Supporting Information for the Manuscript

Synthesis and use of a surface-active initiator in emulsion polymerization under AGET and ARGET ATRP conditions

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Page 03 are the characterization section and Page 04-10 are the ^{1}H NMR and ^{13}C NMR spectra for compounds **4**, **5** and the acid form of **1**; Page 11 is the ^{1}H NMR of the product PMMA.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$.

List of ^{1}H NMR and ^{13}C NMR spectra for compounds 4, 5, the acid form of 1, and the product PMMA.

Page 04	^{1}H NMR of **4**	Page 05	^{13}C NMR of **4**
Page 06	^{1}H NMR of **5**	Page 07	^{13}C NMR of **5**
Page 08	^{1}H NMR of **1**	Page 09	^{13}C NMR of **1**
Page 10	local amplification of ^{13}C NMR of **1**		
Page 11	^{1}H NMR of the product PMMA		

The intermediate 4

IR: *v* 3368, 2930, 2856, 1734, 1396, 1279, 1166 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ4.17 (t, 2H, *J* = 6.61 Hz, OCH_2), 3.63 (t, 2H, *J* = 6.64 Hz, CH_2OH), 2.05 (s, 1H, *OH*), 1.93 (s, 6H, $2CH_3$), 1.70-1.66 (m, 2H, CH_2), 1.58-1.54 (m, 2H, CH_2), 1.36-1.28 (m, 12H, $6CH_2$);

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 66.1, 62.9, 56.0, 32.7, 30.8, 29.5, 29.44, 29.36, 29.1 (2C), 28.3, 25.74, 25.71.

Anal Calcd for $C_{14}H_{27}BrO_3$: C, 52.02; H, 8.42. Found: C, 52.07; H, 8.39.

The intermediate 5

mp 29-31 ^oC.

IR: *v* 3446, 3222, 2927, 2856, 1735, 1462, 1379, 1277, 1165 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ9.5 (*br* s, 1H), 6.49-6.40 (m, 2H, *CH*=*CH*), 4.29 (t, 2H, *J* = 6.59 Hz, OCH_2), 4.17 (t, 2H, *J* = 6.50 Hz, OCH_2), 1.94 (s, 6H, $2CH_3$), 1.74-1.65 (m, 4H, $2CH_2$), 1.32-1.28 (m, 12H, $6CH_2$);

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 167.9, 164.7, 136.4, 129.8, 67.3, 66.1, 56.2, 30.7, 29.3, 29.2, 29.1, 29.03, 28.96, 28.3, 28.1, 25.70, 25.67.

Anal Calcd for $C_{18}H_{29}BrO_6$: C, 51.31; H, 6.94. Found: C, 51.36; H, 6.91.

