

Supporting Information

# End Group Modification of Poly(acrylates)

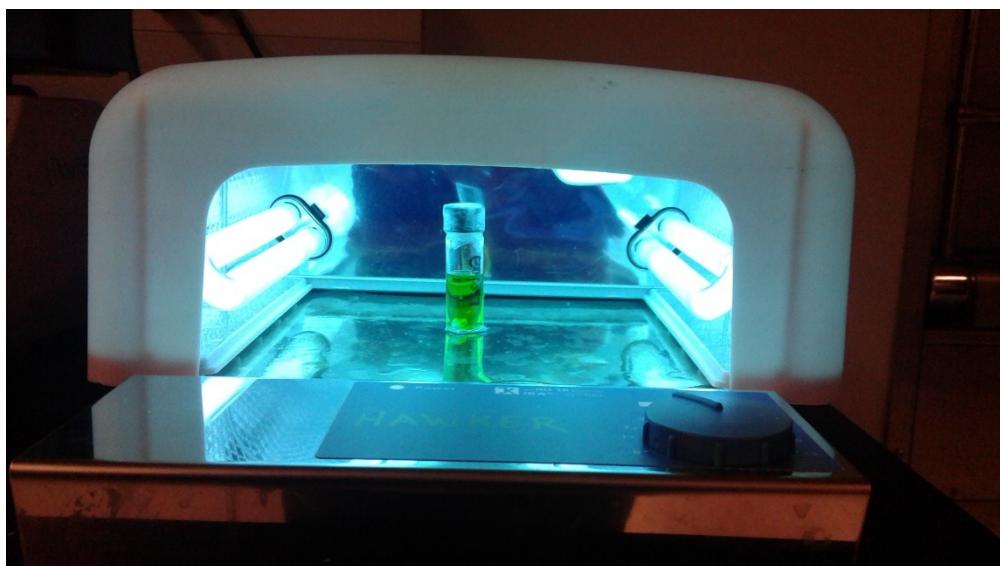
## Obtained via ATRP: A User Guide

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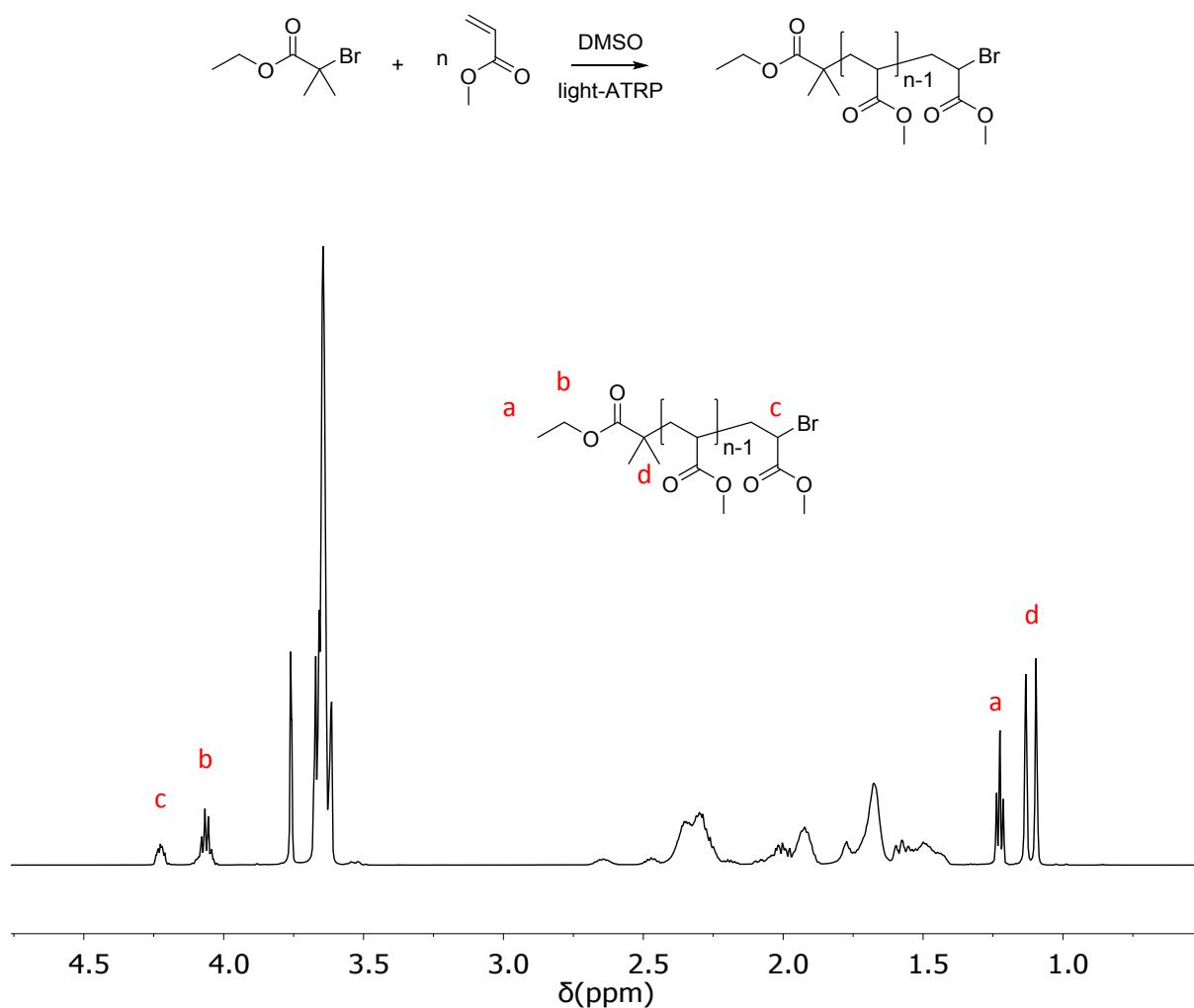
*b - School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332*

*† These authors contributed equally to this work.*

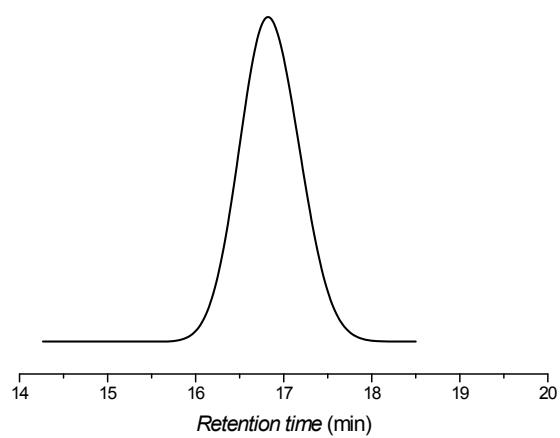


**Figure S1:** Typical setup of a photo-ATRP using a conventional UV nail gel curing lamp.

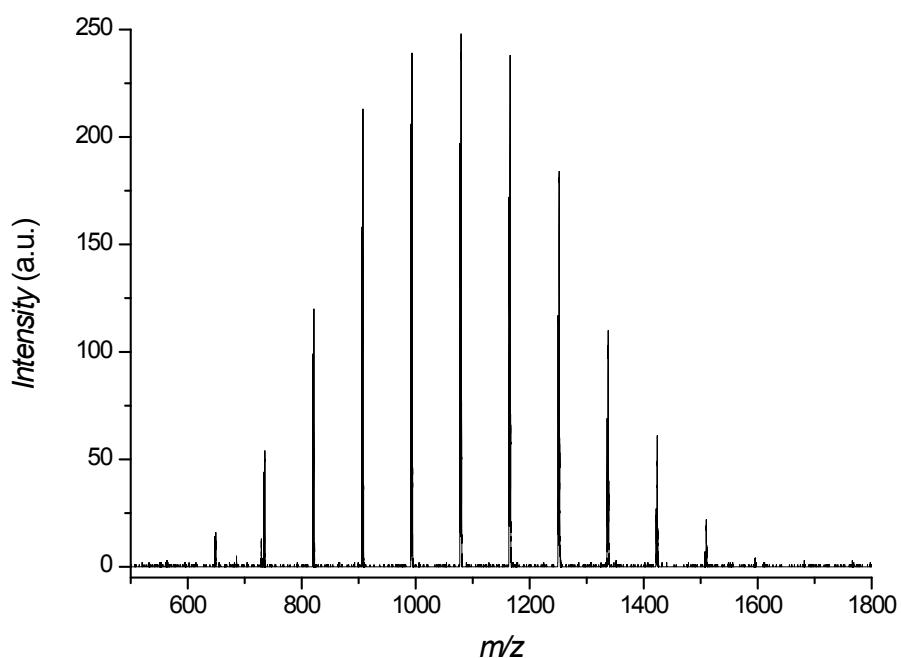
### **Characterization of bromine-terminated poly(MA)**



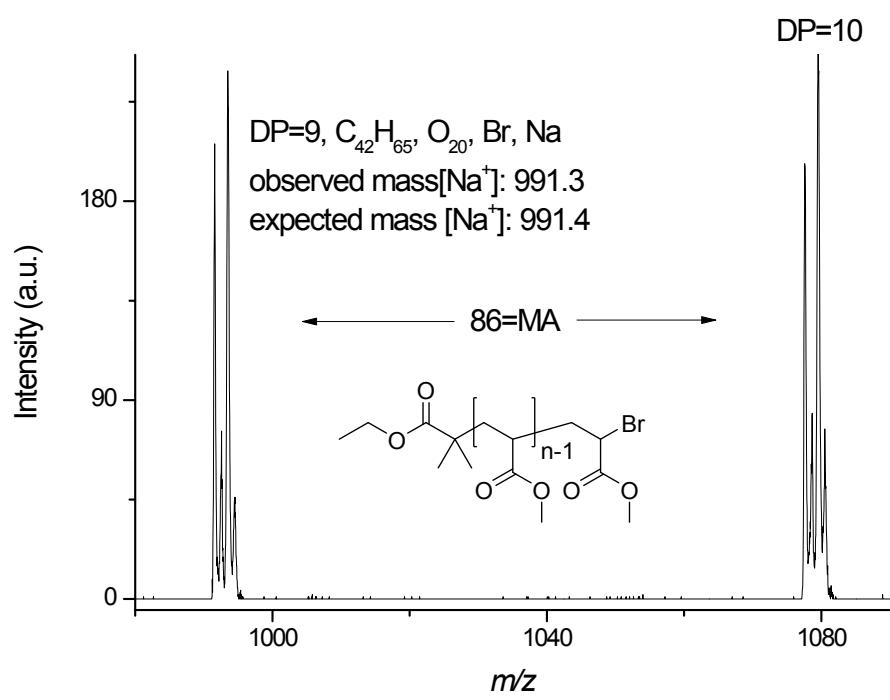
**Figure S2:**  $^1\text{H}$  NMR of bromine-terminated poly(MA) (DP = 10) obtained via photo-ATRP.



**Figure S3:** SEC trace of bromine-terminated poly(MA) (DP = 10),  $M_n = 1100 \text{ g mol}^{-1}$ ,  $D = 1.10$ .

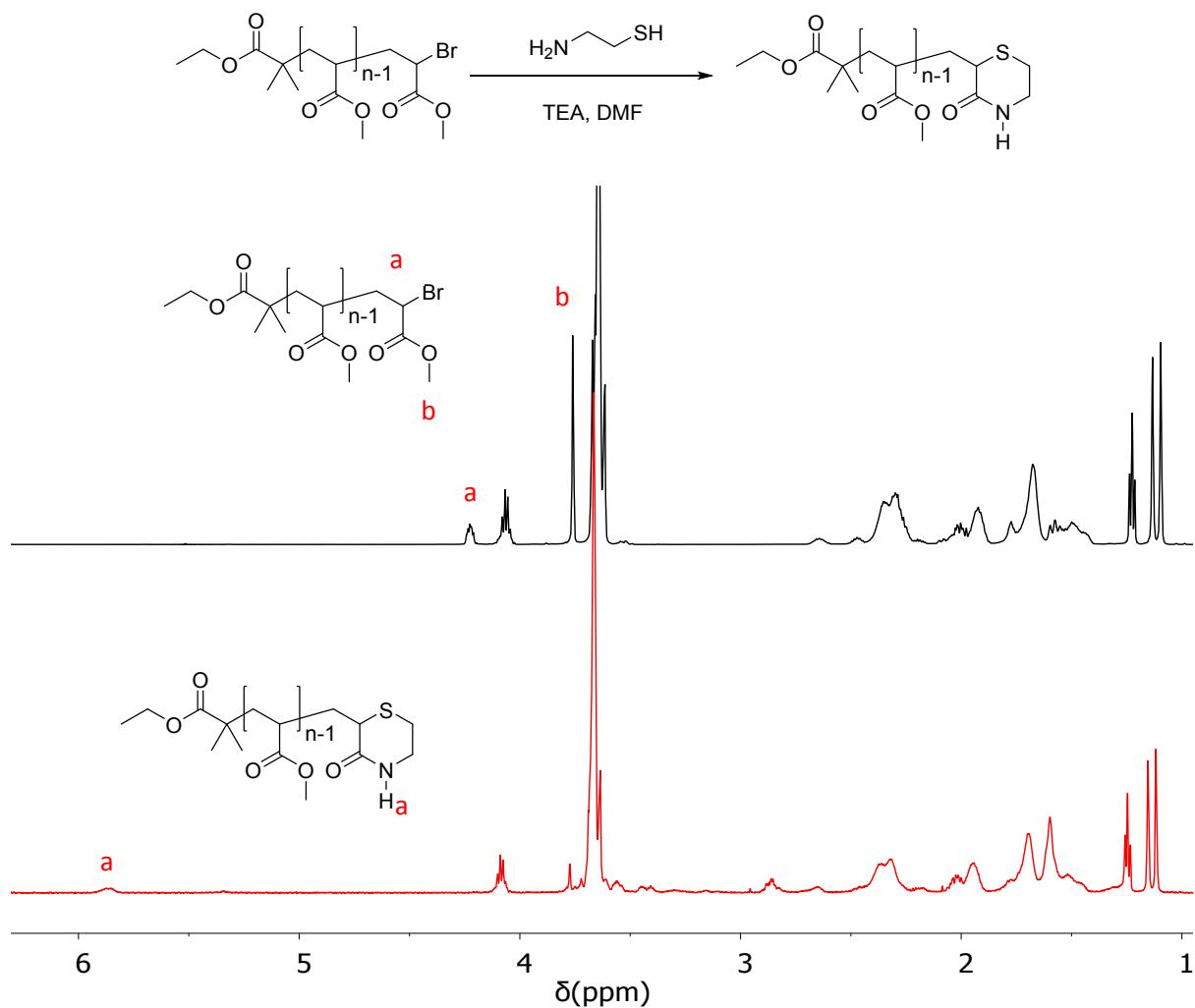


**Figure S4a:** MALDI-ToF-MS of poly(MA) initiated by EBiB and terminated with bromine.

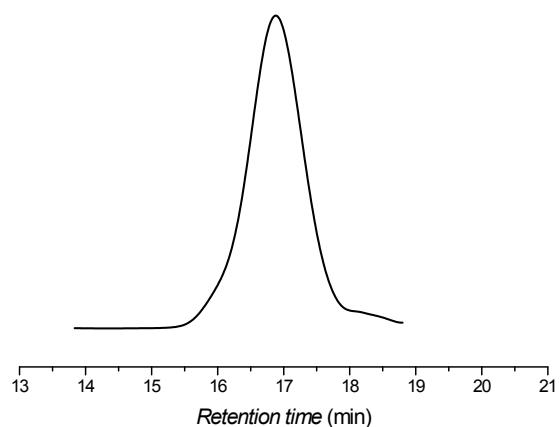


**Figure S4b:** Expanded MALDI-ToF spectrum of poly(MA) initiated by EBiB and terminated with bromine.

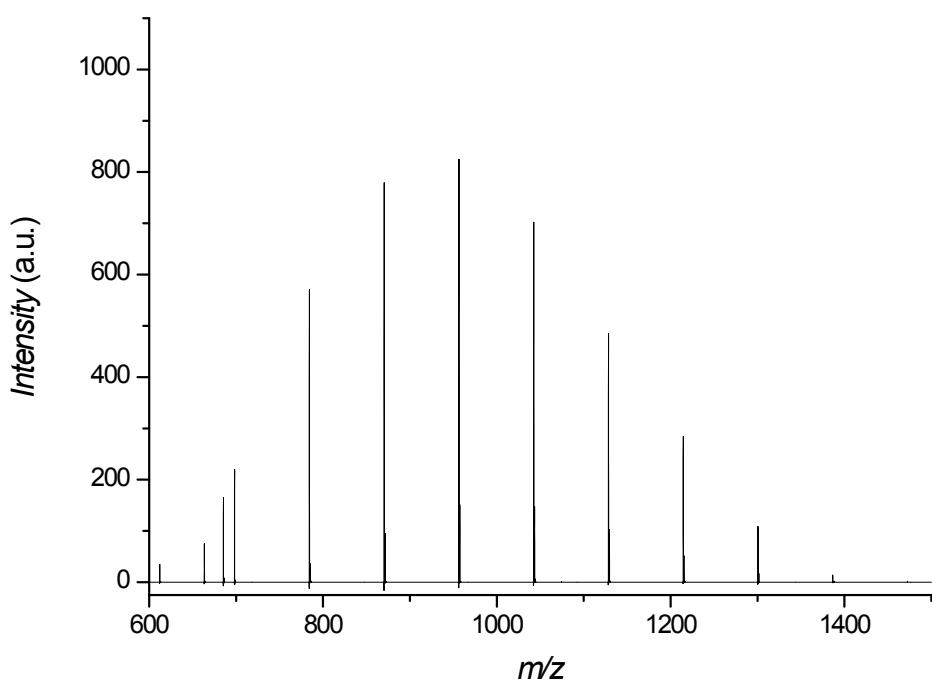
### **Characterization of lactame-terminated poly(MA)**



