

**Electronic Supplementary Information**

**Facile access to functional polyacrylates with dual stimuli  
response and tunable surface hydrophobicity**

Sk Arif Mohammad,<sup>a</sup> Subrata Dolui,<sup>a</sup> Devendra Kumar,<sup>a</sup> Shivshankar R. Mane<sup>b</sup> and Sanjib Banerjee\*<sup>a</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Bhilai, Raipur 492015,  
Chhattisgarh, India

<sup>b</sup>Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune,  
Maharashtra 411008, India

\*Corresponding Author: E-mail: sanjib.banerjee@iitbhilai.ac.in (S. Banerjee)

**Table of contents :**

<b>A. Supporting tables.....</b>	<b>S3</b>
Table S1. Ni-Co mediated RDRP of MA using different ligands and initiators.....	S3
Table S2. Kinetics Study of Ni-Co mediated RDRP of MA .....	S3
<b>B. Supporting scheme.. .....</b>	<b>S4</b>
Scheme S1. Chemical structures of the initiators employed in this study .....	S4
<b>C. Supporting figures.....</b>	<b>S5-S8</b>
Fig. S1 ATR-IR spectra of PMA-Br, PMA- <i>b</i> -PDMAEMA, PMA- <i>b</i> -PTBMA and PMA- <i>b</i> -POFPA .....	S5
Fig. S2 SEC traces of PMA-Br, PMA- <i>b</i> -PDMAEMA, PMA- <i>b</i> -PTBMA and PMA- <i>b</i> - POFPA .....	S6
Fig. S3 Plot of the hydrodynamic diameter ( $D_h$ ) as a function of temperature for aqueous solution of PMA- <i>b</i> -PDMAEMA diblock copolymer .....	S7
Fig. S3 <sup>1</sup> H NMR spectra of PMA-Br and PMA- <i>b</i> -PTBMA before and after hydrolysis of the <i>tert</i> -butyl ester groups.....	S8
Fig. S4 <sup>1</sup> H NMR spectrum of PMA- <i>b</i> -PMAA .....	S9
Fig. S5 <sup>13</sup> C NMR spectrum of PMA- <i>b</i> -PMAA .....	S10

## A. Supporting tables

**Table S1** Reaction conditions and results for the Ni-Co alloy mediated RDRP of MA in DMSO

Entry	Reaction condition	Time (h)	Conv. <sup>b</sup> (%)	$M_{n,theo.}^c$ (g mol <sup>-1</sup> )	$M_{n,SEC}^d$ (g mol <sup>-1</sup> )	$\mathcal{D}^d$
P1	MA/EBiB/Ni-Co/Me <sub>6</sub> TREN	0.5	100	17400	17100	1.17
P2	MA/MBP/Ni-Co/Me <sub>6</sub> TREN	0.5	91	16300	14300	1.22
P3	MA/BEB/Ni-Co/ Me <sub>6</sub> TREN	0.5	79	14400	12900	1.29
P4	MA/EBiB/Ni-Co/bpy	0.5	41	7250	6300	1.48
P5	MA/EBiB/Ni-Co/PMDETA	0.5	67	11700	10400	1.54
P6	MA/EBiB/Ni-Co	24	0	-	-	-
P7	MA/EBiB/Me <sub>6</sub> TREN	24	0	-	-	-

at 25 °C.<sup>a</sup>

<sup>a</sup>Reaction Conditions:  $[MA]_0/[I]_0 = 200$ . <sup>b</sup>Determined gravimetrically based on monomer feed.

<sup>c</sup>Calculated using yield as conversion and the following equation:  $M_{n,theo} = ([MA]_0/[I]_0 \times \text{yield} \times M_{MA}) + M_I$ , where  $M_{MA}$  (= 86.09 g mol<sup>-1</sup>),  $M_{EBiB}$  (= 195.05 g mol<sup>-1</sup>),  $M_{MBP}$  (= 167.00 g mol<sup>-1</sup>) and  $M_{BEB}$  (= 185.06 g mol<sup>-1</sup>) are the molecular weight of MA, MBP, EBiB and BEB, respectively. <sup>d</sup>Obtained from SEC measurements.