The initiator/surfactant 1

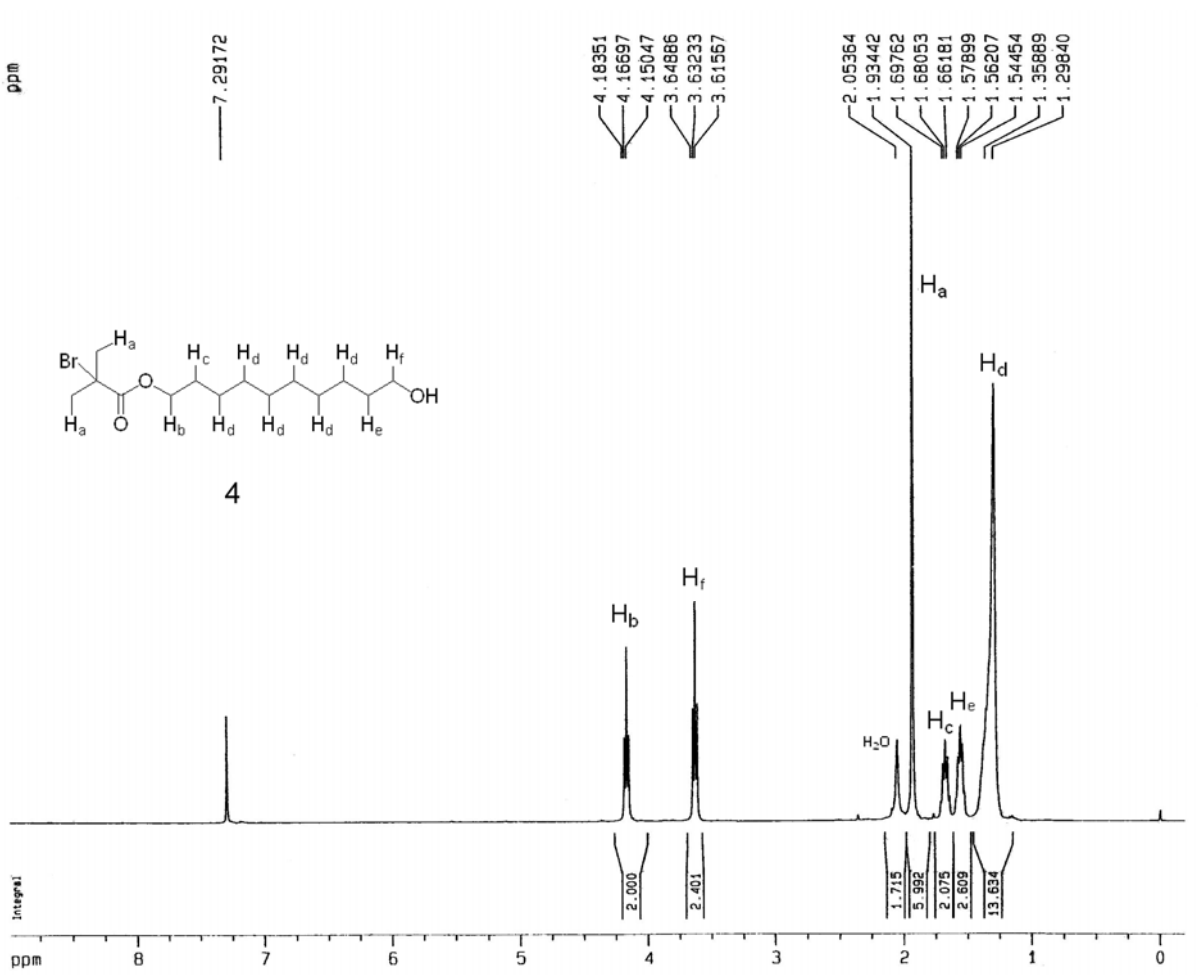
IR: *v* 3440 (*br*), 2930, 2856, 1733, 1637, 1400, 1275, 1227, 1166, 1045, 691cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ4.04 (t, 4H, *J* = 10.88 Hz, $2OCH_2$), 3.99-3.97 (m, 2H, CH_2), 3.57 (t, 1H, *J* = 6.62 Hz, *CH*), 1.86 (s, 6H, $2CH_3$), 1.62-1.49 (m, 4H, $2CH_2$), 1.48-1.18 (m, 12H, $6CH_2$);