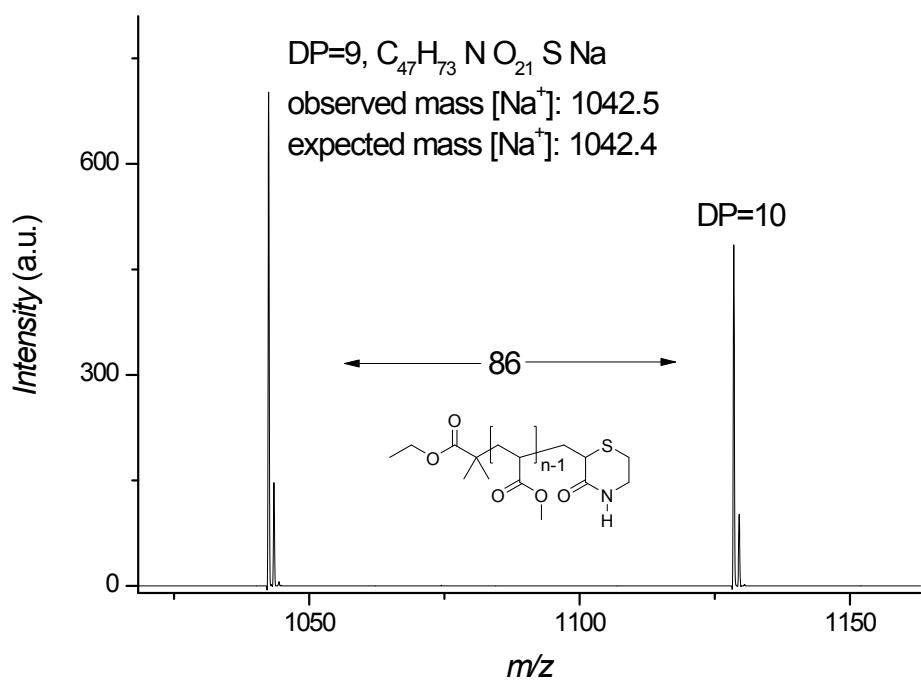
**Figure S5:**  $^1\text{H}$  NMR spectra of the transformation of bromine-terminate poly(MA) (top) to lactame-terminated poly(MA) (bottom).



**Figure S6:** SEC trace of lactame-terminated poly(MA),  $M_n = 1000 \text{ g mol}^{-1}$ ,  $D = 1.10$ .

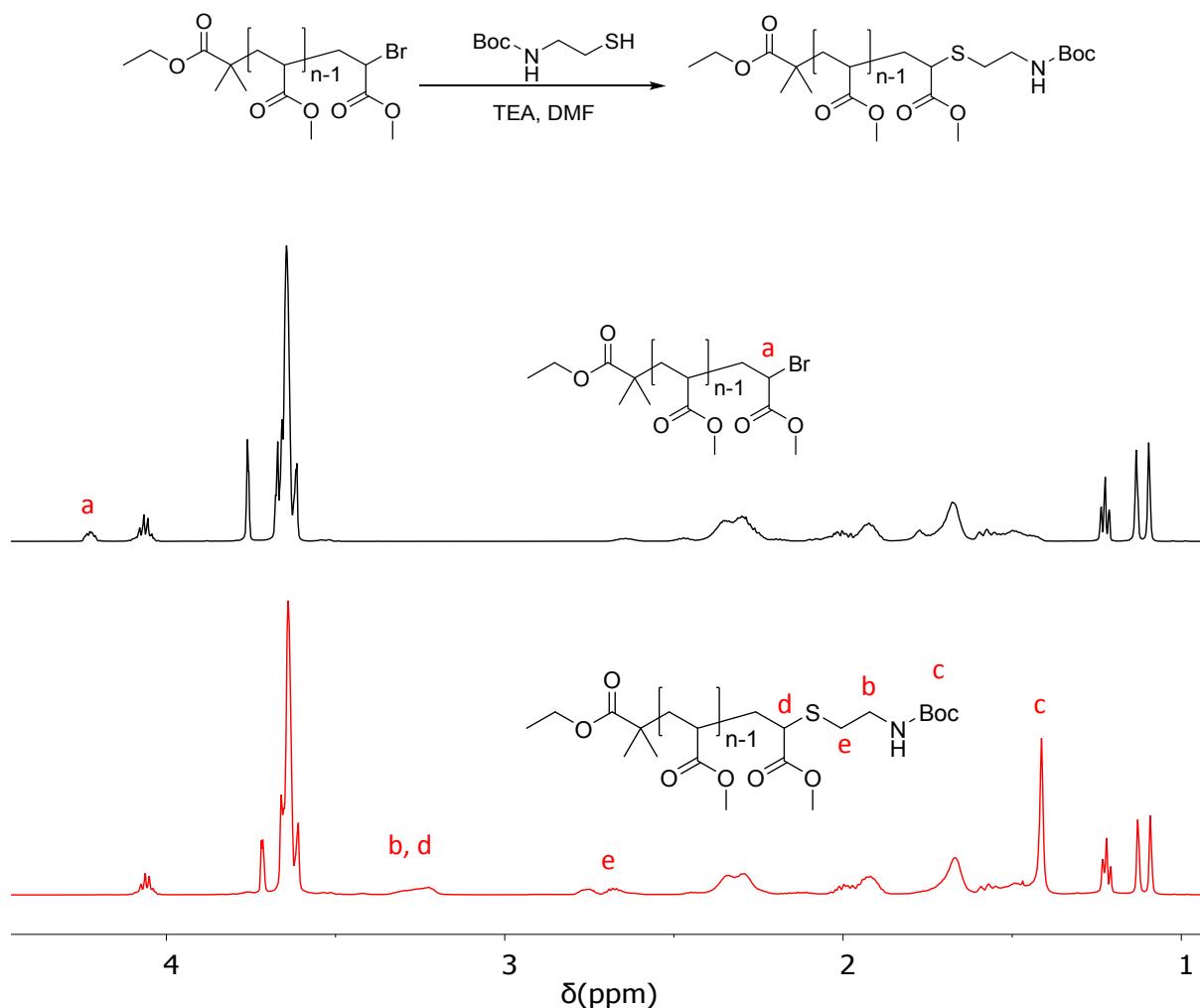


**Figure S7a:** MALDI-ToF-MS spectrum of lactame-terminated poly(MA).

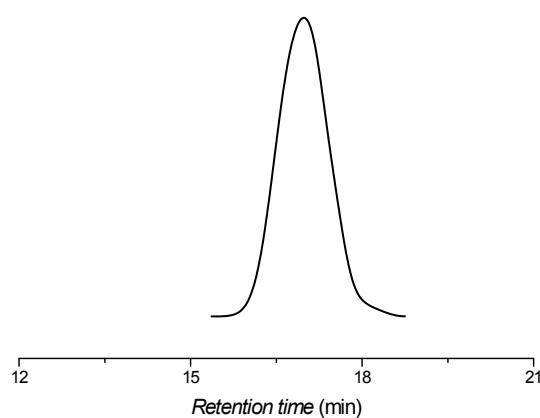


**Figure S7b:** Expanded MALDI-ToF-MS spectrum of lactame-terminated poly(MA).

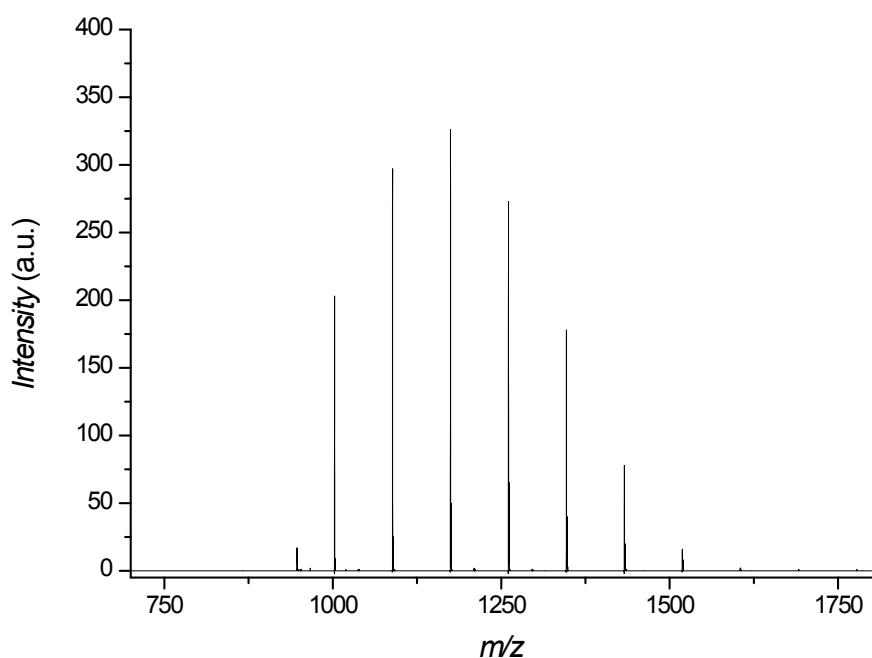
**Characterization of Boc-protected-amine terminated poly(MA)**



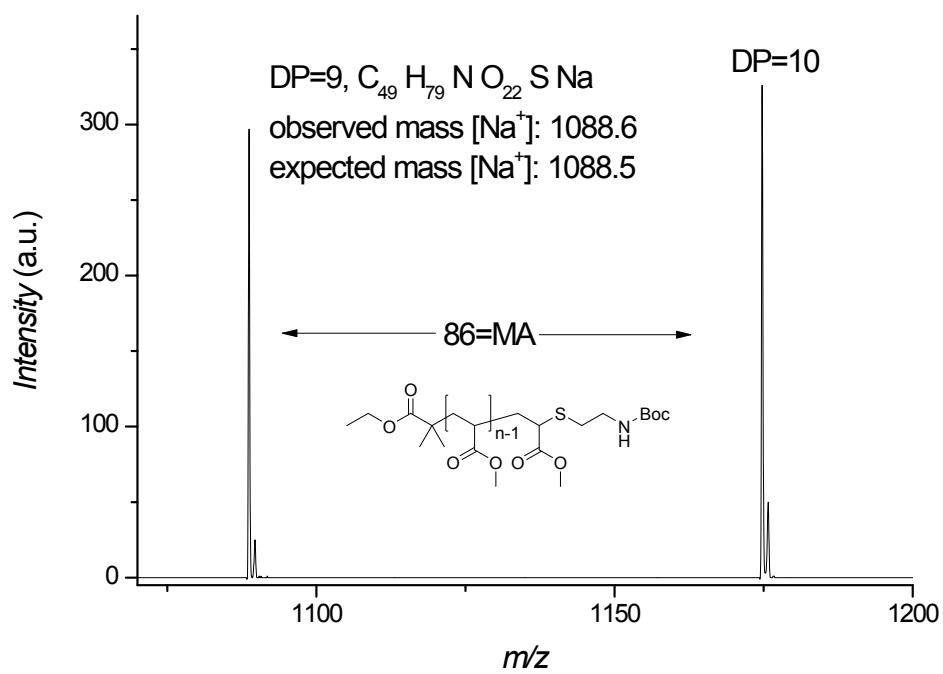
**Figure S8:** <sup>1</sup>H NMR spectra of the transformation from bromine-terminated poly(MA) (top) to Boc-amine-terminated poly(MA) (bottom).



**Figure S9:** SEC trace of Boc-amine-terminated poly(MA),  $M_n = 1000 \text{ g mol}^{-1}$ ,  $D = 1.20$ .

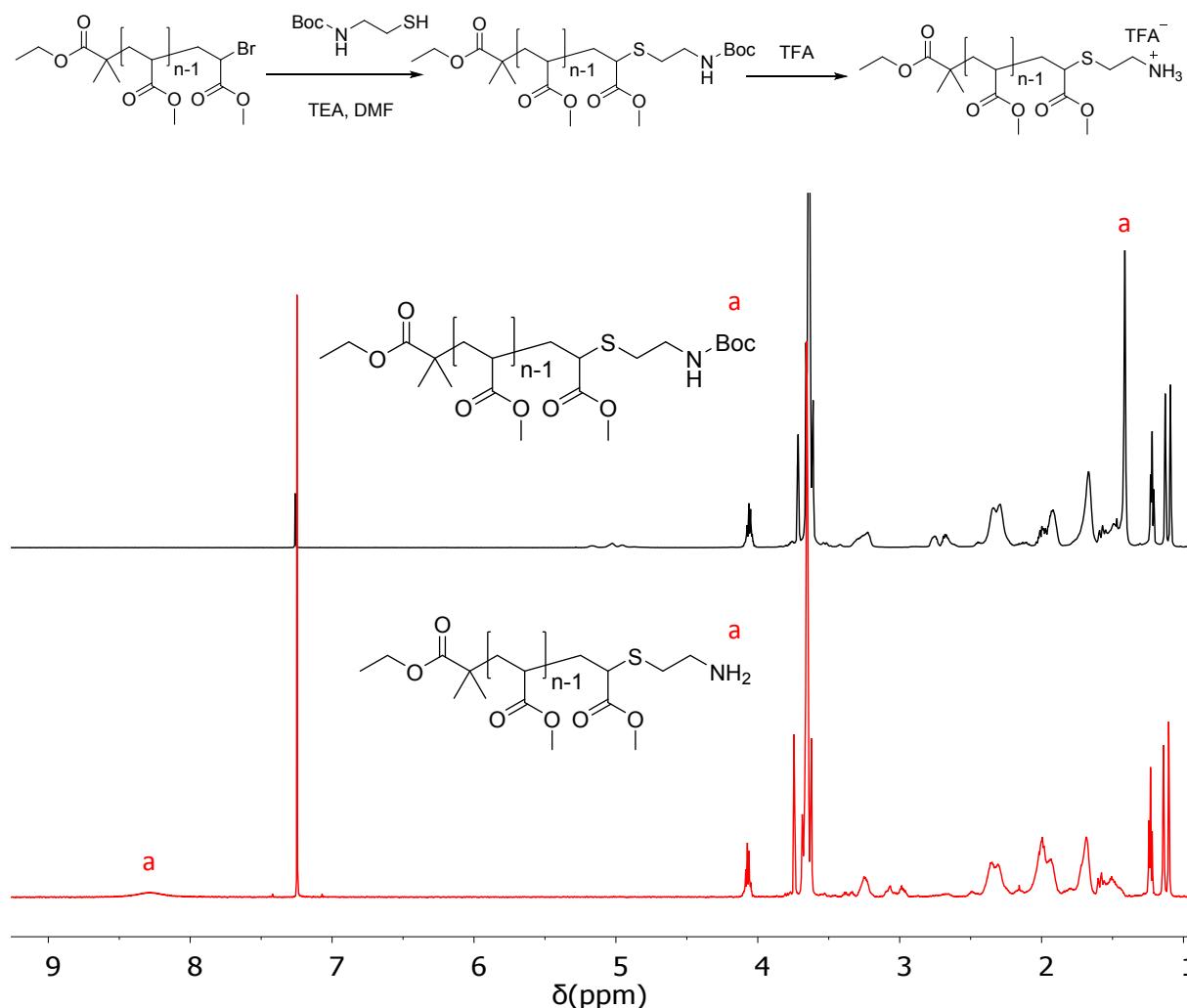


**Figure S10a:** MALDI-ToF-MS spectrum of Boc-amine-terminated poly(MA).

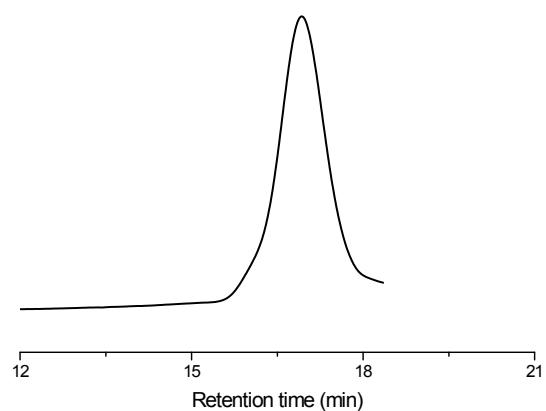


**Figure S10b:** Expanded of MALDI-ToF-MS spectrum Boc-amine-terminated poly(MA).

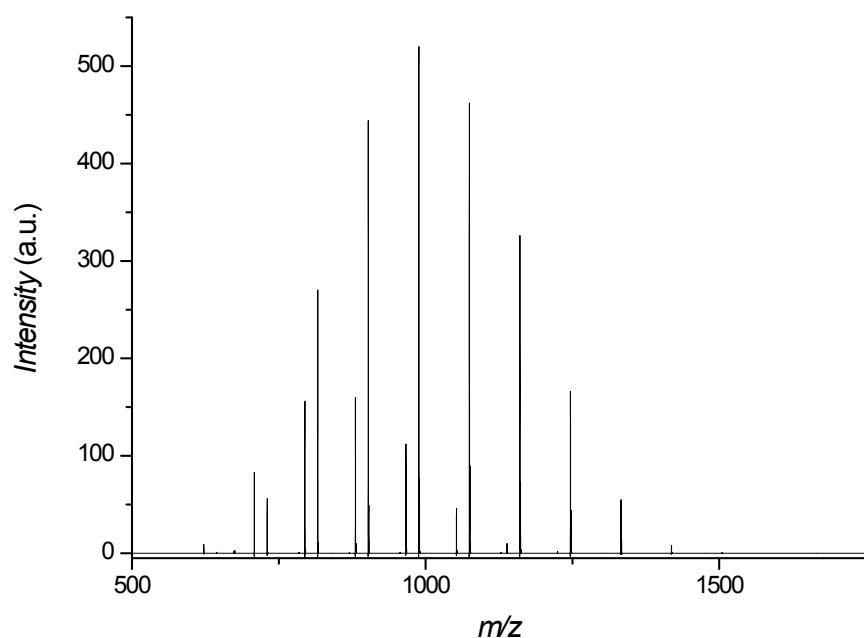
### **Characterization of amine-terminated poly(MA)**



