Supporting Information

Highly Stretchable Free Standing Poly(acrylic acid)-*block*-Poly(vinyl alcohol) Films Obtained from Cobalt Mediated Radical Polymerization

Fu-Sheng Wang,[†] Tzu-Fang Wang,[‡] Hung-Hsun Lu,[†] Wai-Sam Ao-Ieong,[‡] Jane Wang,[‡] Hsin-Lung Chen,*[,‡] Chi-How Peng*[,†]

[†] Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University 101, Sec 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan
[‡] Department of Chemical Engineering, National Tsing Hua University 101, Sec 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan

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1. Synthesis of the PVAc-Co^{III}(salen*) macroinitiator and chain extension of MA from PVAc-Co^{III}(salen*).

The synthesis was held under the condition of Co^{II}(salen*):AIBN:VAc = 1:5:1500 in bulk of VAc at 55 °C. The total volume of the solution was 5 ml and the weight of Co^{II}(salen*) was 22 mg. The polymerization was stopped at conversion = 40.2% to give a PVAc-Co^{III}(salen*) macroinitiator which M_n and PDI equal to 51.2k and 1.19 respectively. Residual VAc was removed by vacuum. Then, 15 ml benzene solution of 2.47 M MA and 26 mg Co^{II}(salen*) was added for block copolymer synthesis at 50 °C. The addition of extra Co^{II}(salen*) was to prevent the formation of dead PVAc chains[1]. The conversion reached 51.8% within 240 mins.

2. Synthesis of the PMA-Co^{III}(salen*) macroinitiator and chain extension of VAc from PMA-Co^{III}(salen*).

The synthesis was held under the condition of Co^{II}(salen*):AIBN:MA = 1:5:1000 at 55°C in 15 ml benzene solution with [MA] = 3.68 M. The polymerization was stopped at conversion = 20.1% to give a PMA-Co^{III}(salen*) macroinitiator which M_n and PDI equal to 15.6k and 1.40 respectively. Benzene and residual MA was removed by vacuum. The polymer was dissolved by 30 ml DCM and added to 300 ml hexane dropwisely to precipitate the macro-initiator for removing unreacted Co^{II}(salen*) and AIBN. 1 g PMA-Co(salen*) (0.064 mmole) and 0.042 g AIBN (0.256 mmole) was dissolved in 10 ml VAc. The solution was stirred at 50 °C.

3. Synthesis of the PVAc-Co^{III}(TMP) macroinitiator and chain extension of MA from PVAc-Co^{III}(TMP).

The synthesis was held under the condition of Co^{II}(TMP):AIBN:VAc = 1:5:1500 in bulk of VAc at 55 °C. The total volume of the solution was 5 ml and the weight of Co^{II}(TMP) was 31 mg. The polymerization was stopped at conversion = 21.0% to give a PVAc-Co^{III}(TMP) macroinitiator which M_n and PDI equal to 27.0k and 1.21 respectively. Residual VAc was removed by vacuum. Then, 10 ml benzene solution of 2.47 M MA was added for block copolymer synthesis at 50 °C. The polymerization reached 76.7% within 180 mins. The reaction reached conversion 17.3% within 400 mins. A 180 minutes long induction period was observed.

4. Synthesis of the PMA-Co^{III}(TMP) macroinitiator and chain extension of VAc from PMA-Co^{III}(TMP).

The synthesis was held under the condition of Co^{II}(TMP):AIBN:MA = 1:5:1000 at 55 °C in 10 ml benzene solution with [MA] = 3.68 M. The polymerization was

stopped at conversion = 23.2% to give a PMA-Co^{III}(TMP) macroinitiator which M_n and PDI equal to 20.0k and 1.22. Benzene and residual MA was removed by vacuum. 13 ml VAc was then added for the synthesis of block copolymer at 50 °C. The reaction reached conversion 18.9% within 65 mins. A 30 minutes long induction period was observed.

NMR spectra and GPC traces of the block copolymers.