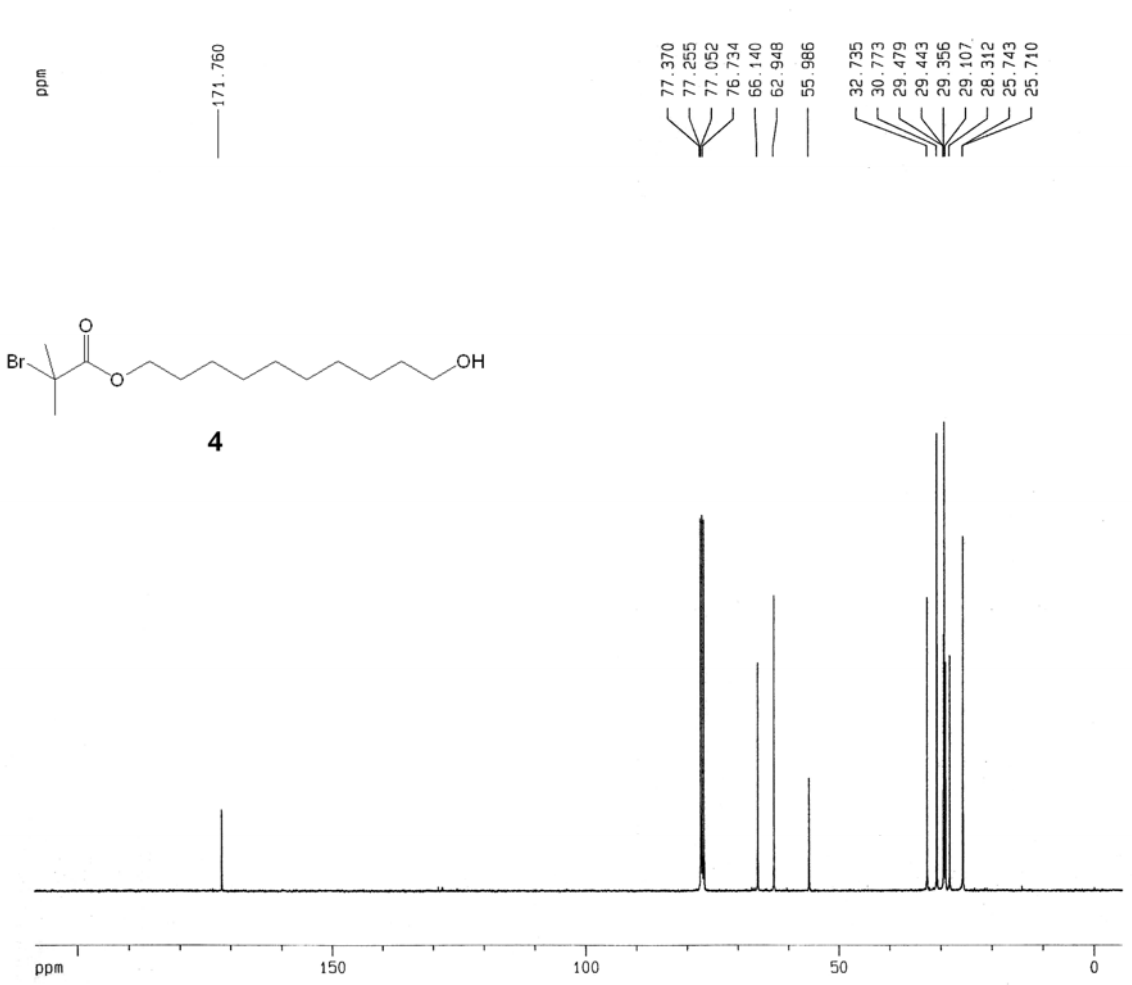
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 171.8, 169.0, 66.1, 65.9, 63.0, 56.0, 30.8 (2C), 29.44, 29.35, 29.10, 28.56, 28.52, 25.84, 25.75, 25.71.

Anal Calcd for $C_{18}H_{31}BrO_9S$: C, 42.91; H, 6.24. Found: C, 42.95; H, 6.21.

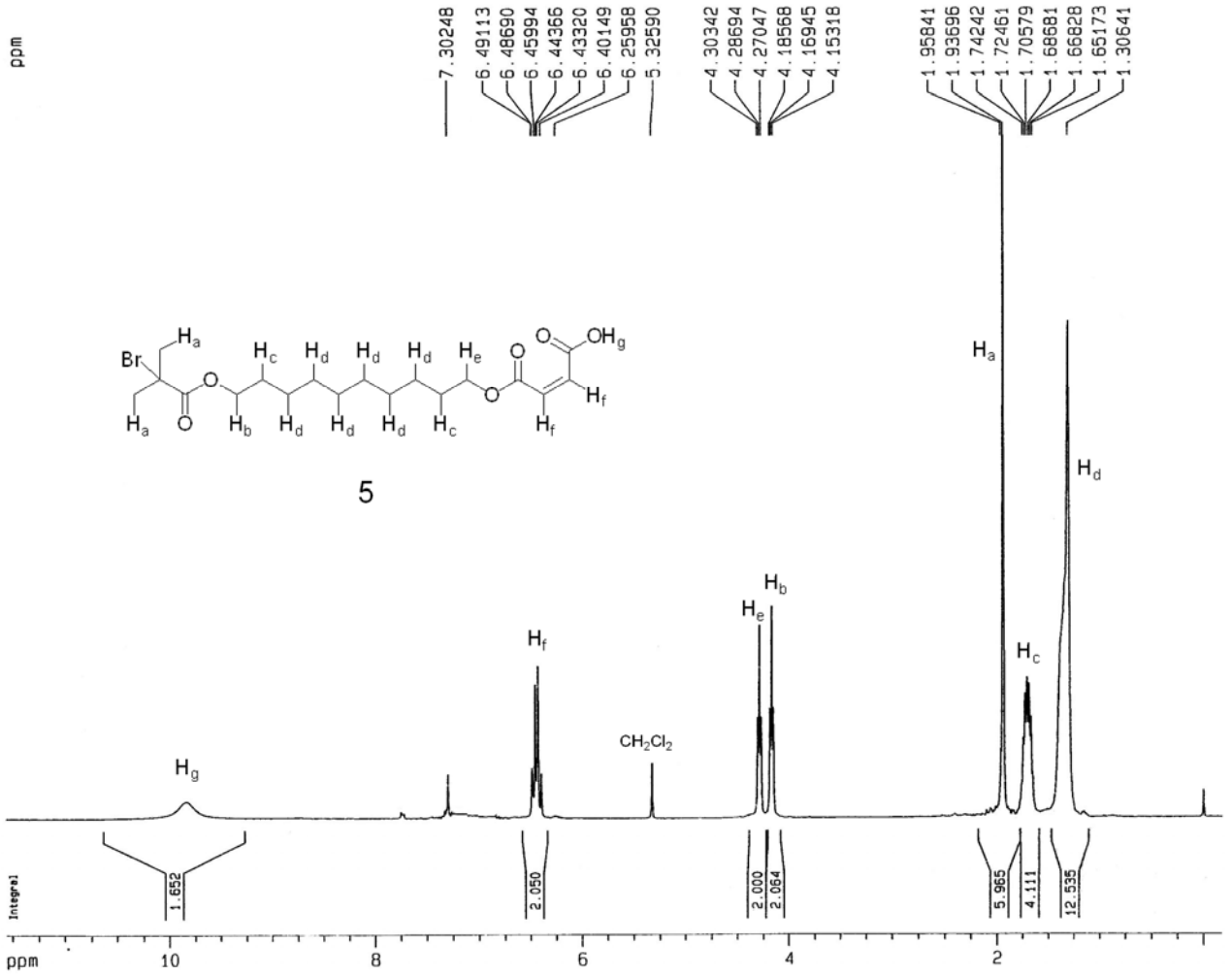
Compound **4**: ^{1}H NMR(400MHz, $CDCl_3$)