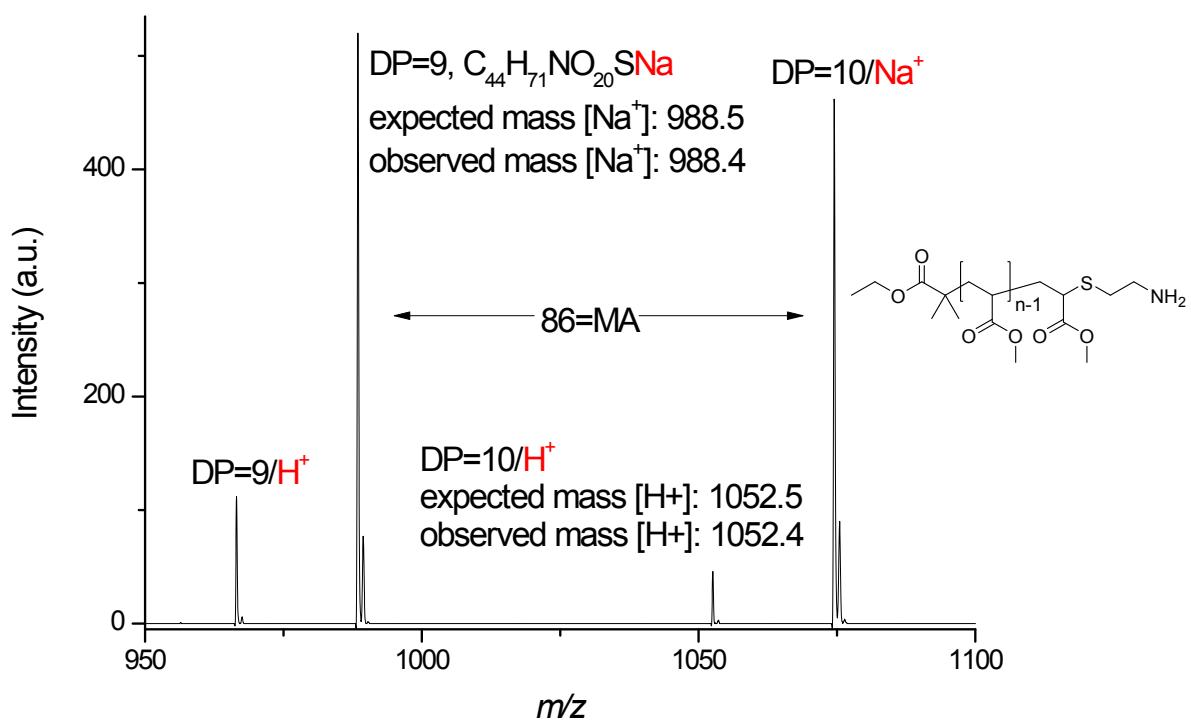
**Figure S11:** <sup>1</sup>H NMR spectra of the transformation from the Boc-amine-terminated poly(MA) (top) to amine-terminated poly(MA) (bottom).



**Figure S12:** SEC trace of amine-terminated poly(MA),  $M_n = 1100 \text{ g mol}^{-1}$ ,  $D = 1.20$ .

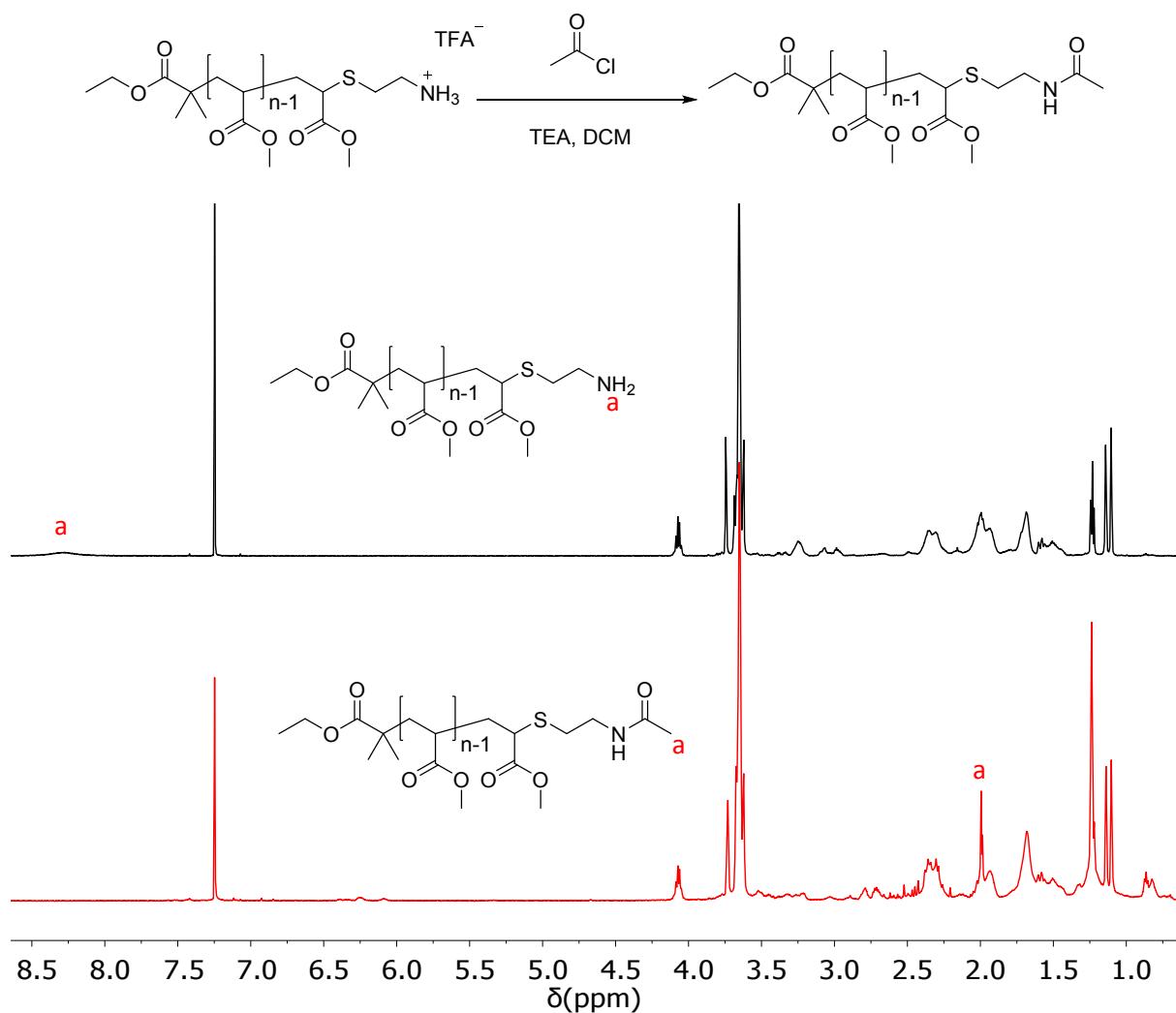


**Figure S13a:** MALDI-ToF-MS spectrum of amine-terminated poly(MA).

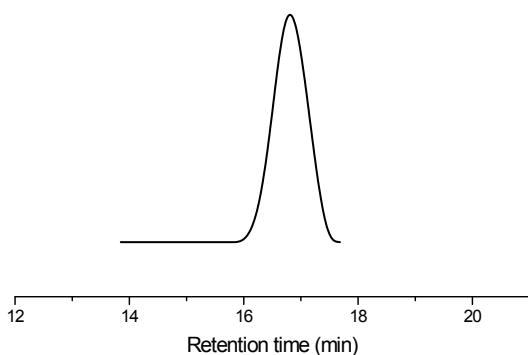


**Figure S13b:** Expanded MALDI-ToF-MS spectrum of amine-terminated poly(MA).

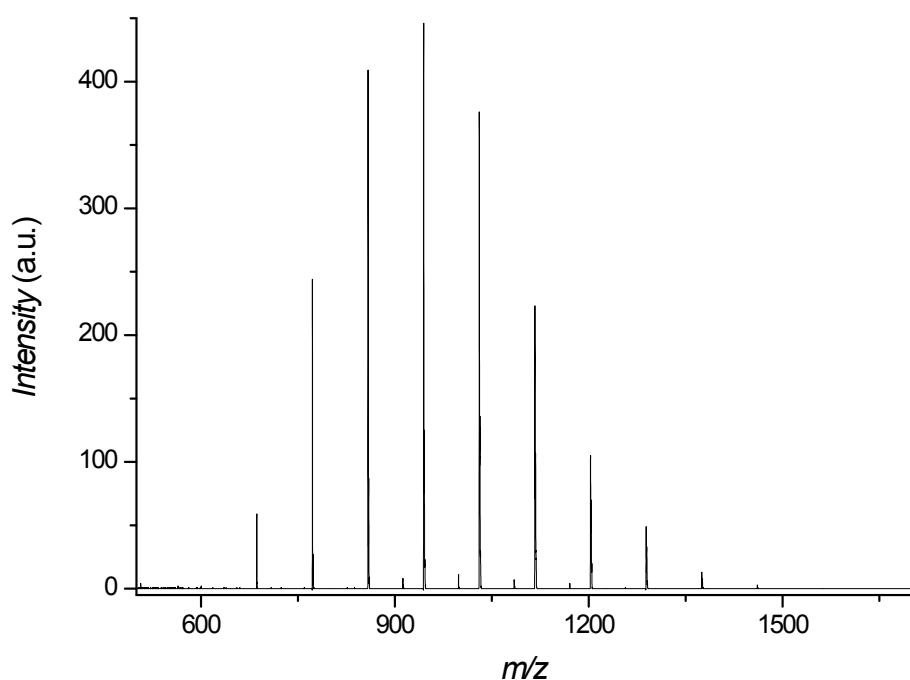
### Characterization of acetyl-terminated poly(MA)



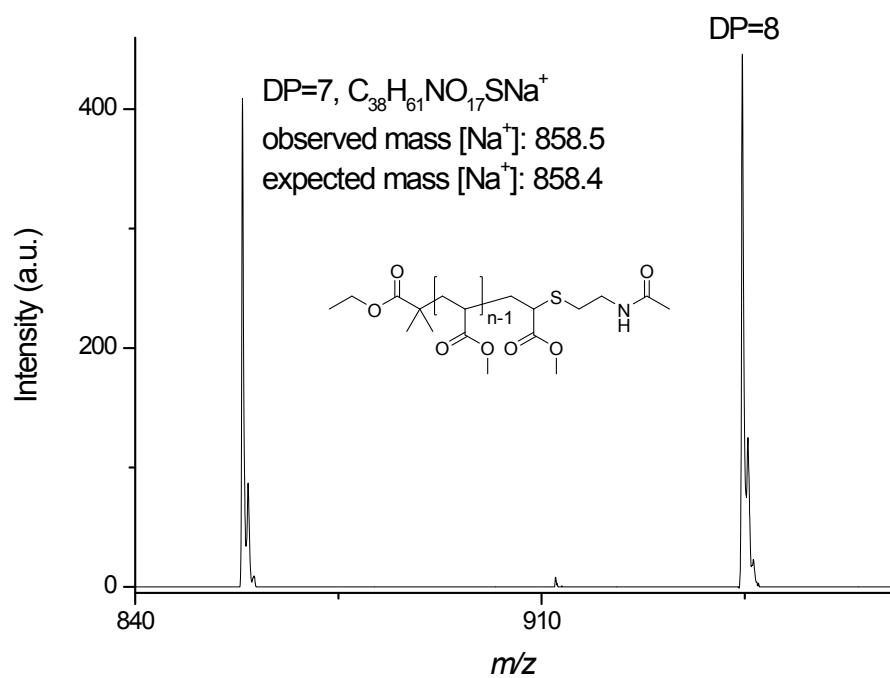
**Figure S14:** <sup>1</sup>H NMR spectra of the reaction from amine-terminated poly(MA) (top) to acetyl-terminated poly(MA) (bottom).



**Figure S15:** SEC trace of acetyl-terminated poly(MA),  $M_n = 1200 \text{ g mol}^{-1}$ ,  $D = 1.15$ .

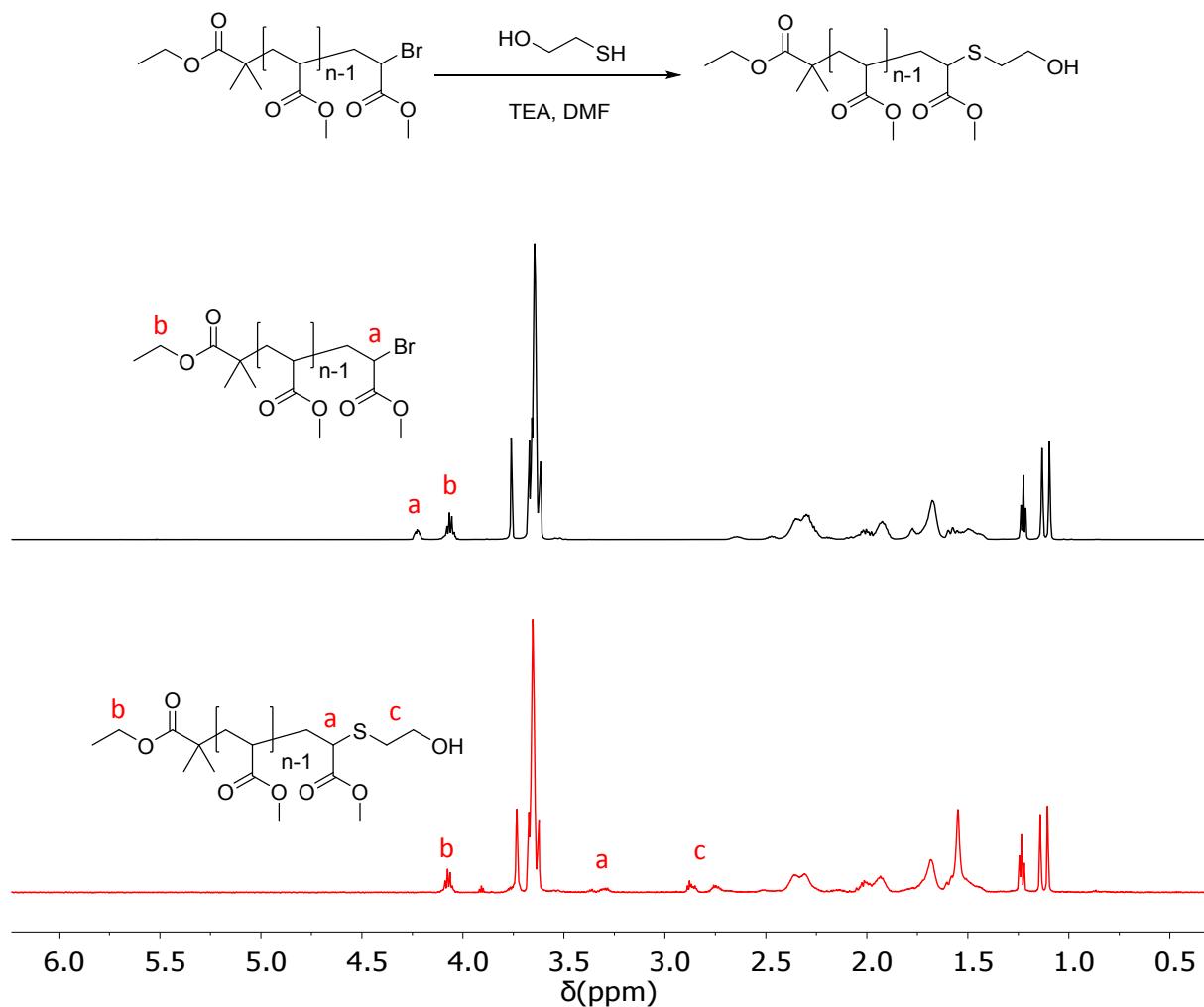


**Figure S16a:** MALDI-ToF-MS spectrum of acetyl-terminated poly(MA).

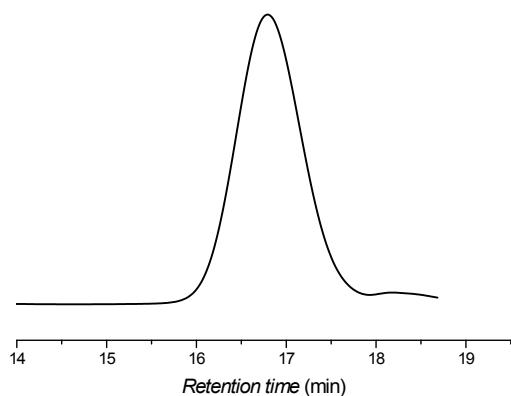


**Figure S16b:** Expanded MALDI-ToF-MS spectrum of acetyl-terminated poly(MA).

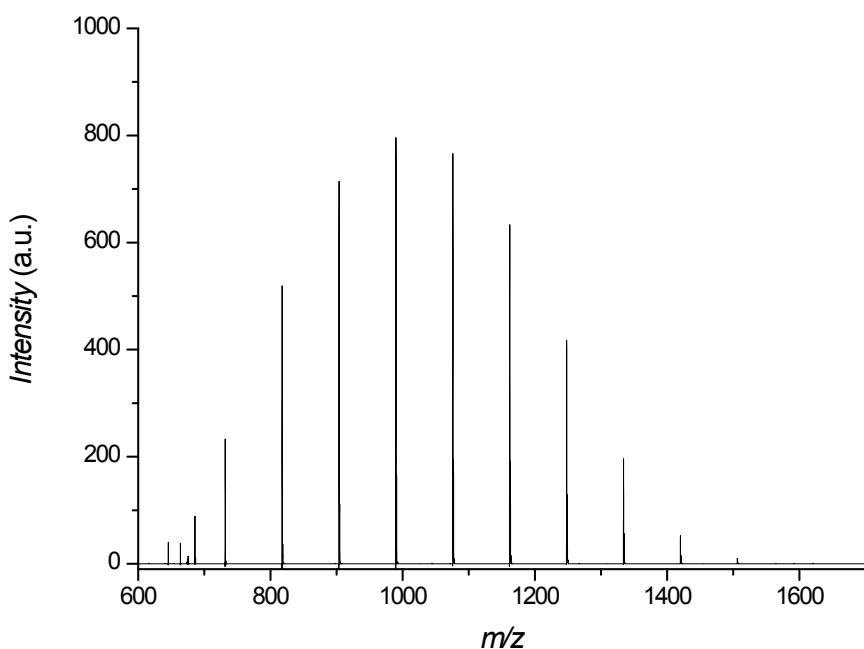
### **Characterization of hydroxyl-terminated poly(MA)**