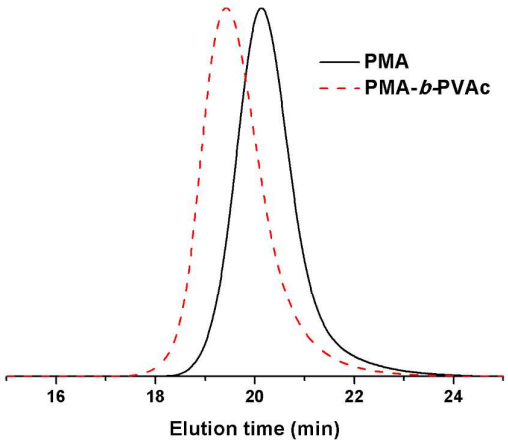

Figure S1. GPC traces of the synthesis of block copolymer PMA_{976}-*b*-$PVAc_{2041}$.

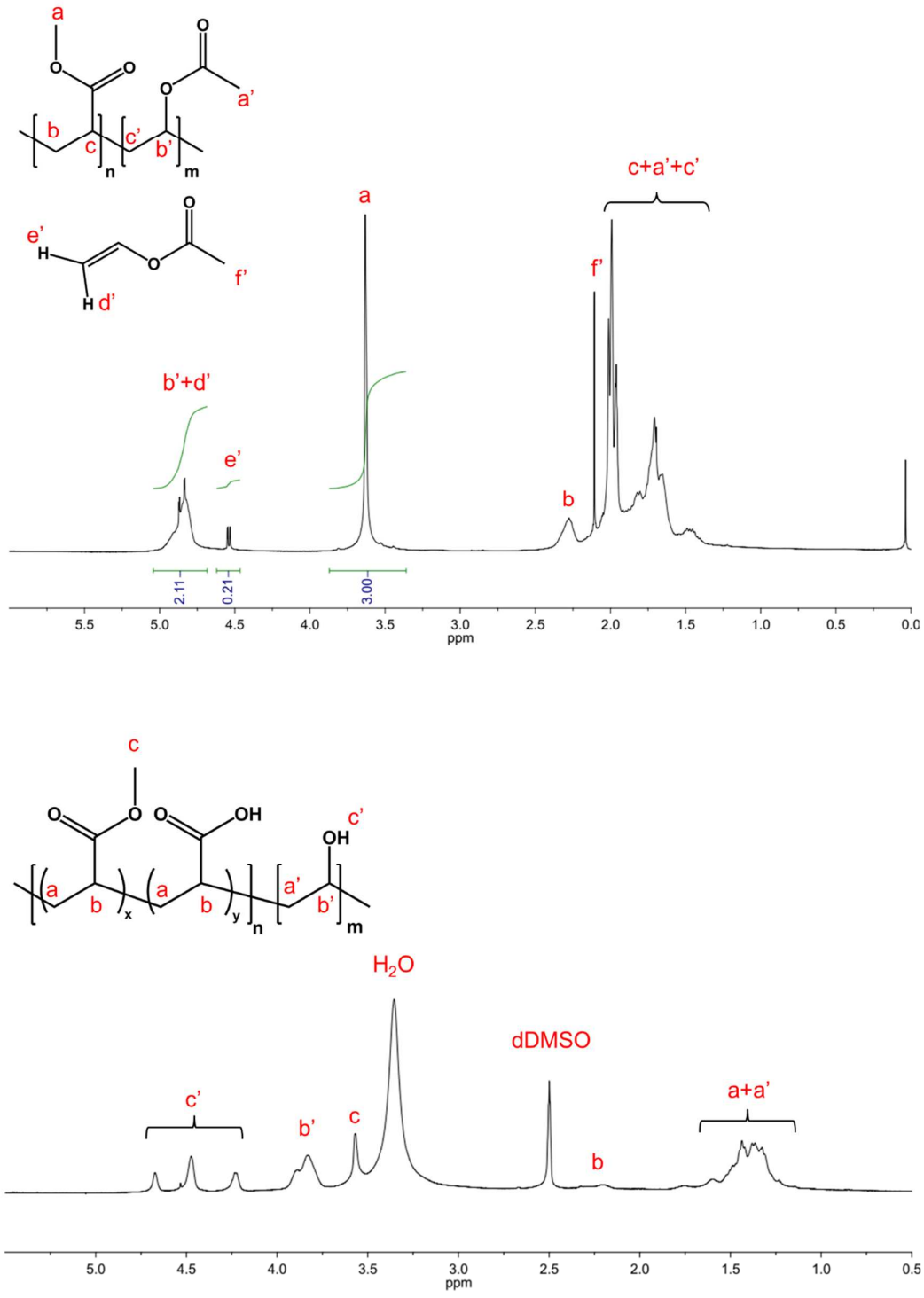

Figure S2. NMR spectrum of PMA_{976}-*b*-$PVAc_{2041}$ ($CDCl_3$) and hydrolyzed product PAA-*b*-PVA (*d*-DMSO).