**Table S2.** Reaction conditions and results for the kinetics study of Ni-Co alloy mediated

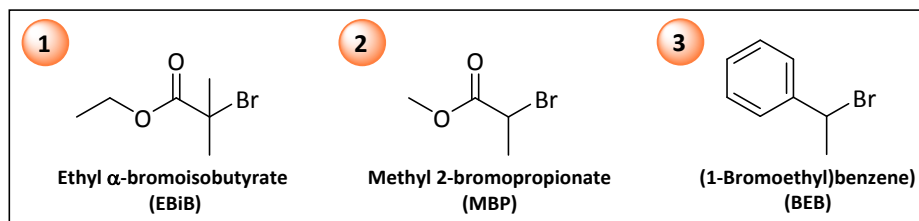
Entry	Time (min)	Conv. (%)	$M_{n,theo.}^b$ (g mol <sup>-1</sup> )	$M_{n,SEC}^c$ (g mol <sup>-1</sup> )	$\mathcal{D}^c$
P1	2	22	4000	3900	1.29
P2	5	43	7600	8100	1.26
P3	10	74	12900	12600	1.24
P4	15	87	15200	14800	1.21
P5	20	94	16400	16100	1.18
P6	30	100	17400	26900	1.17

RDRP of MA in DMSO at 25 °C using EBiB as the initiator.<sup>a</sup>

<sup>a</sup>Reaction Conditions:  $[MA]_0/[EBiB]_0 = 200$ . <sup>b</sup> Determined gravimetrically based on monomer feed. <sup>c</sup>Calculated using yield as conversion and the following equation:  $M_{n,theo} = ([MA]_0/[EBiB]_0 \times \text{yield} \times M_{MA}) + M_{EBiB}$ , where  $M_{MA}$  (= 86.09 g mol<sup>-1</sup>) and  $M_{EBiB}$  (= 195.05 g

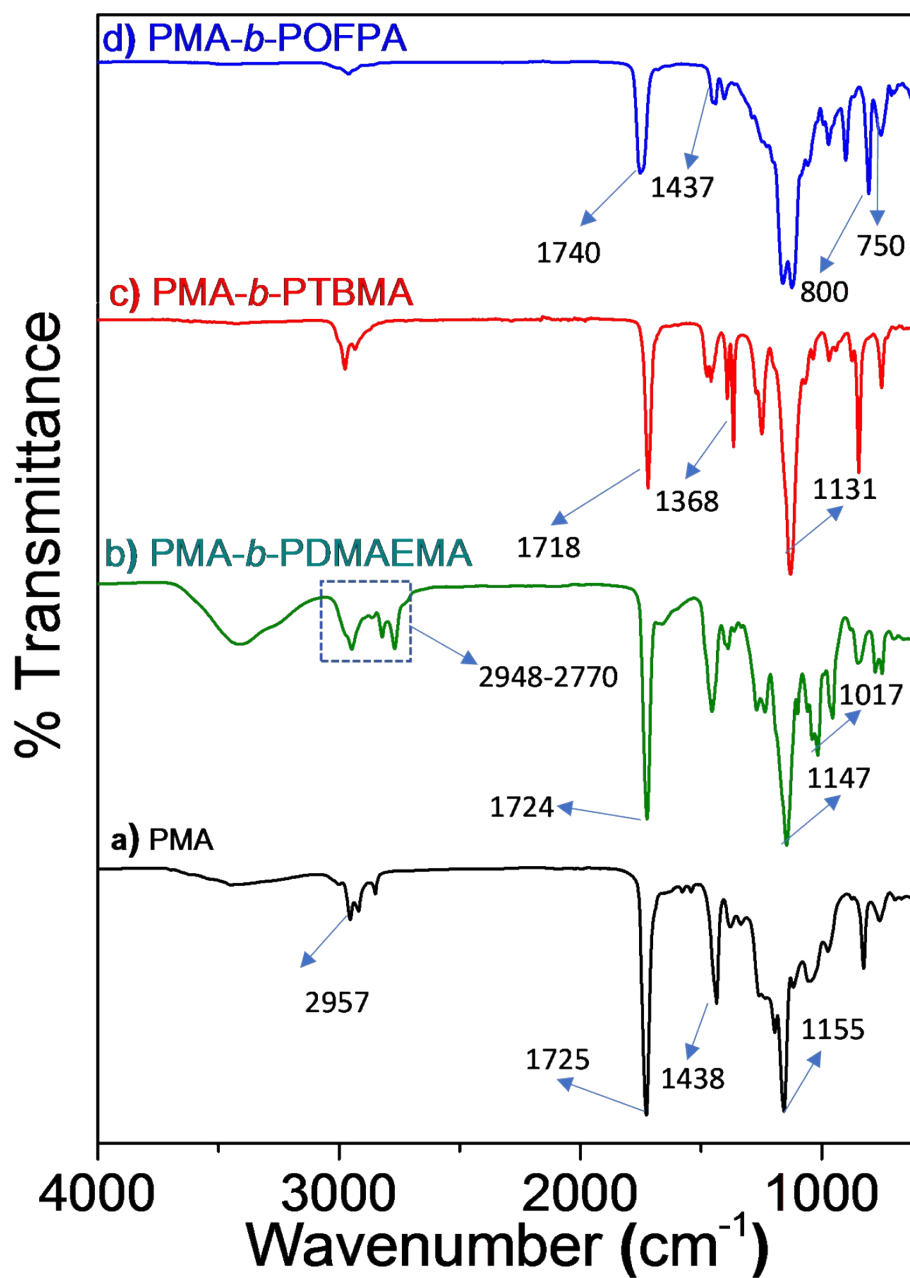
mol<sup>-1</sup>) are the molecular weight of MA and EBiB, respectively. <sup>d</sup>Obtained from SEC measurements.