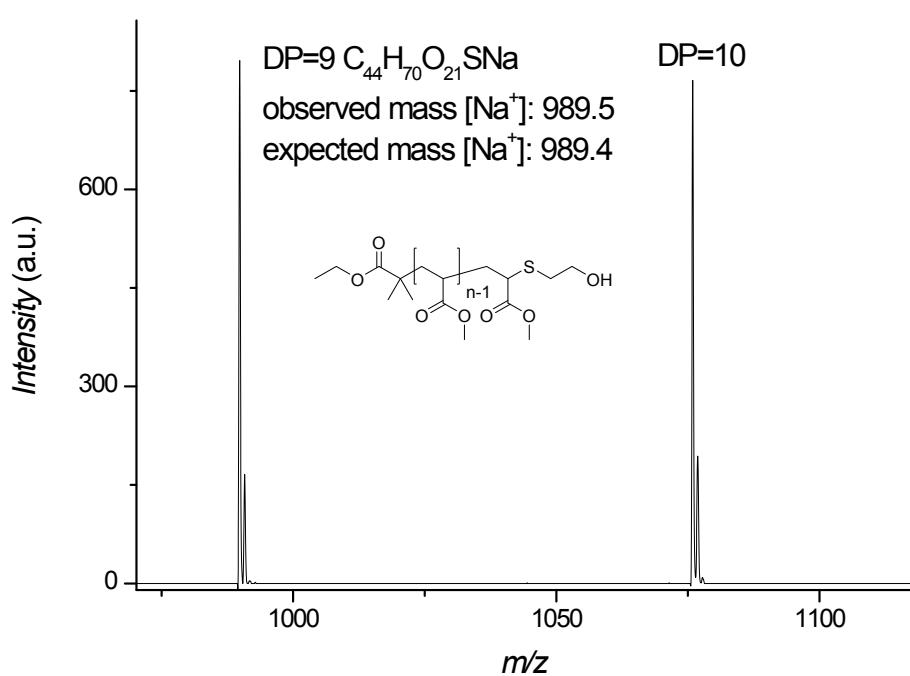
**Figure S17:** <sup>1</sup>H NMR spectra of the reaction from bromine-terminated poly(MA) (top) to hydroxyl-terminated poly(MA) (bottom).



**Figure S18:** SEC trace of hydroxyl-terminated poly(MA),  $M_n = 1100 \text{ g mol}^{-1}$ ,  $D = 1.10$ .

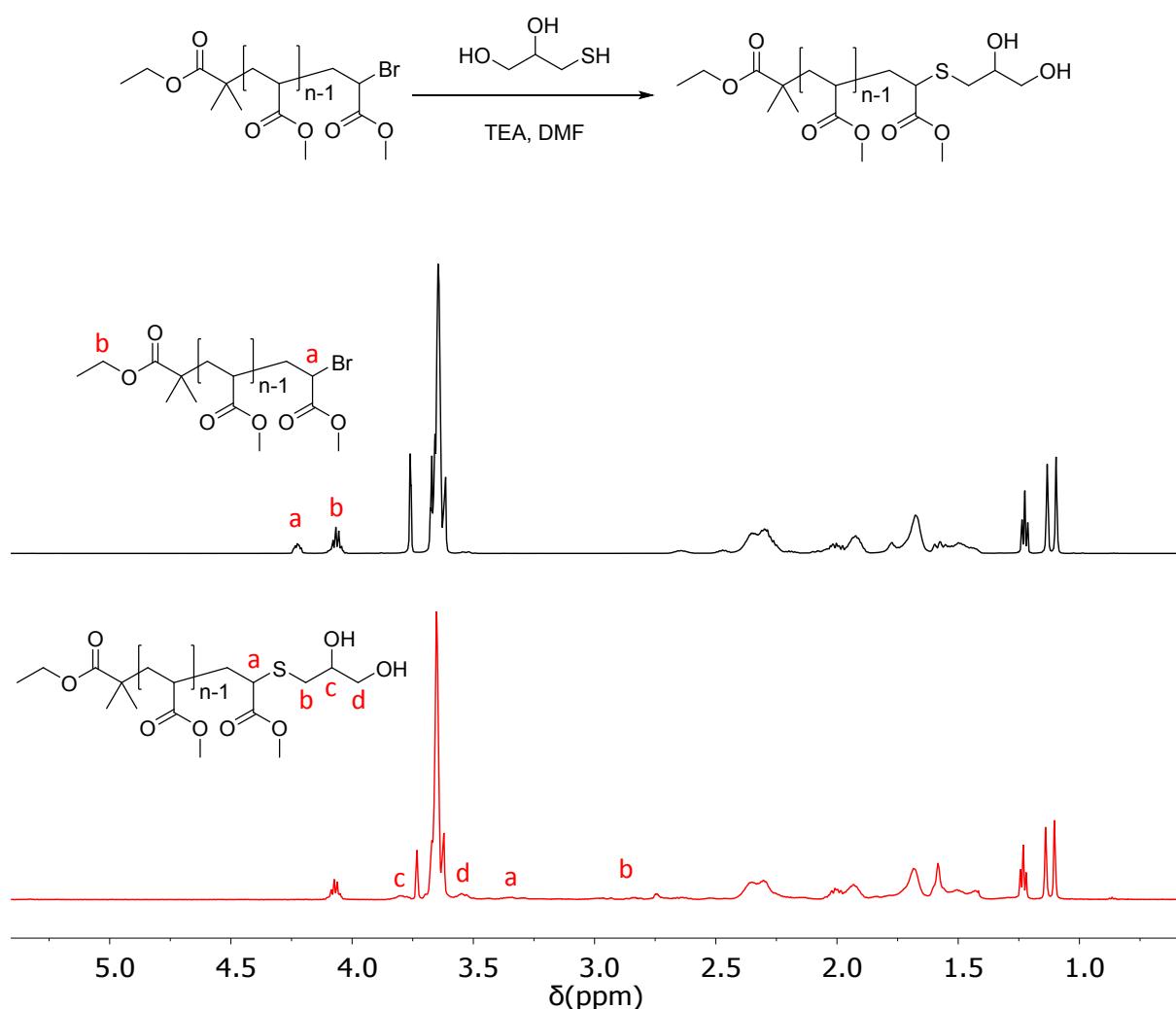


**Figure S19a:** MALDI-ToF-MS spectrum of hydroxyl-terminated poly(MA).

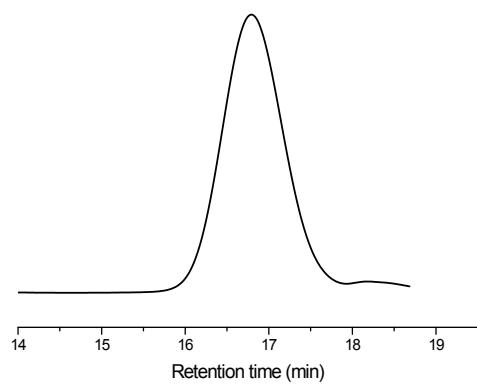


**Figure S19b:** Expanded MALDI-ToF-MS spectrum of hydroxyl-terminated poly(MA).

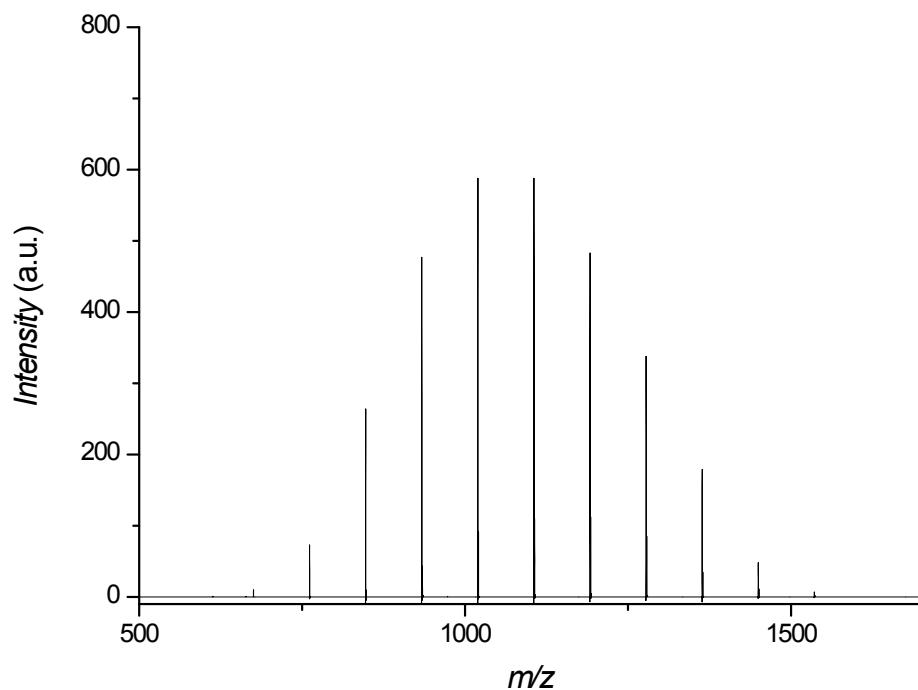
### **Characterization of di-hydroxyl-terminated poly(MA)**



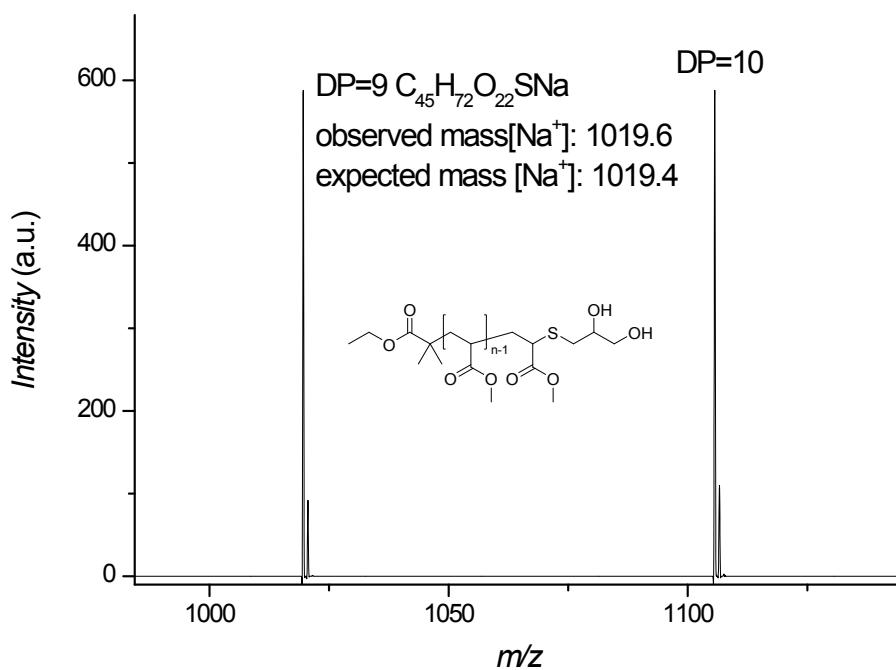
**Figure S20:**  $^1\text{H}$  NMR spectra of the reaction from bromine-terminated poly(MA) (top) to di-hydroxyl-terminated poly(MA) (bottom).



**Figure S21:** SEC trace of di-hydroxyl-terminated poly(MA),  $M_n = 1200 \text{ g mol}^{-1}$ ,  $D = 1.10$ .



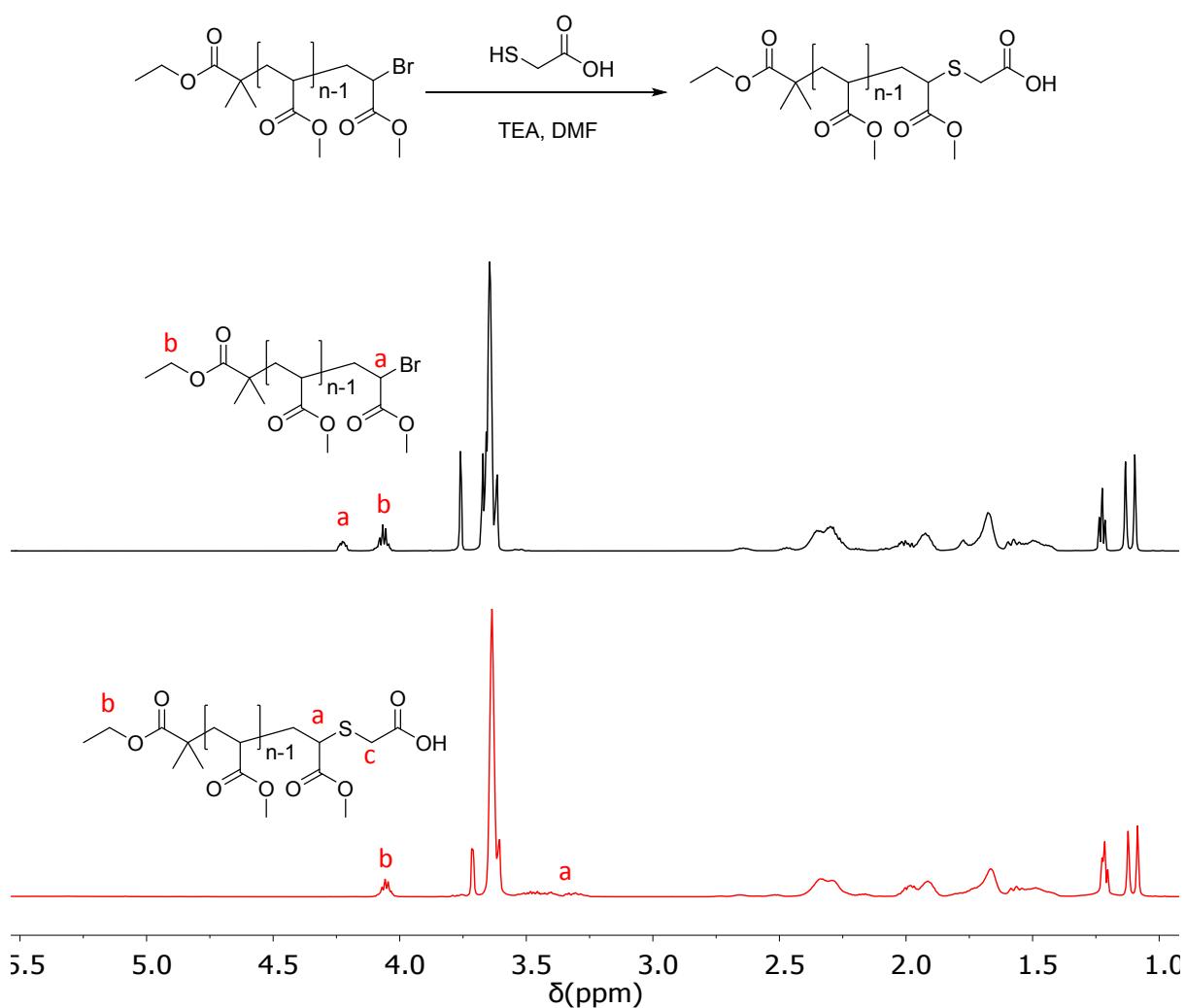
**Figure S22a:** MALDI-ToF-MS spectrum of di-hydroxyl-terminated poly(MA).