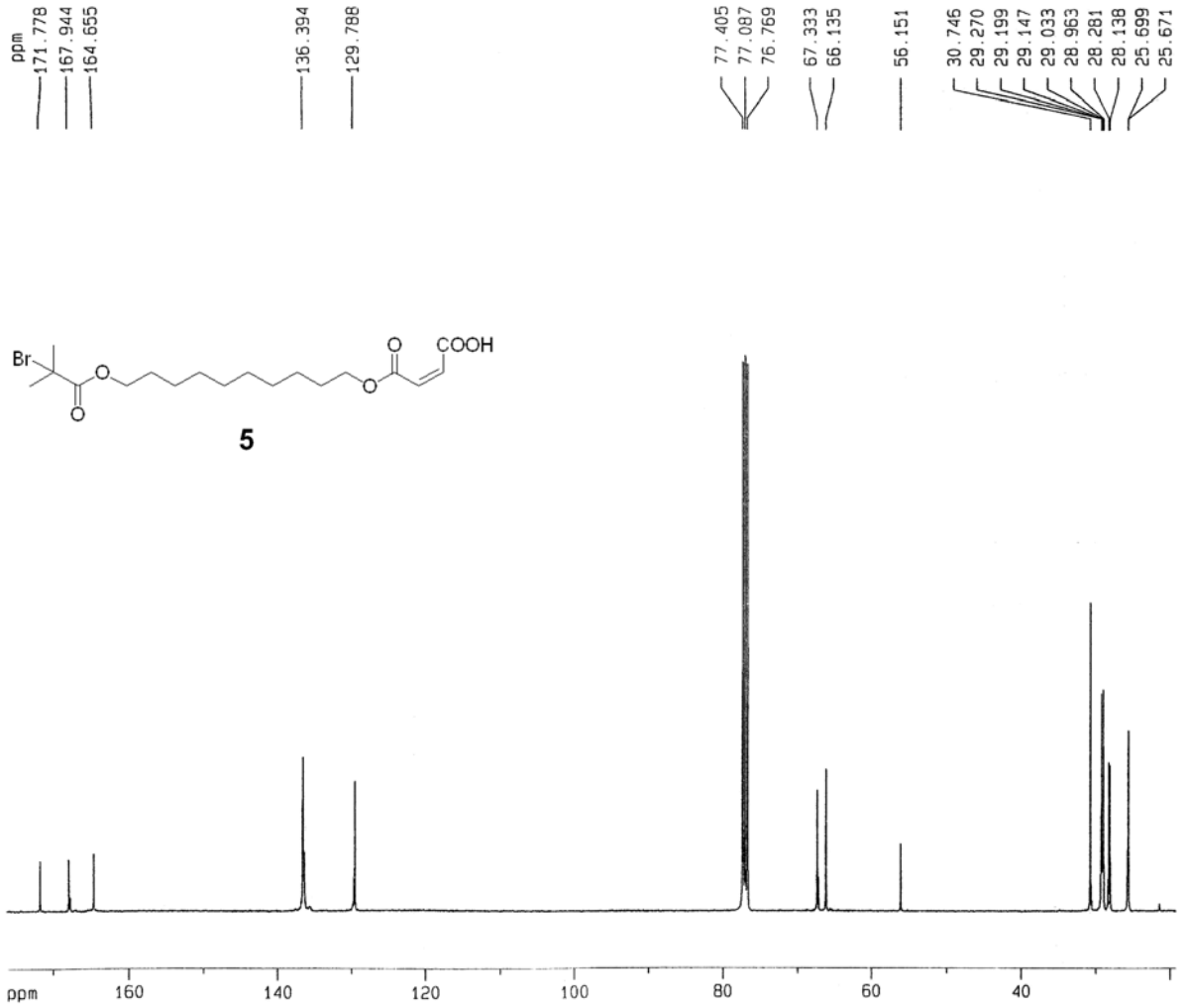
Compound **4**: ^{13}C NMR(100MHz, $CDCl_3$)