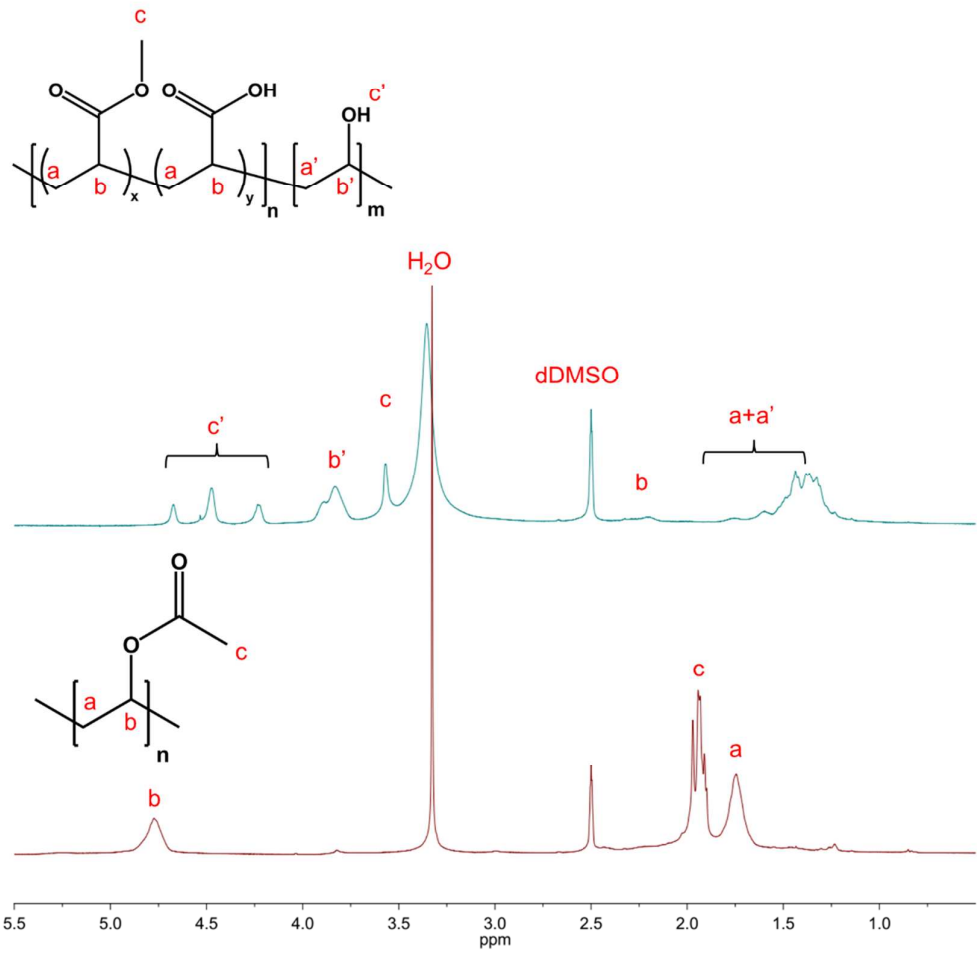

Figure S3. The comparison of the NMR spectrum for PVAc and PAA-*b*-PVA in *d*-DMSO. (Peak a and b were not observed in PAA-*b*-PVA, indicating that the hydrolysis approached more than 99%)