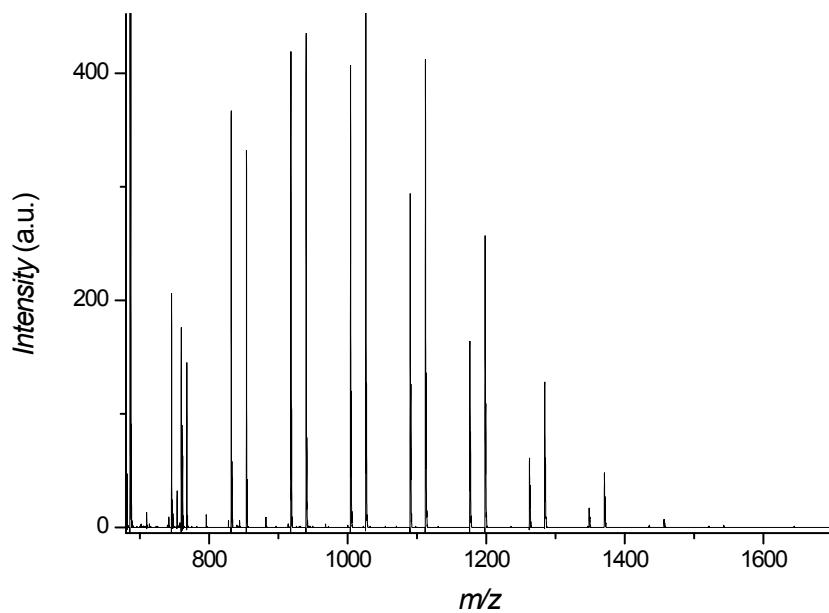
**Figure S22b:** Expanded MALDI-ToF-MS spectrum of di-hydroxyl-terminated poly(MA).



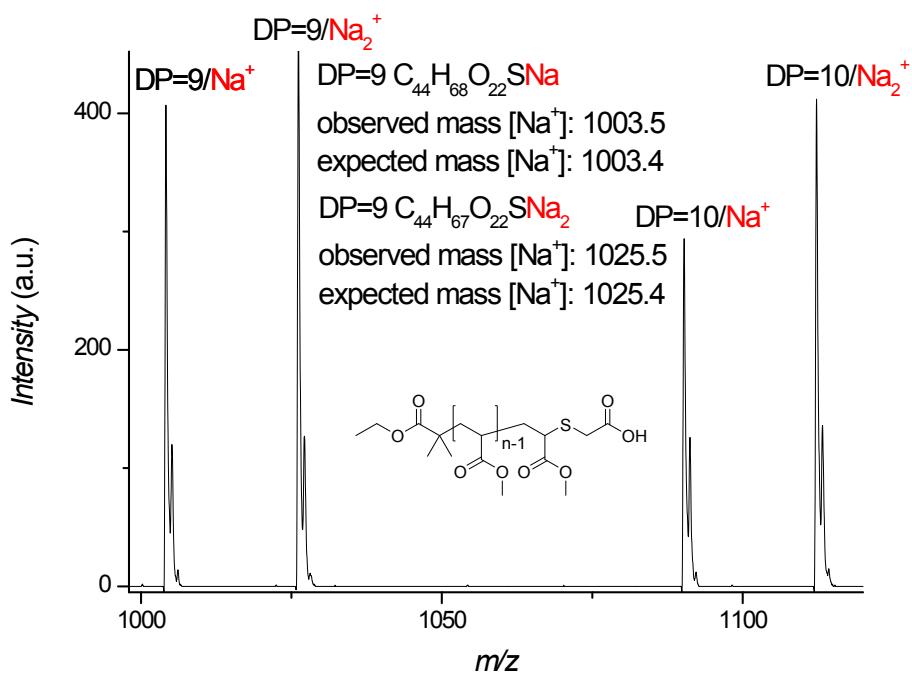
### **Characterization of carboxylic acid-terminated poly(MA)**



**Figure S23:**  $^1\text{H}$  NMR spectra for the transformation of bromine-terminate poly(MA) (top) to carboxylic acid-terminated poly(MA) (bottom).

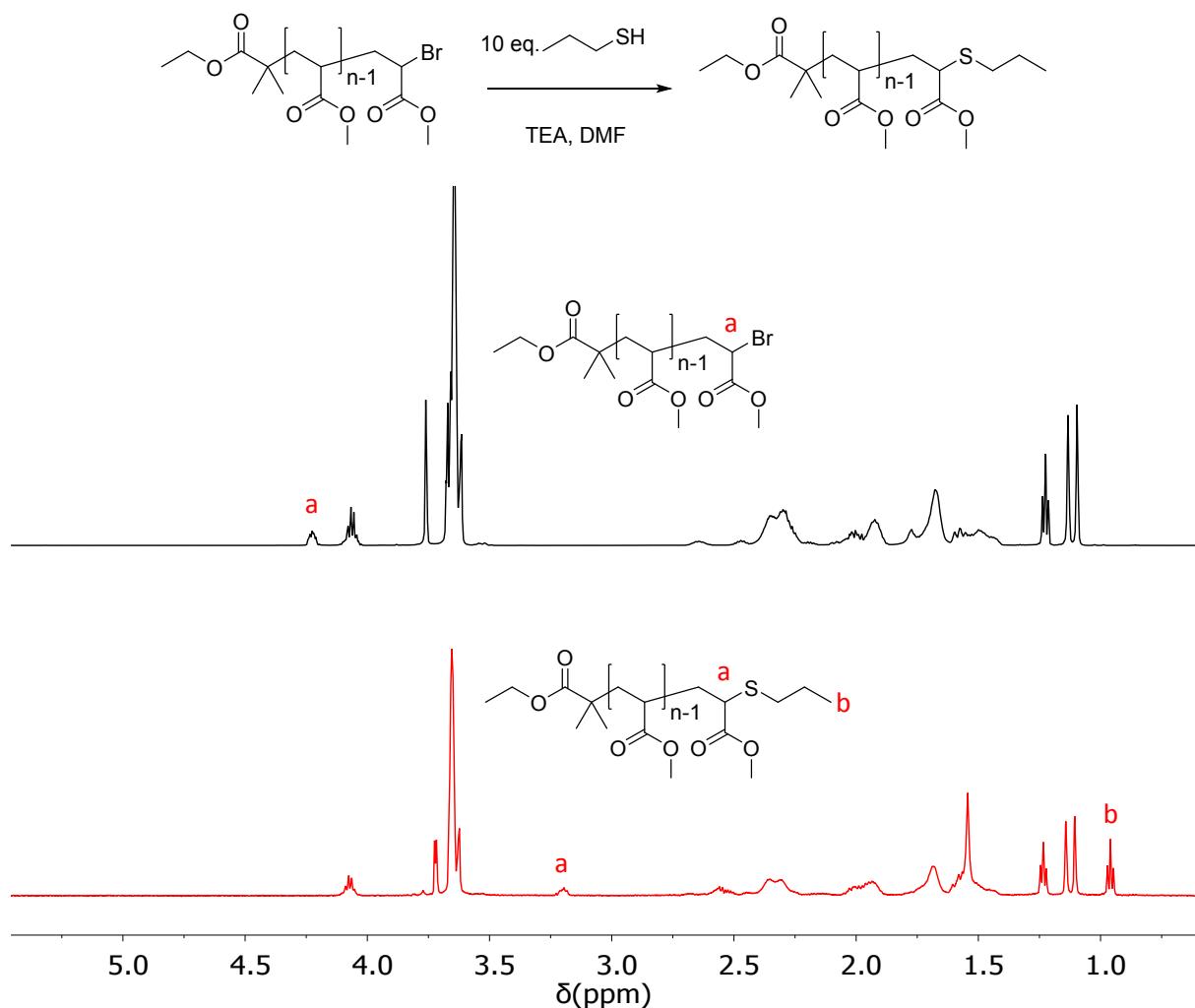


**Figure S24a:** MALDI-ToF-MS spectrum of carboxylic acid-terminated poly(MA).

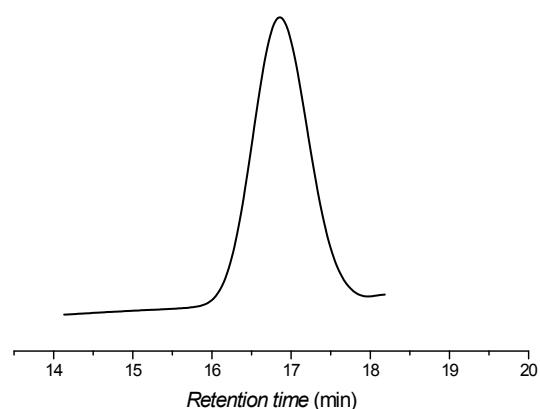


**Figure S24b:** Expanded MALDI-ToF-MS spectrum of carboxylic acid-terminated poly(MA).

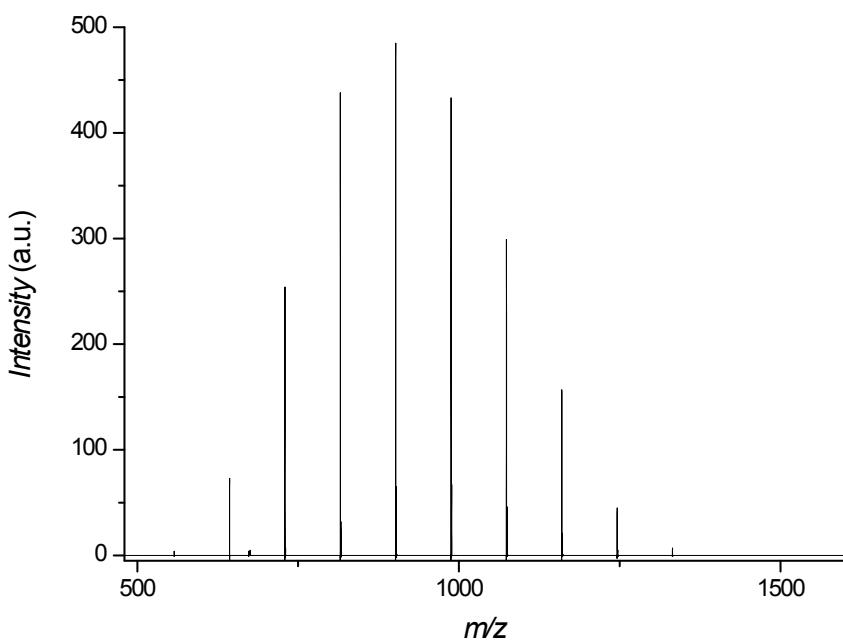
### Characterization of propane-terminated poly(MA)



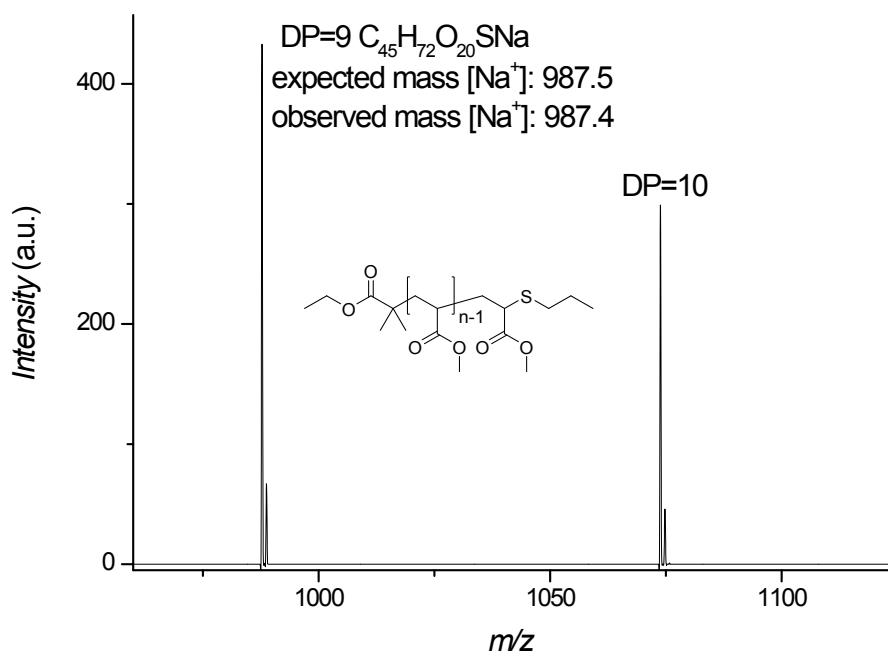
**Figure S25:**  $^1\text{H}$  NMR spectra for the transformation of bromine-terminate poly(MA) (top) to propane-terminated poly(MA) (bottom).