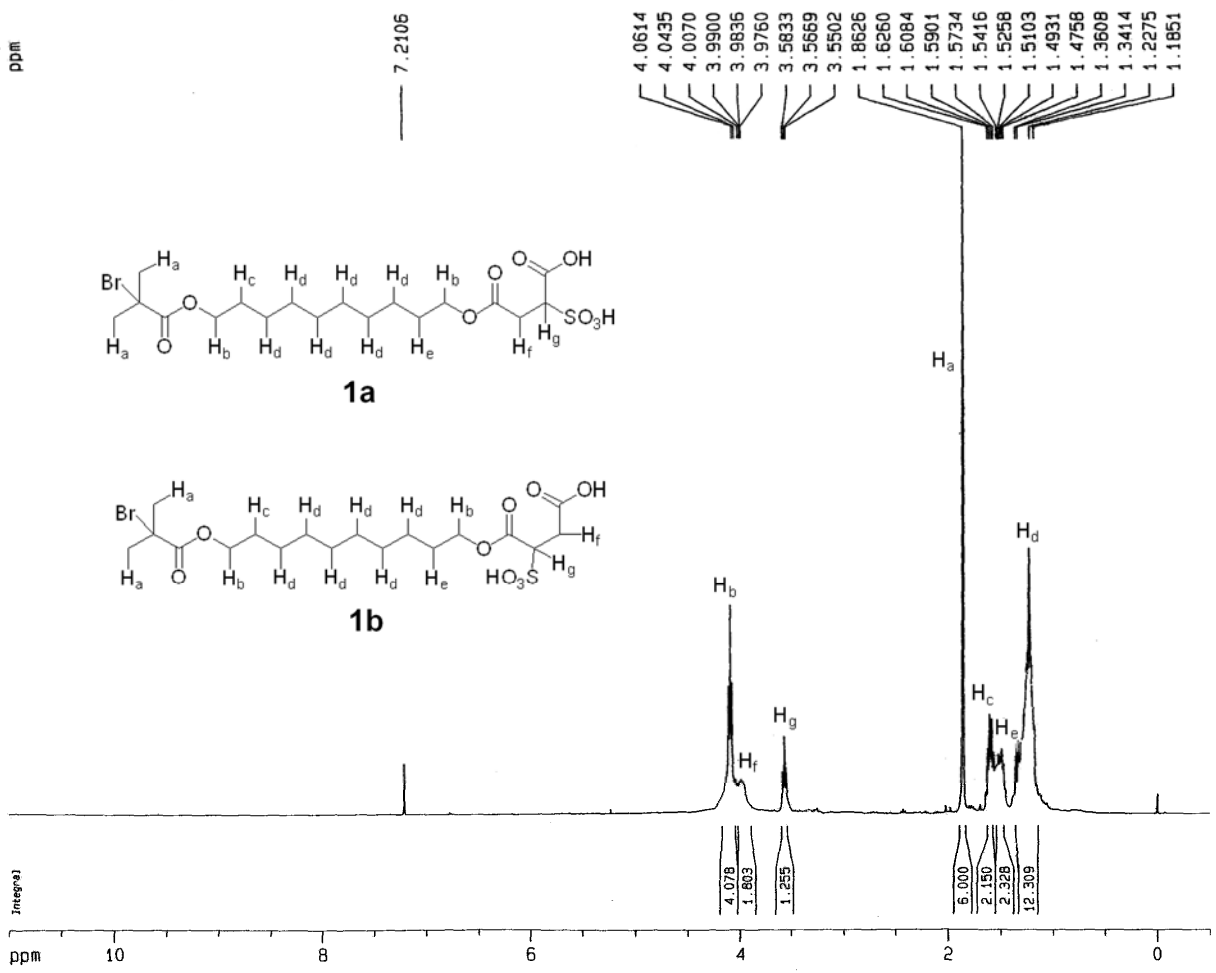
Compound **5**: ^{1}H NMR(400MHz, $CDCl_3$)