## B. Supporting scheme

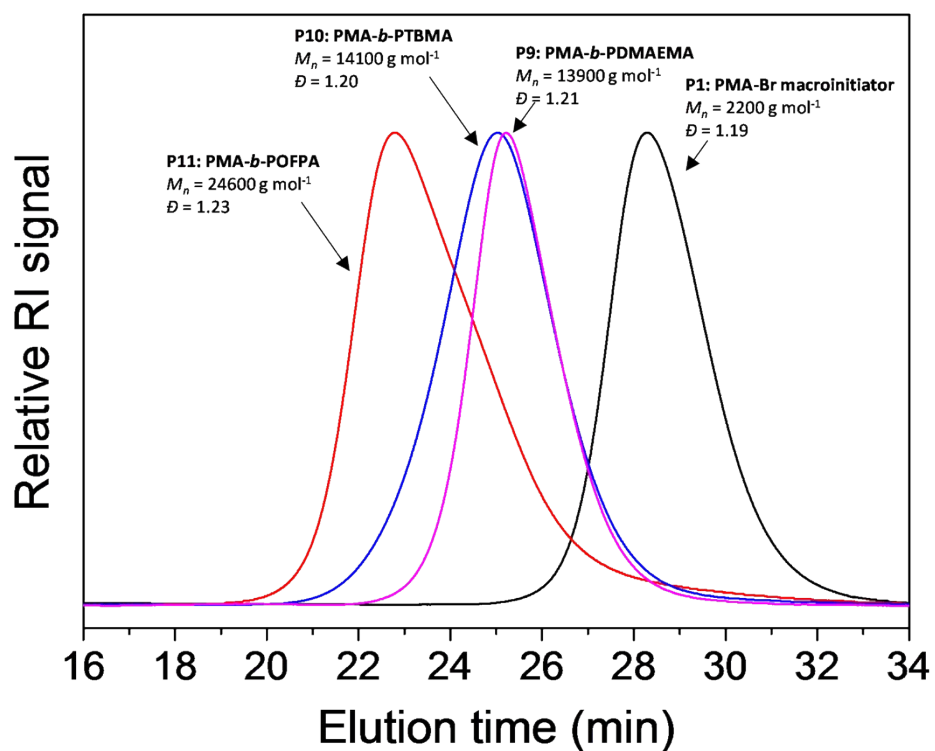


**Scheme S1** Chemical structures of the initiators employed in this study.

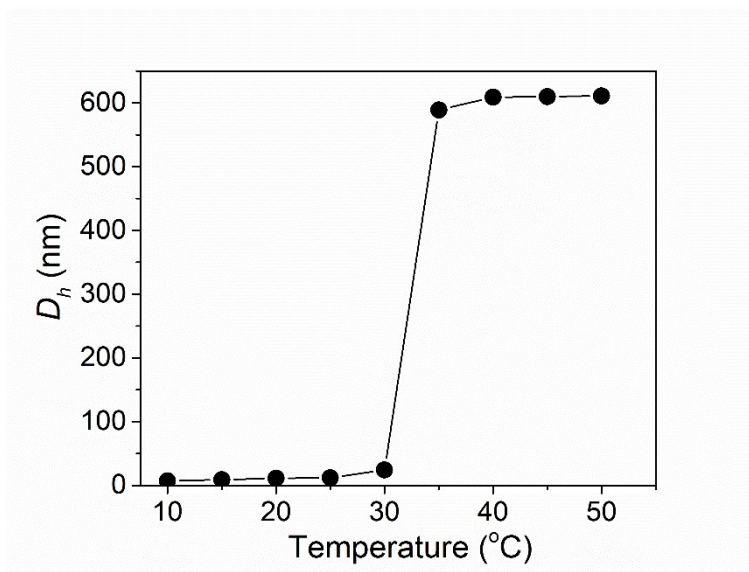