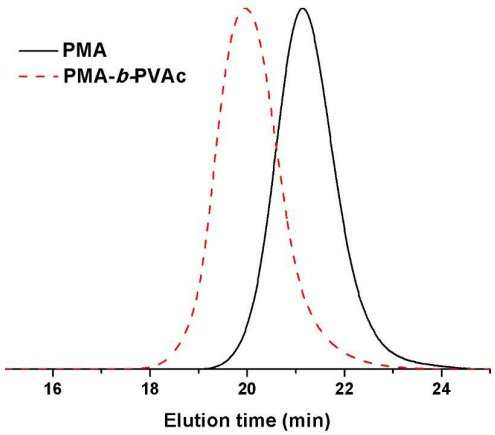

Figure S4. GPC traces of the synthesis of block copolymer PMA_{1034}-*b*-$PVAc_{1191}$.

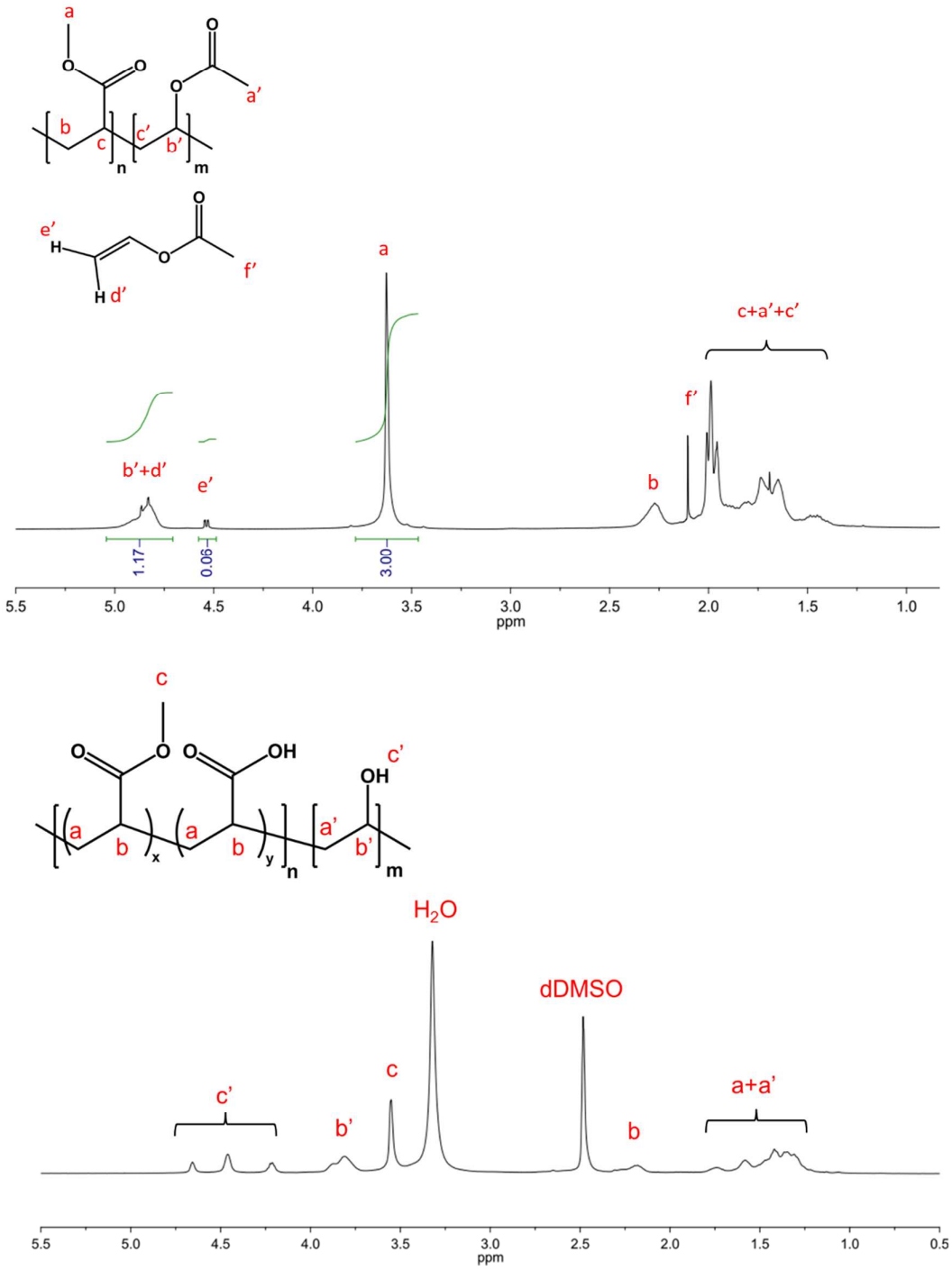

Figure S5. NMR spectrum of PMA_{1034}-*b*-$PVAc_{1191}$ ($CDCl_3$, up) and hydrolyzed product PAA-*b*-PVA (*d*-DMSO, down).

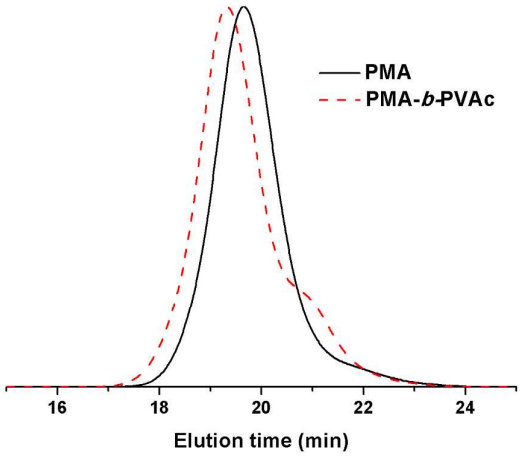

Figure S6. GPC traces of the synthesis of block copolymer PMA_{1348}-*b*-$PVAc_{148}$.