**Figure S26:** SEC trace of propane-terminated poly(MA),  $M_n = 1100 \text{ g mol}^{-1}$ ,  $D = 1.14$ .

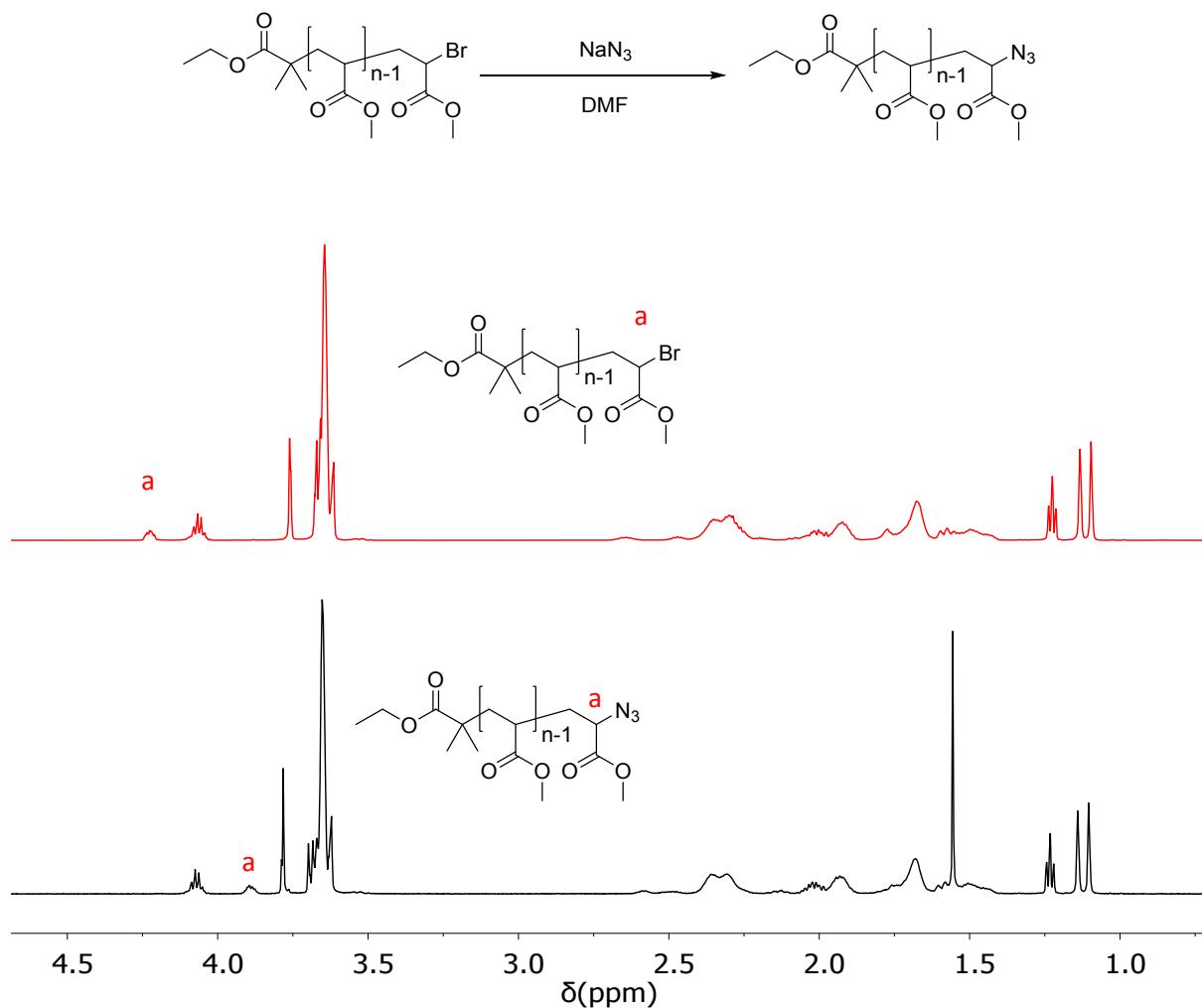


**Figure S27a:** MALDI-ToF-MS spectrum of propane-terminated poly(MA).

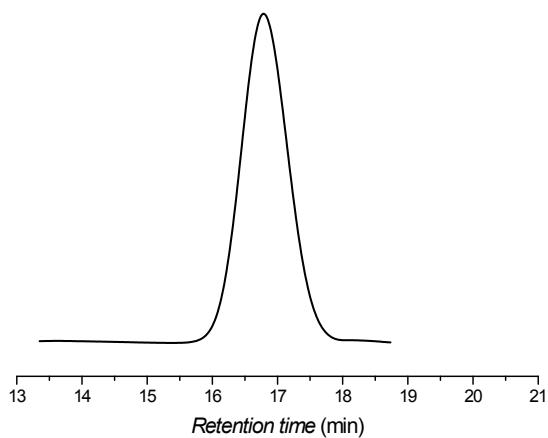


**Figure S27b:** Expanded MALDI-ToF-MS spectrum of propane-terminated poly(MA).

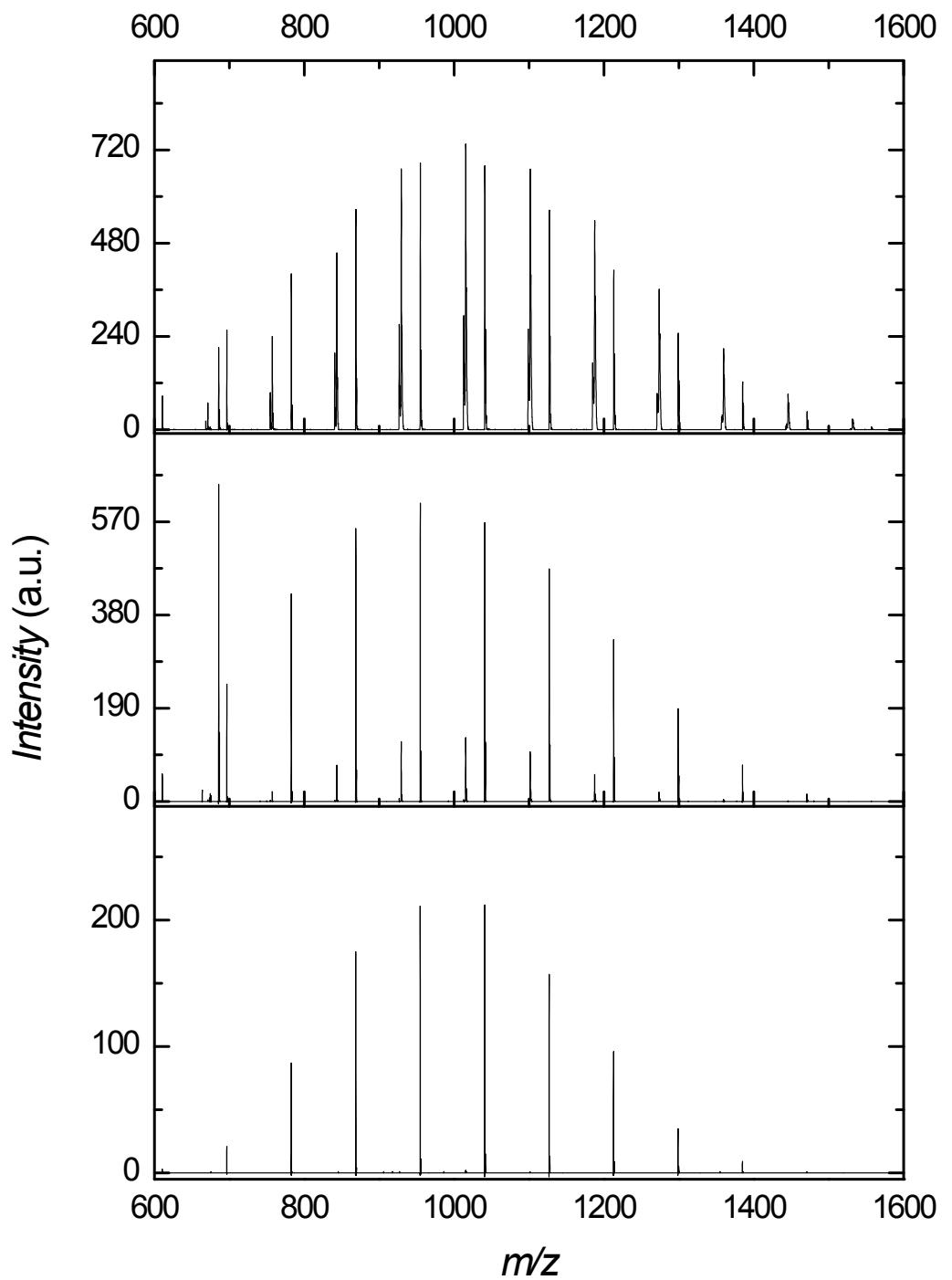
### Characterization of azide-terminated poly(MA)



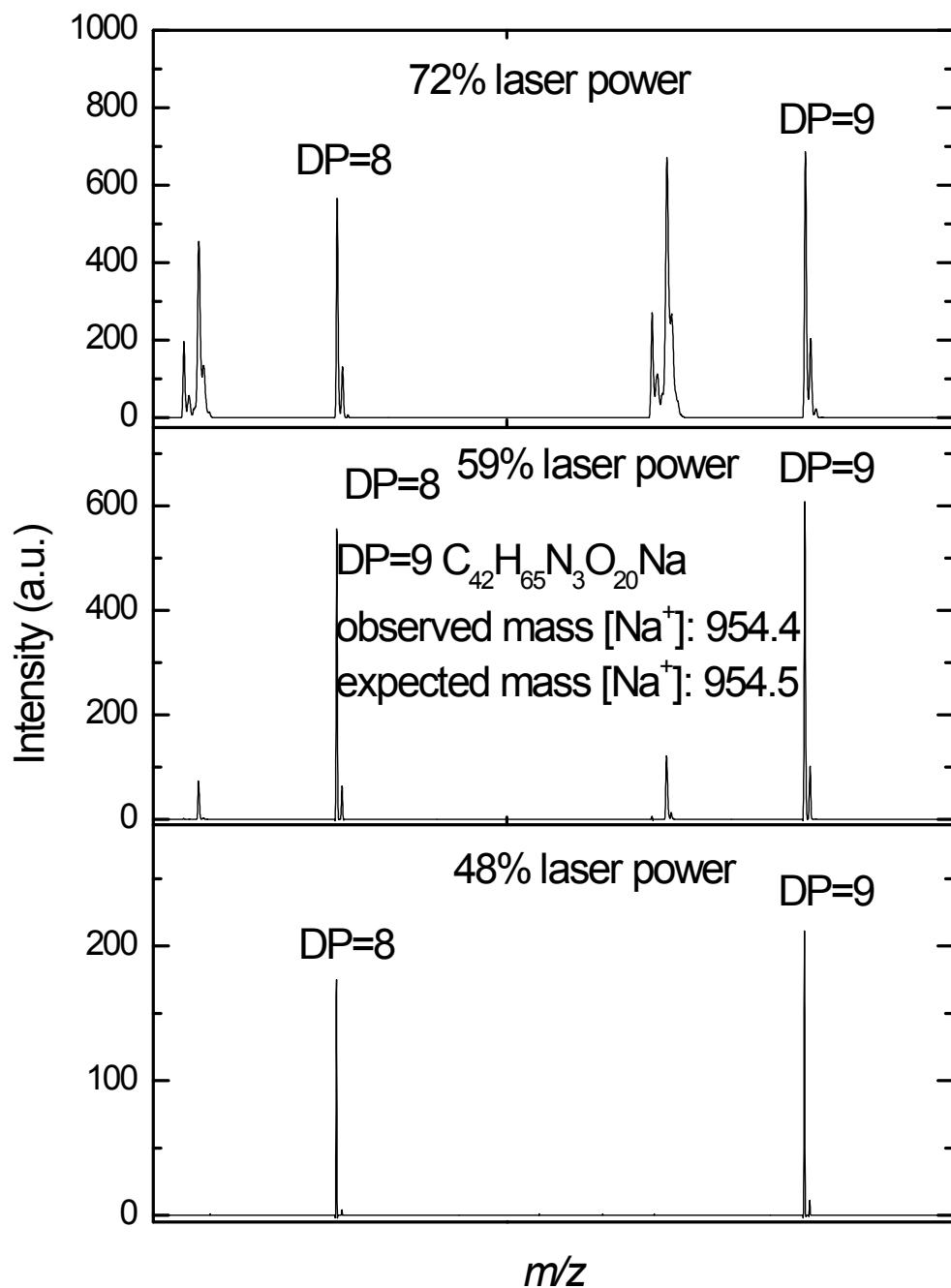
**Figure S28:** <sup>1</sup>H NMR spectra for the transformation of bromine-terminate poly(MA) (top) to azide-terminated poly(MA) (bottom).



**Figure S29:** SEC trace of azide-terminated poly(MA),  $M_n = 1000 \text{ g mol}^{-1}$ ,  $D = 1.11$ .

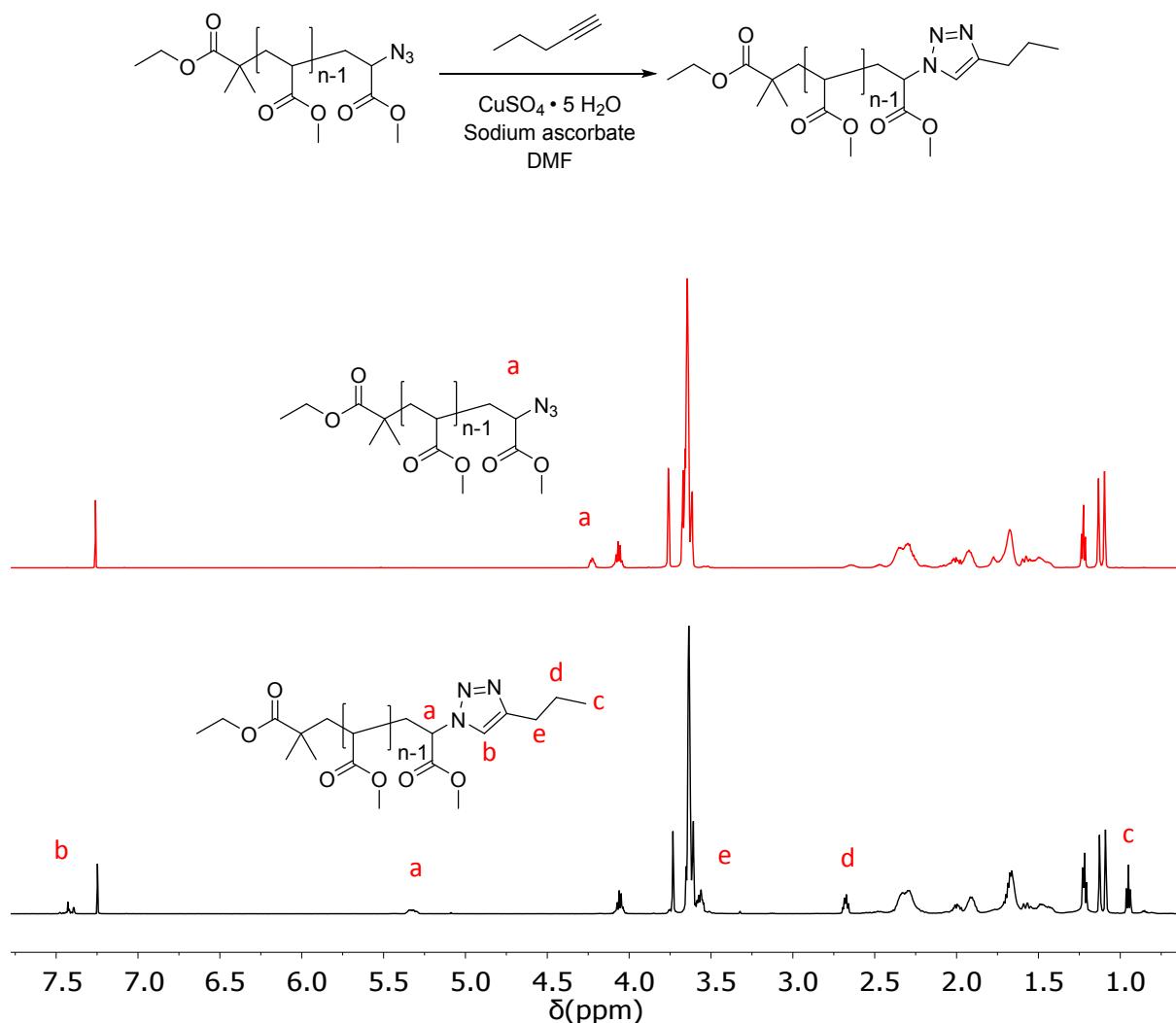


**Figure S30a:** MALDI-ToF-MS spectra of azide-terminated poly(MA) utilizing different laser power (with increased laser power, from bottom to top, the fragmentation increases considerably).

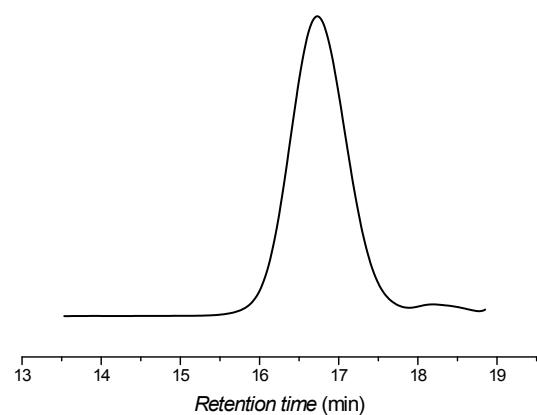


**Figure S30b:** Expanded MALDI-ToF-MS spectra of azide-terminated poly(MA) utilizing different laser power (with increased laser power, from bottom to top, the fragmentation increases considerably).

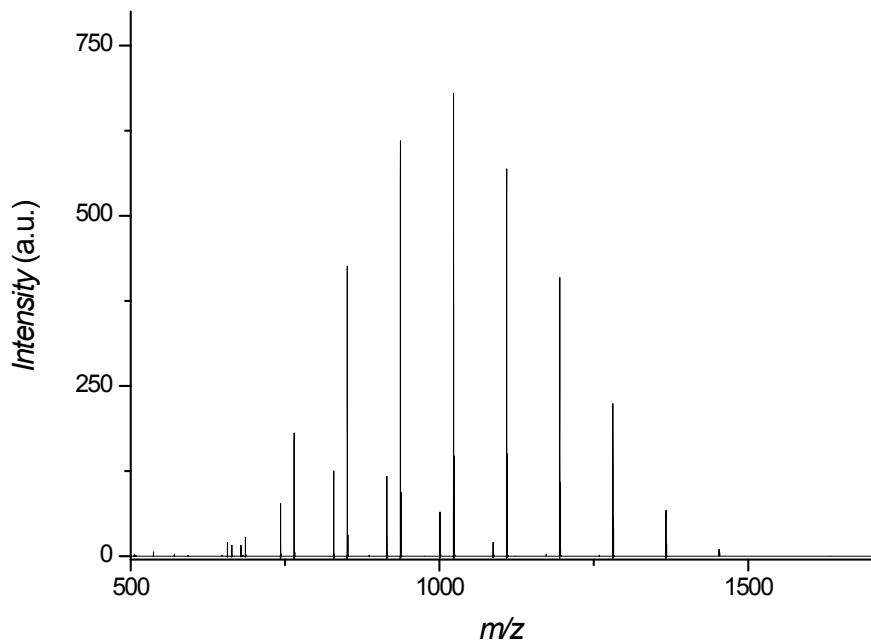
**Characterization of triazole-terminated poly(MA)**



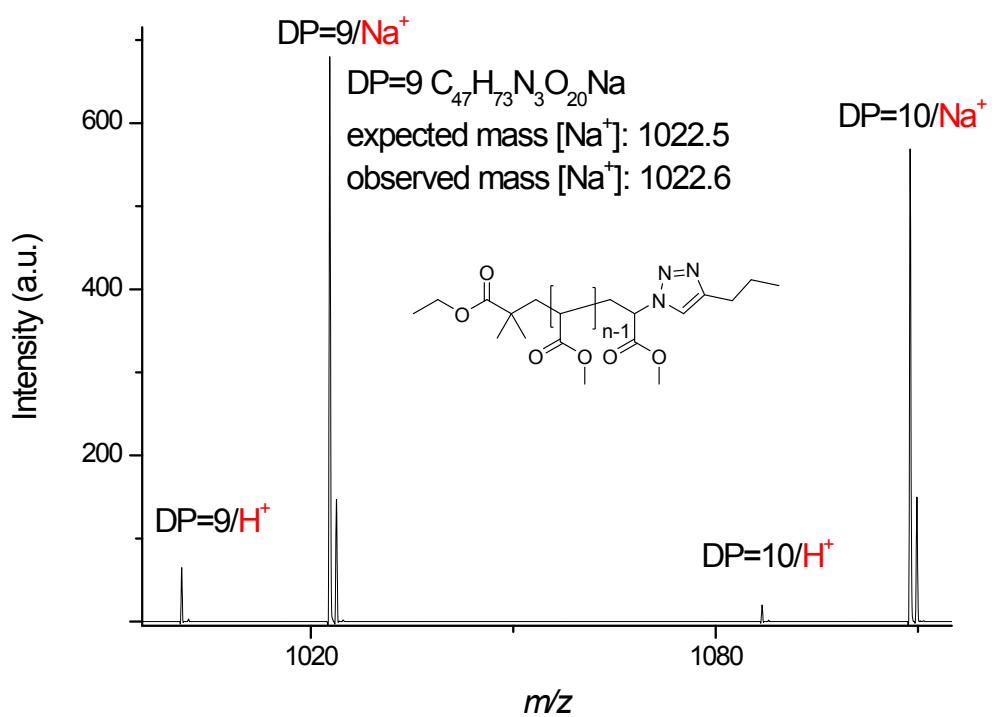
**Figure S31:** <sup>1</sup>H NMR spectra for the transformation of azide-terminated poly(MA) (top) to triazole-terminated poly(MA) (bottom).