### C. Supporting figures



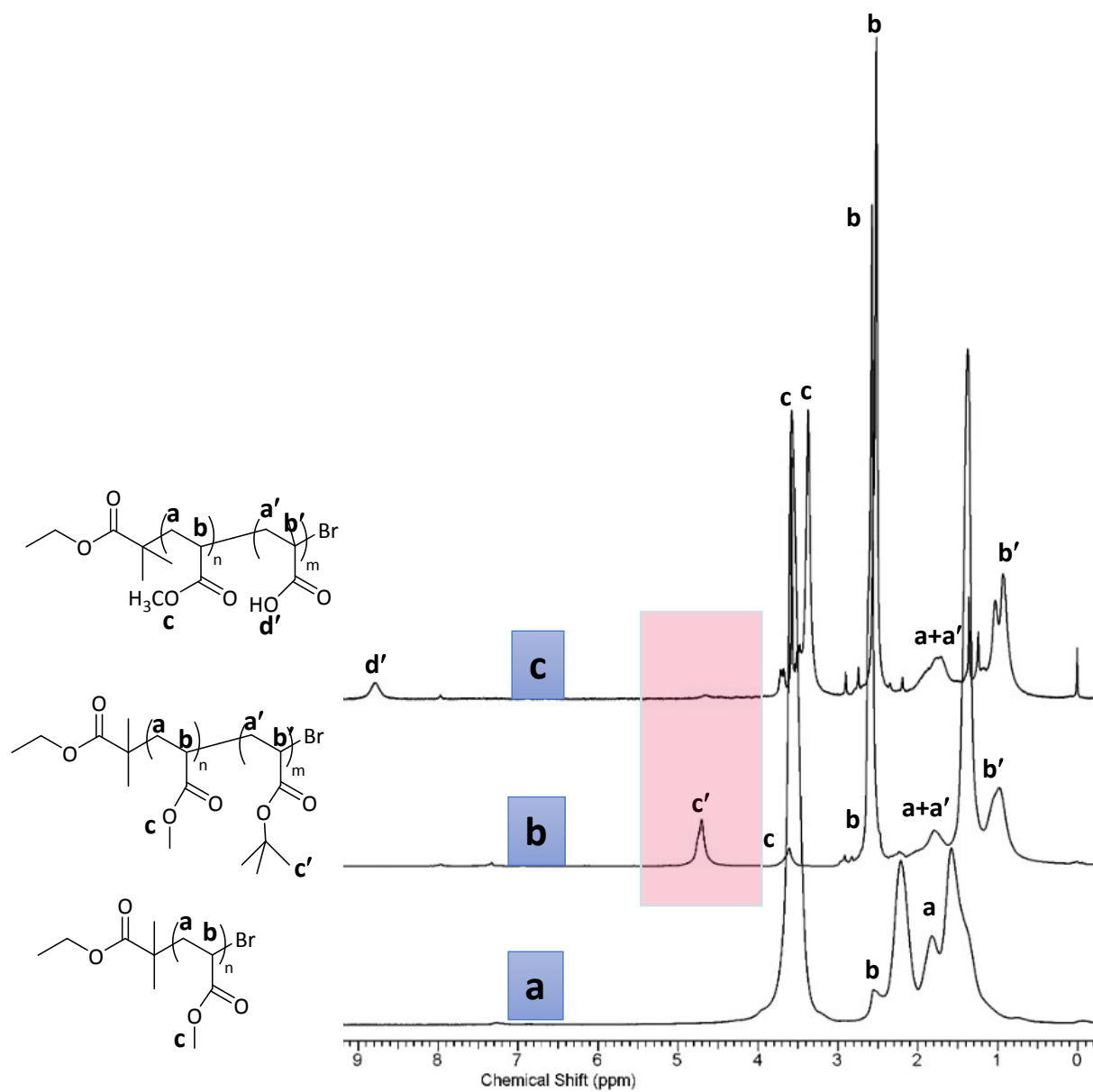
**Fig. S1** ATR-IR spectra of PMA-Br (P1, Table 1) (a), PMA-*b*-PDMAEMA (P9, Table 1) (b), PMA-*b*-PTBMA (P10, Table 1) (c) and PMA-*b*-POFPA (P11, Table 1) (d).