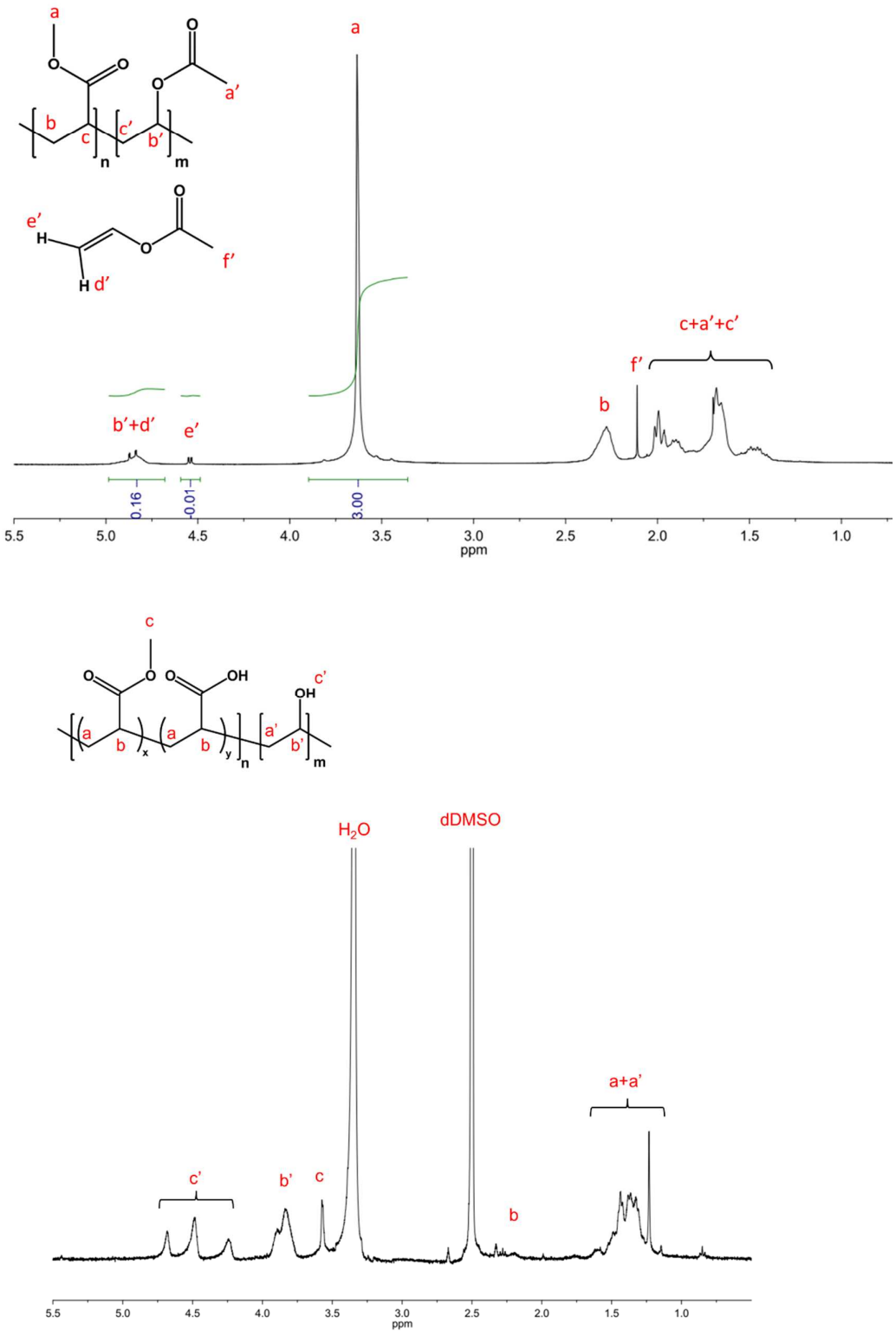

Figure S7. NMR spectrum of PMA_{1348}-*b*-$PVAc_{148}$ ($CDCl_3$) and hydrolyzed product PAA-*b*-PVA (*d*-DMSO).

Titration of PAA, PVA and PAA-*b*-PVA block copolymer.

0.25 g polymer was dissolved water solution and titrated to pH 12.0 by 0.1 M $NaOH_{(aq)}$. Then the solution was titrated with 0.1 M $HCl_{(aq)}$ (Figure S8, S9). The first derivative titration curve shows that the infection point of PAA were 3 ml and 16 ml. For the