**Figure S32:** SEC trace of triazole-terminated poly(MA),  $M_n = 1200 \text{ g mol}^{-1}$ ,  $D = 1.11$ .

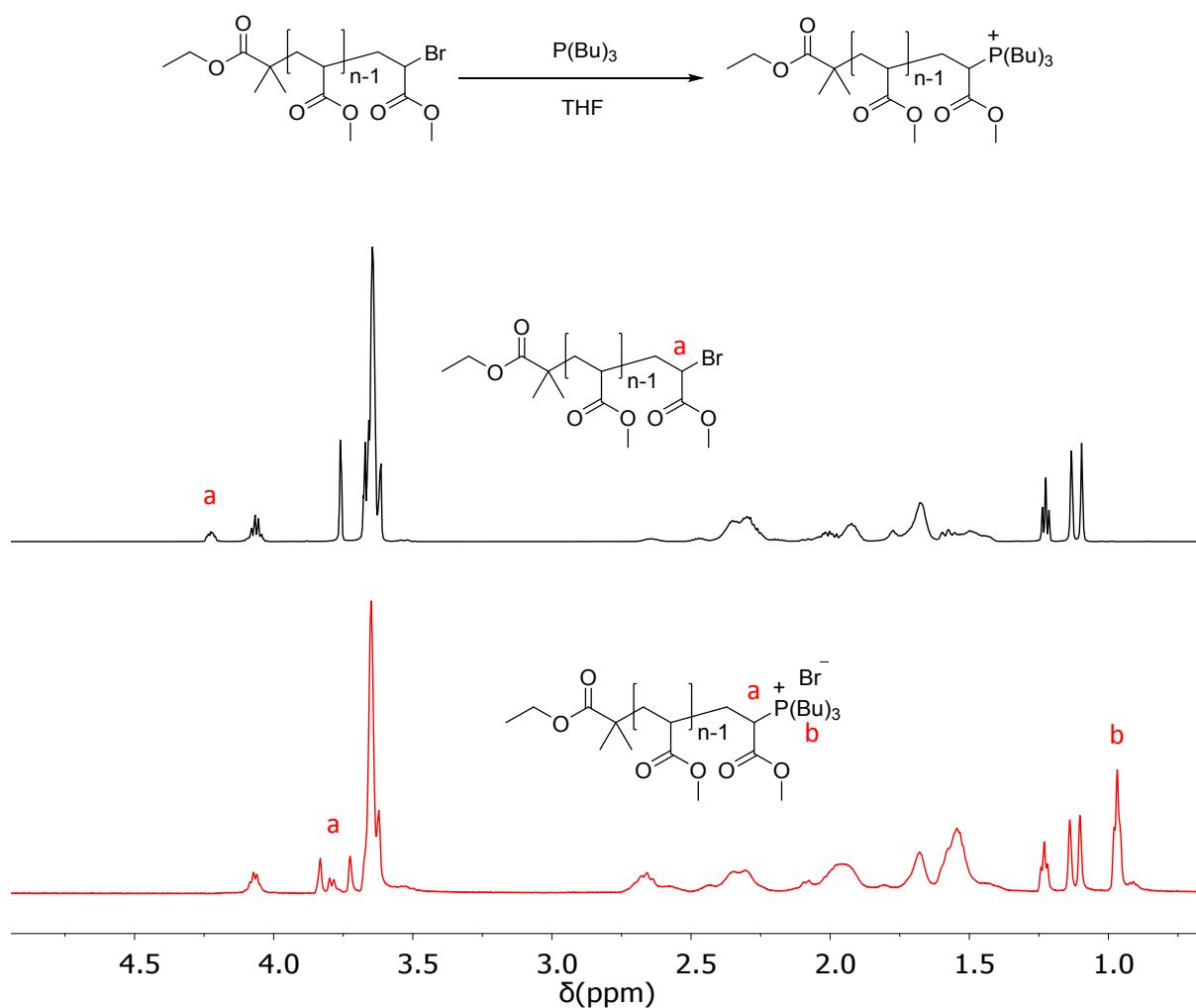


**Figure S33a:** MALDI-ToF-MS spectrum of triazole-terminated poly(MA).

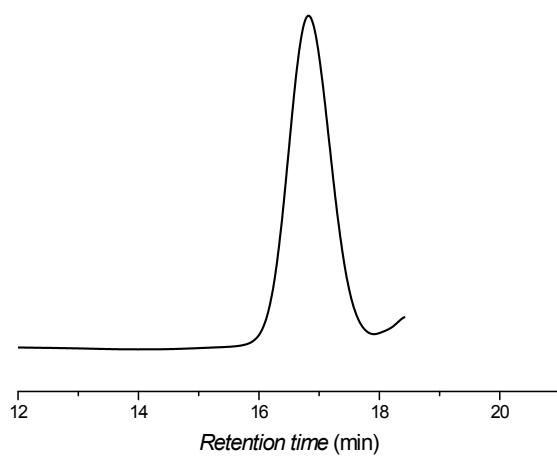


**Figure S33b:** Expanded MALDI-ToF-MS spectrum of triazole-terminated poly(MA).

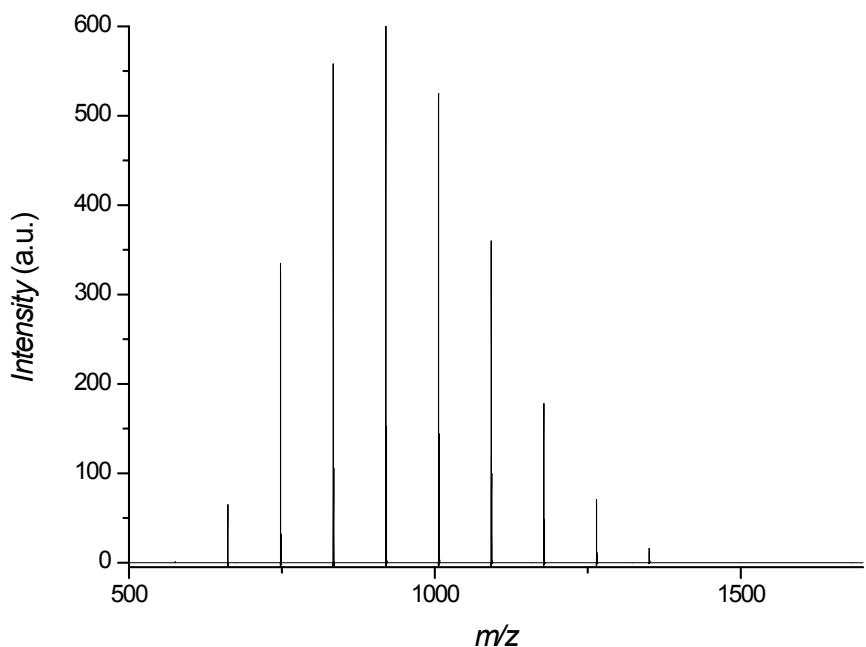
### Characterization of phosphonium-terminated poly(MA)



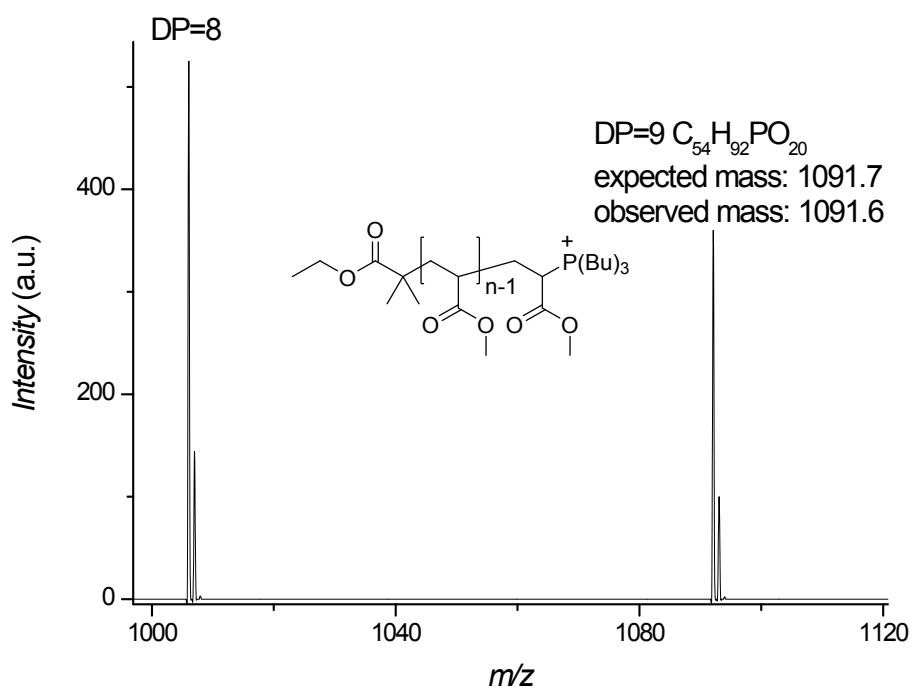
**Figure S34:** <sup>1</sup>H NMR spectra for the transformation of bromine-terminate poly(MA) (top) to phosphonium-terminated poly(MA) (bottom).



**Figure S35:** SEC trace of phosphonium-terminated poly(MA),  $M_n = 1100 \text{ g mol}^{-1}$ ,  $D = 1.12$ .

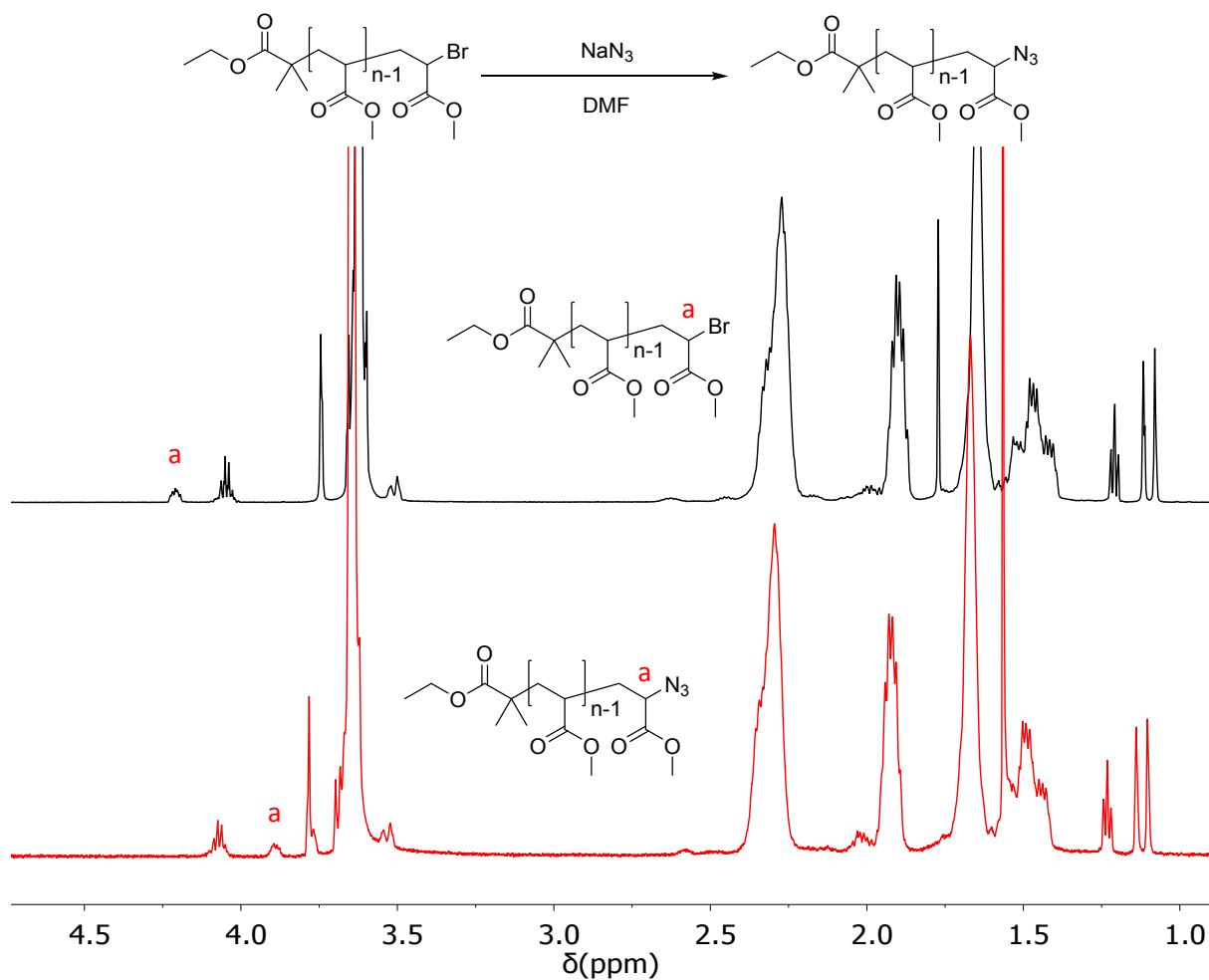


**Figure S36a:** MALDI-ToF-MS spectrum of phosphonium-terminated poly(MA).

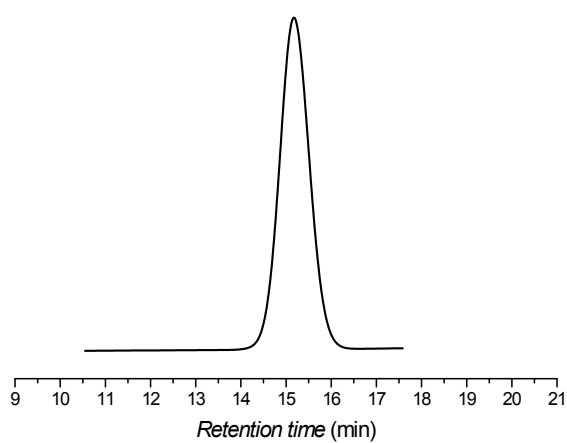


**Figure S36b:** Expanded MALDI-ToF-MS spectrum of phosphonium-terminated poly(MA).

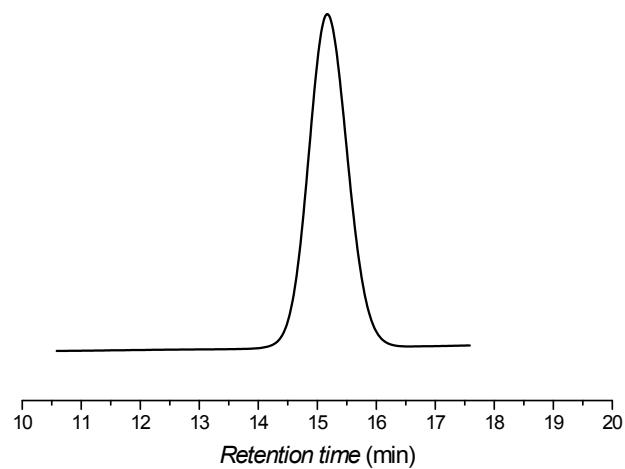
### **Characterization of poly(MA) of higher MW and its modifications**



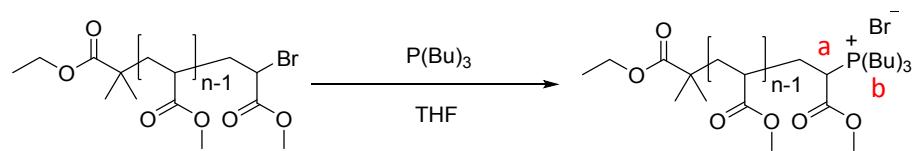
**Figure S37:** <sup>1</sup>H NMR spectra of the transformation of higher MW bromine-terminated poly(MA) (top) to azide-terminated poly(MA) (bottom).