**Fig. S2** SEC traces of PMA-Br (P1, Table 1), PMA-*b*-PDMAEMA (P9, Table 1), PMA-*b*-PTBMA (P10, Table 1) and PMA-*b*-POFPA (P11, Table 1).

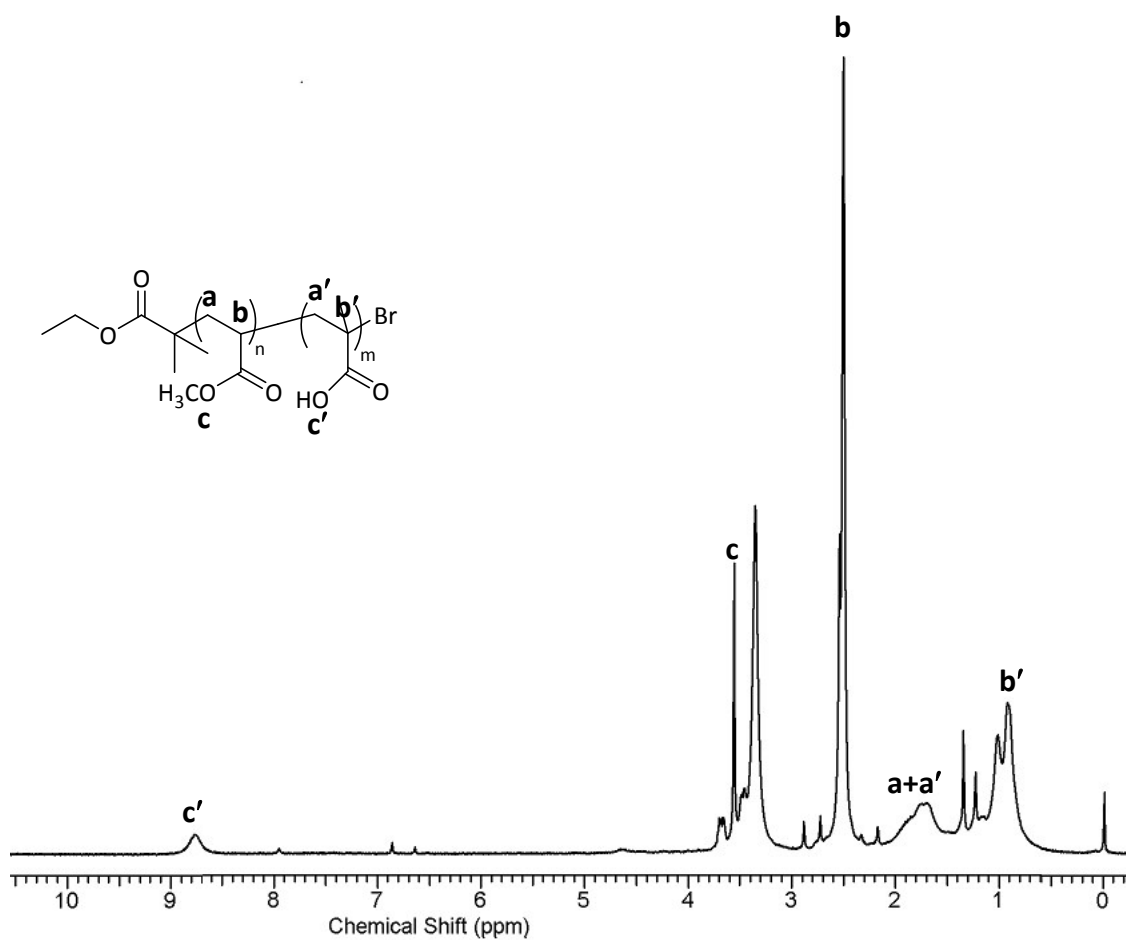


**Fig. S3** Plot of the hydrodynamic diameter ( $D_h$ ) as a function of temperature for an aqueous solution of PMA-*b*-PDMAEMA diblock copolymer at pH 10.5.

