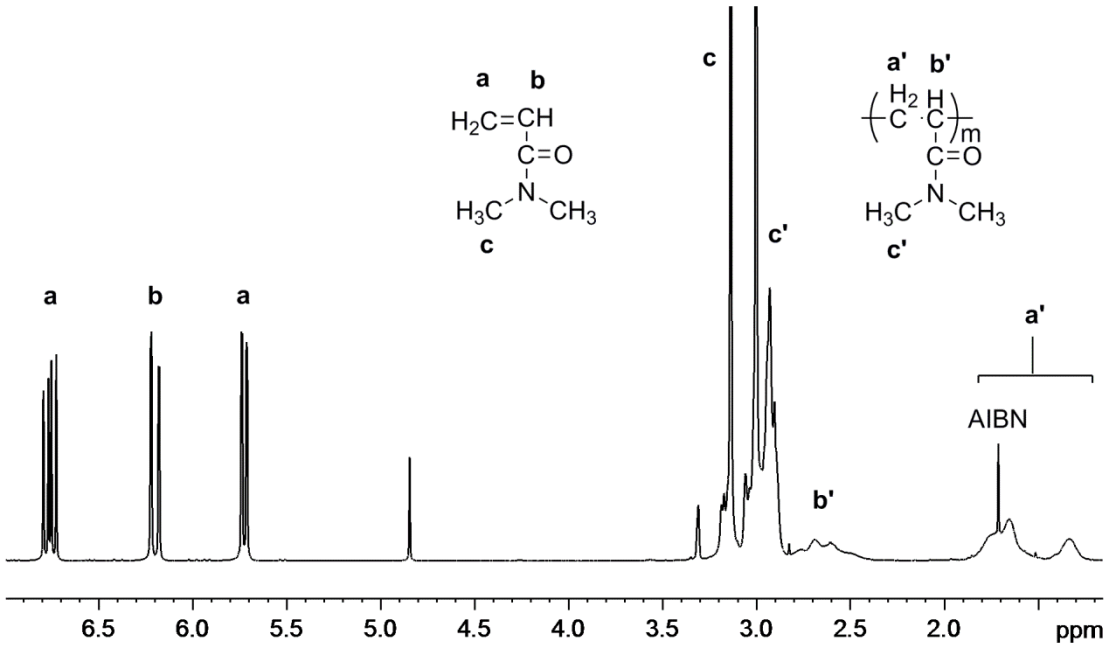


Fig. S11 ^{1}HNMR spectrogram of N,N-dimethylacrylamide and poly(N,N-dimethylacrylamide) in CD_3OD.

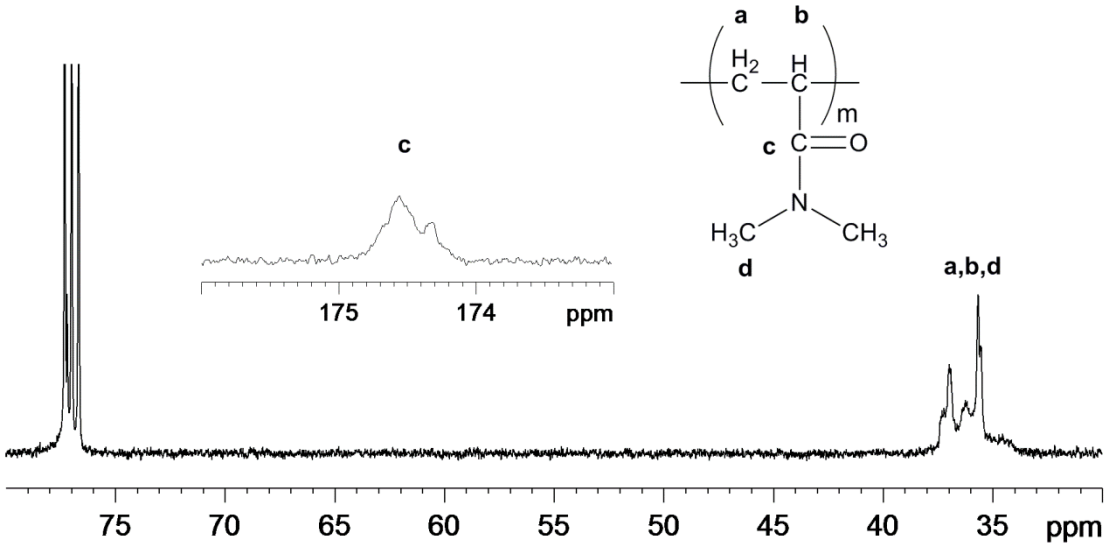


Fig. S12 ^{13}CNMR spectrogram of poly(N,N-dimethylacrylamide) in $CDCl_3$.

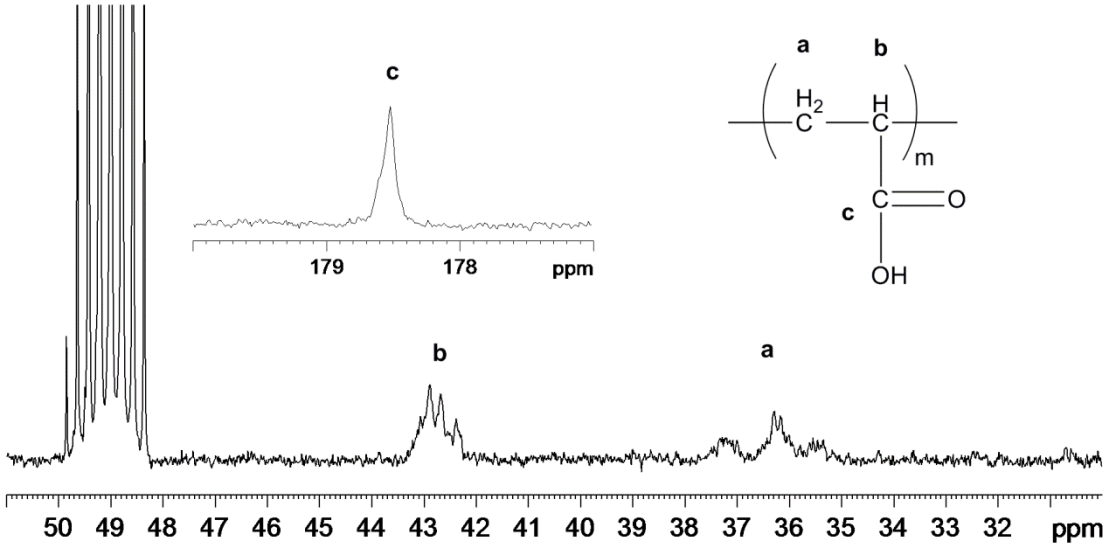


Fig. S13 ^{13}CNMR spectrogram of poly(acrylic acid) in CD_3OD.

Reference:

1. L. Couvreur, C. Lefay, J. Belleney, B. Charleux, O. Guerret and S. Magnet, *Macromolecules*, 2003, **36**, 8260-8267.
2. S. Graham, P. A. G. Cormack and D. C. Sherrington, *Macromolecules*, 2005, **38**, 86-90.
3. B. B. Wayland, L. Basickes, S. Mukerjee, M. L. Wei and M. Fryd, *Macromolecules*, 1997, **30**, 8109-8112.