block copolymer the peak were at 2 ml and 7.5 ml. The results suggest that the block copolymer contains about 0.125 g PAA. Since the formula molecular weight for PAA and PVA was 74 and 43, the ratio of PAA and PVA for the block copolymer was 0.125/74 : 0.125/43 ≈ 1: 2.

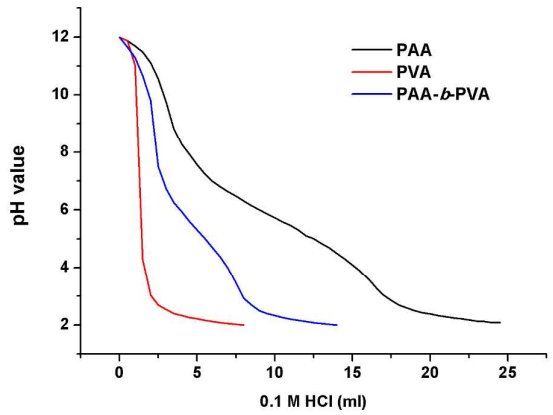

Figure S8. Titration curve of PAA, PVA and PAA-*b*-PVA.

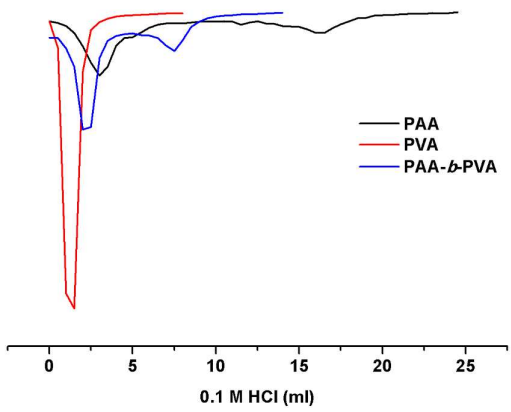

Figure S9. First derivative titration curve of PAA, PVA and PAA-*b*-PVA.