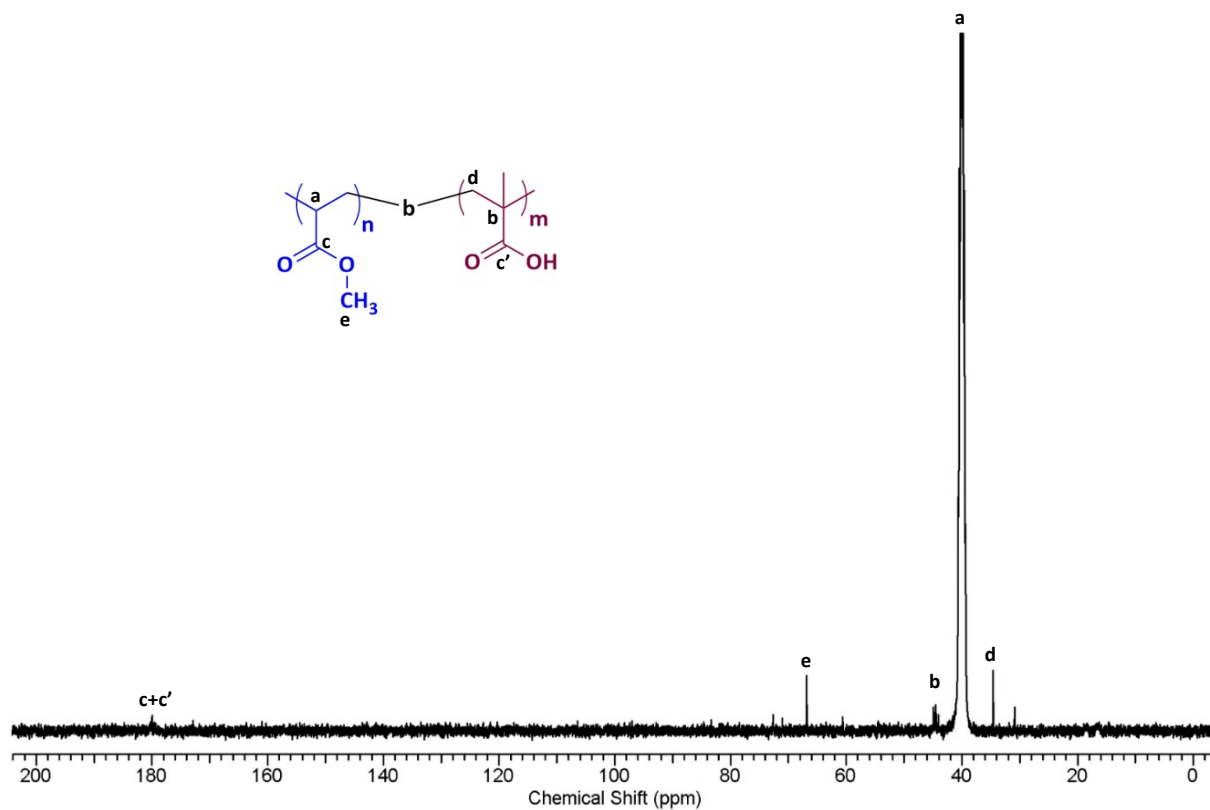


**Fig. S4**  $^1\text{H}$  NMR spectra of PMA-Br (P1, Table 1) (a); PMA-*b*-PTBMA (P10, Table 1) before (b) and after hydrolysis (c) of the *tert*-butyl ester groups.





**Fig. S5** <sup>1</sup>H NMR spectrum of PMA-*b*-PMAA (P8, Table 1) obtained via hydrolysis of PMA-*b*-PTBMA.



**Fig. S6**  $^{13}\text{C}$  NMR spectrum of PMA-*b*-PMAA (P8, Table 1) obtained via hydrolysis of PMA-*b*-PTBMA.