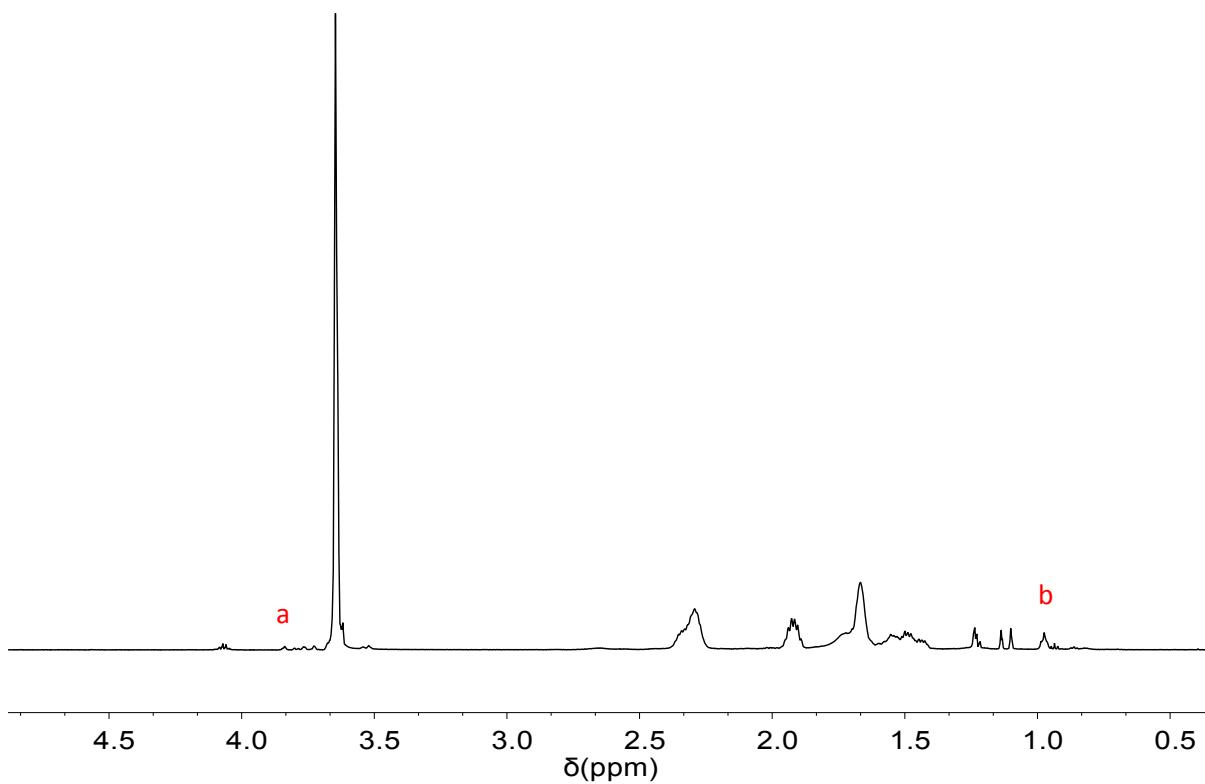


**Figure S38:** SEC trace of higher MW bromine-terminated poly(MA),  $M_n = 6400 \text{ g mol}^{-1}$ ,  $D = 1.09$ .



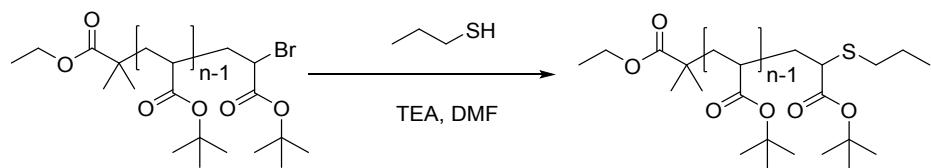
**Figure S39:** SEC trace of higher MW azide-terminated poly(MA),  $M_n = 6400 \text{ g mol}^{-1}$ ,  $D = 1.09$ .

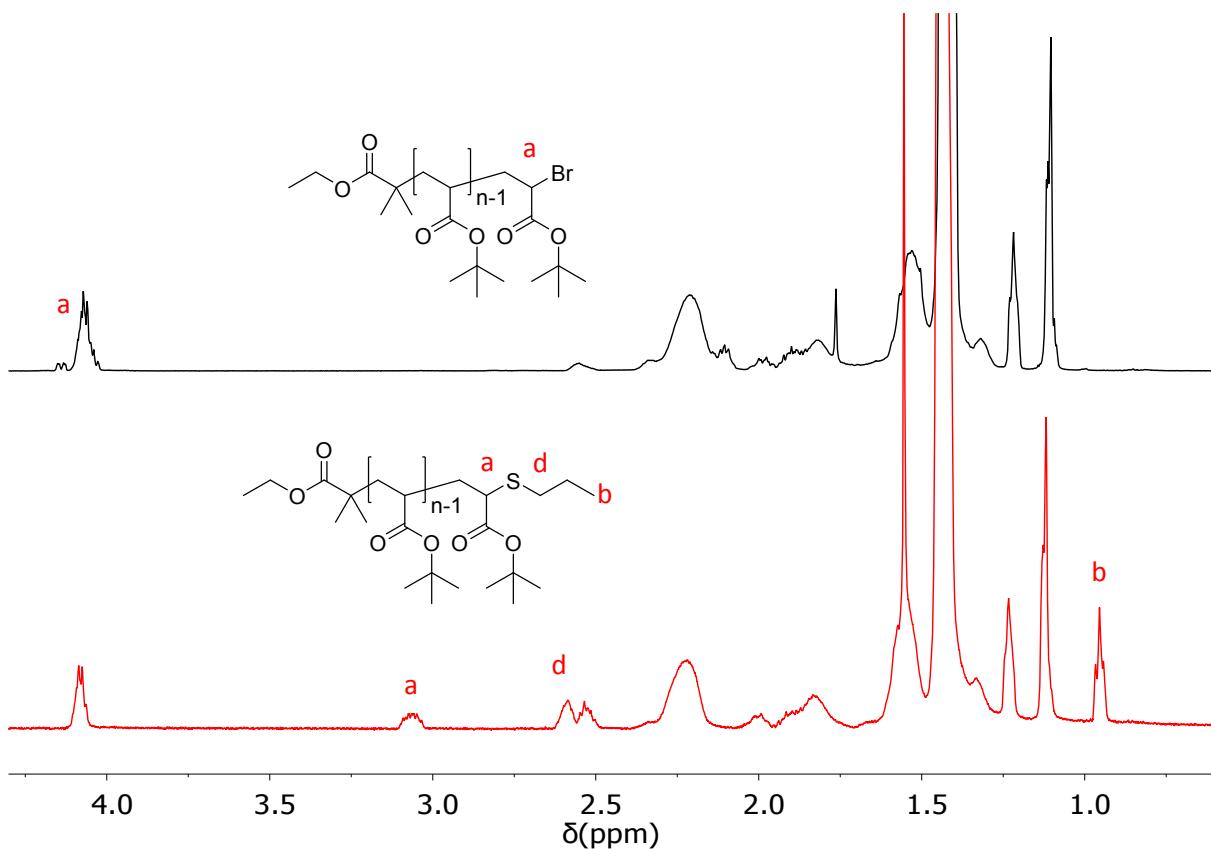




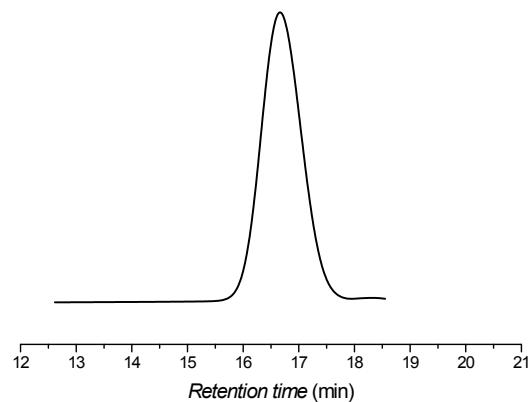
**Figure S40:** <sup>1</sup>H NMR spectrum of the higher MW phosphonium-terminated poly(MA).

**Characterization of bromine-terminated poly(tBA) and propane-terminated poly(tBA)**

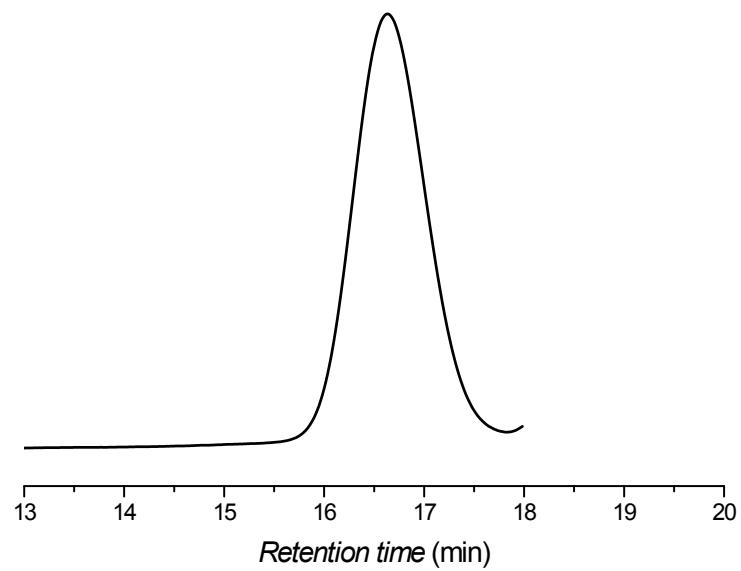




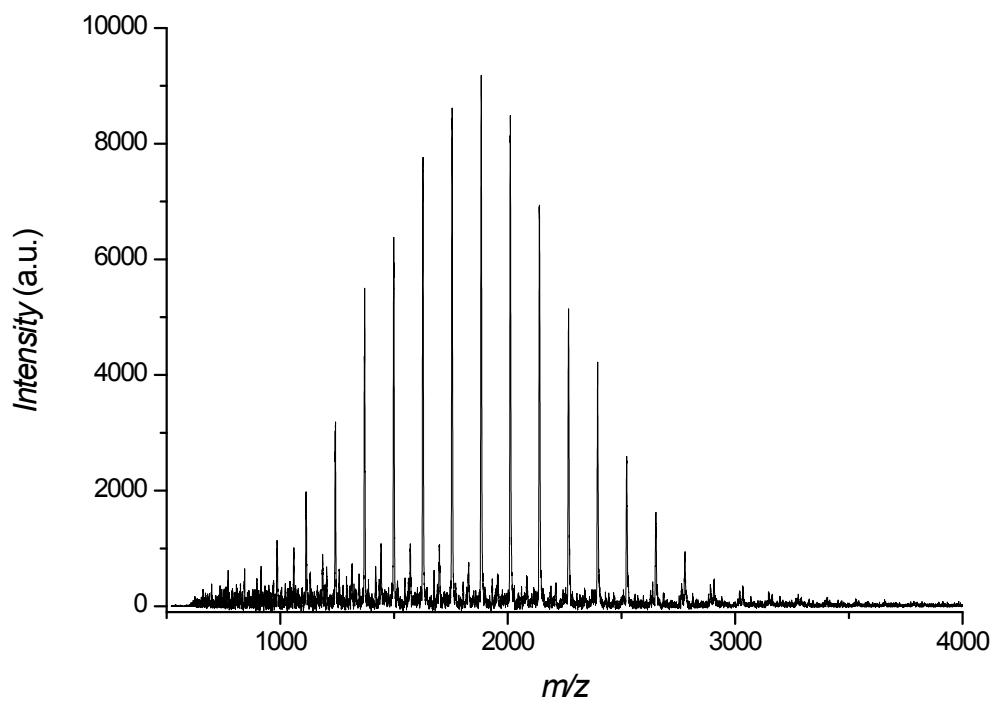
**Figure S41:**  $^1\text{H}$  NMR spectra of the transformation of bromine-terminated poly(tBA) (top) to propane-terminated poly(tBA) (bottom).



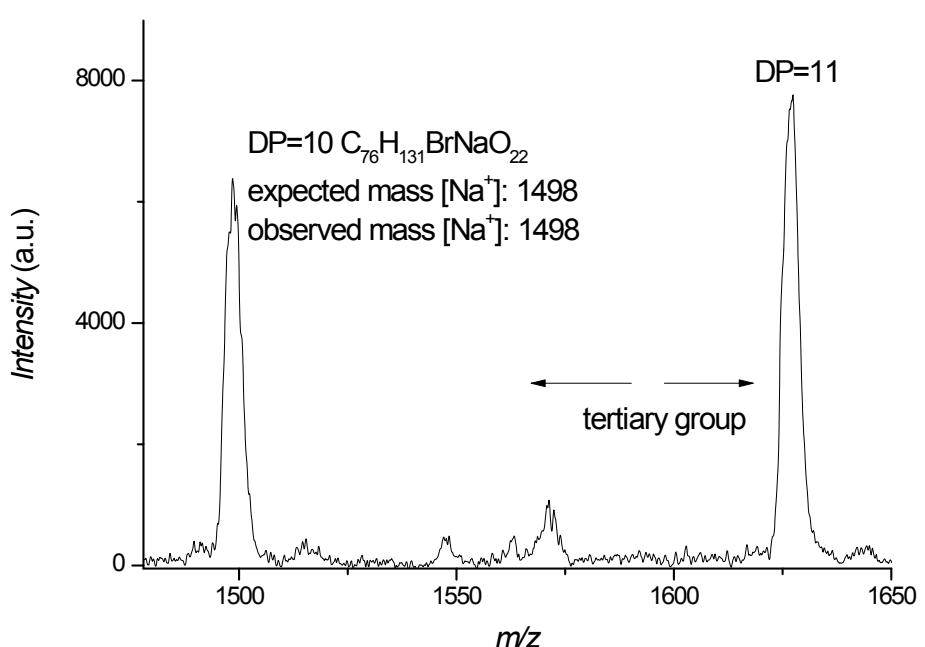
**Figure S42:** SEC trace of bromine-terminated poly(tBA),  $M_n = 1300 \text{ g mol}^{-1}$ ,  $D = 1.15$ .



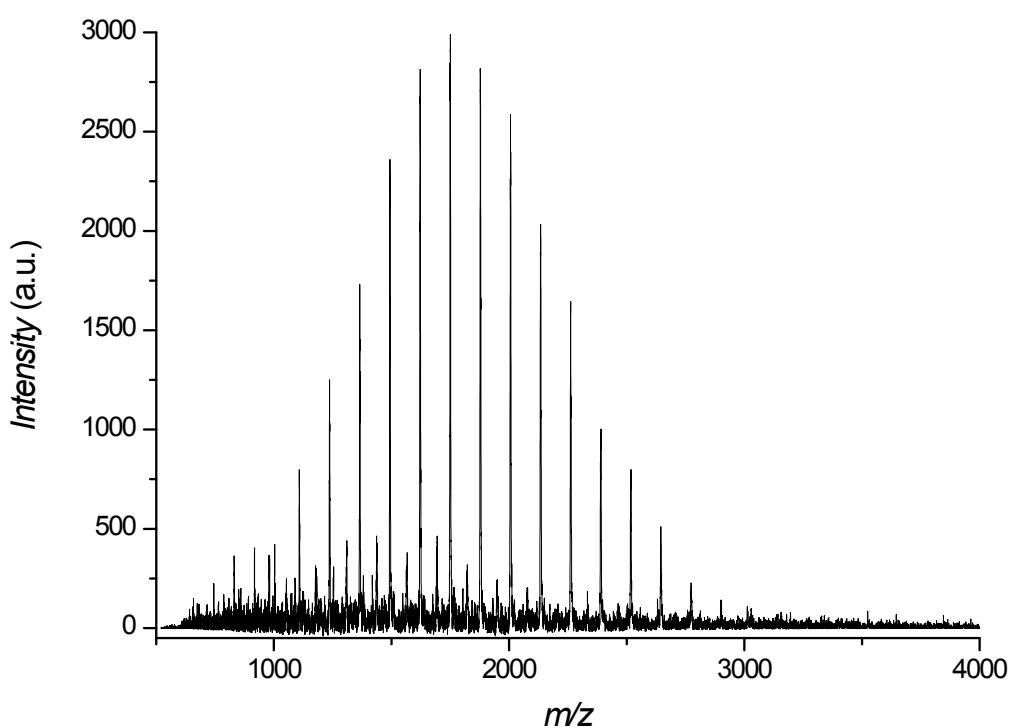
**Figure S43:** SEC of propane-terminated poly(tBA),  $M_n = 1400 \text{ g mol}^{-1}$ ,  $D = 1.12$ .



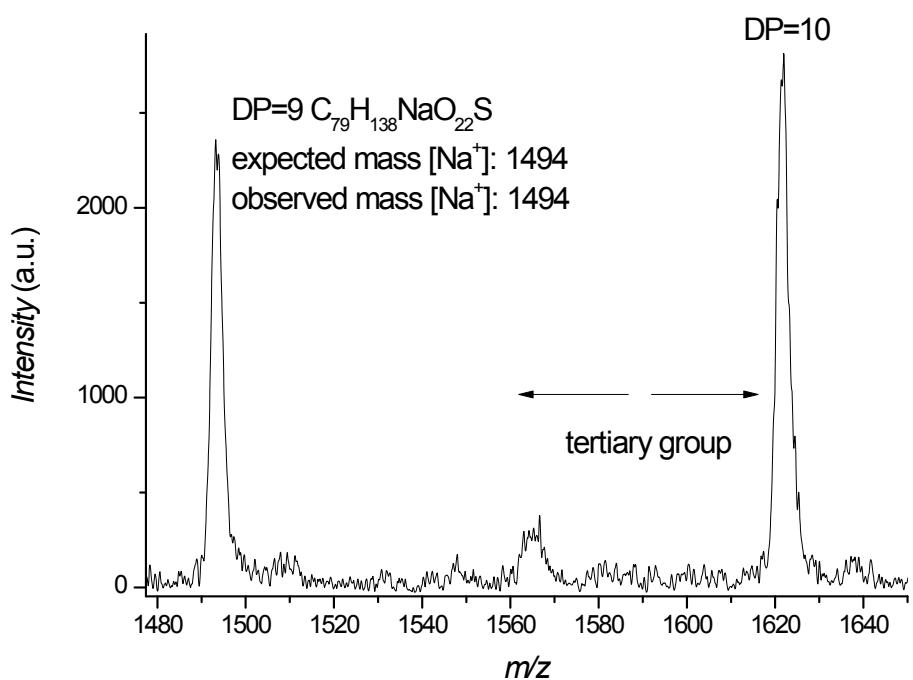
**Figure S44a:** MALDI-ToF-MS spectrum of bromine-terminated poly(tBA).



**Figure S44b:** Expanded MALDI-ToF-MS spectrum of bromine-terminated poly(tBA).



**Figure S45a:** MALDI-ToF-MS spectrum of propane-terminated poly(tBA).



**Figure S45b:** Expanded MALDI-ToF-MS spectrum of propane-terminated poly(tBA).