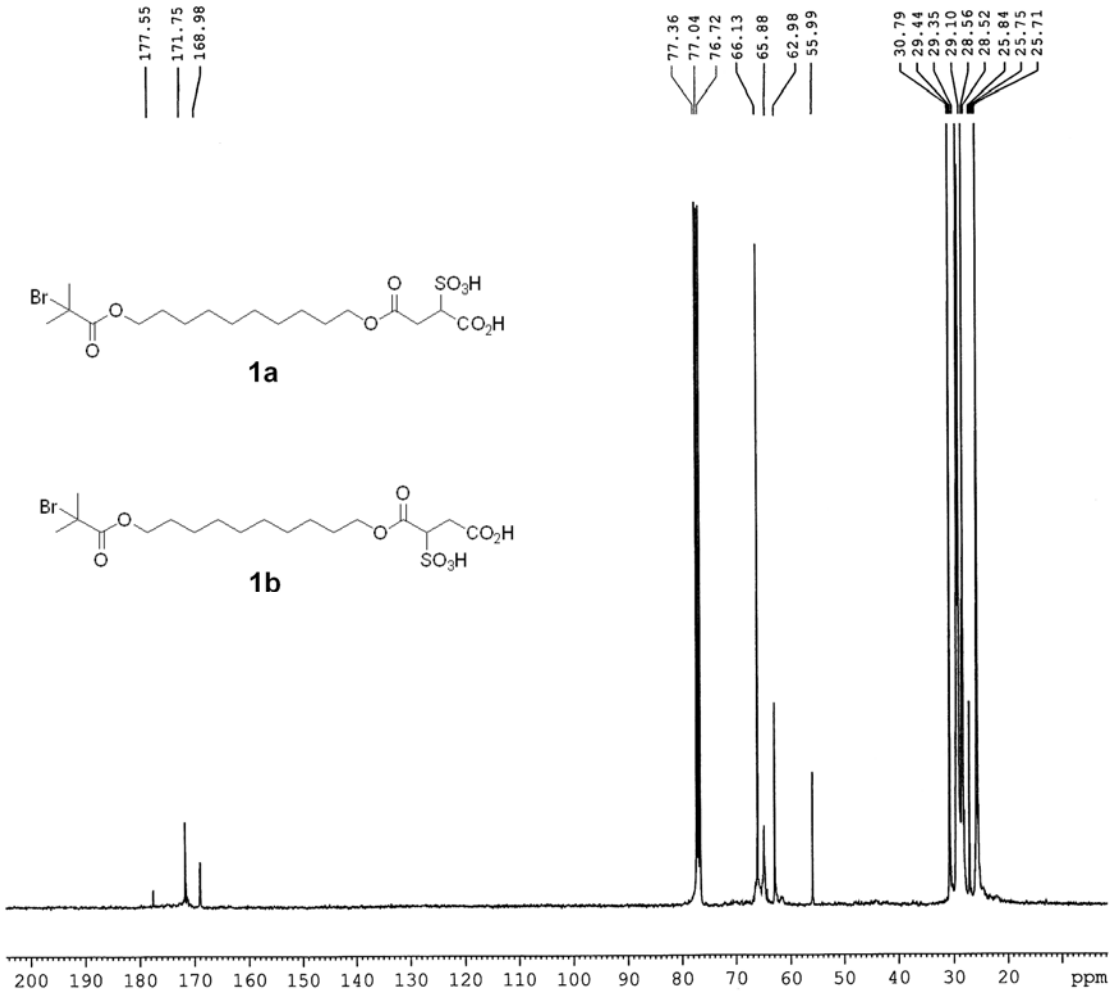
Compound **5**: ^{13}C NMR(100MHz, $CDCl_3$)



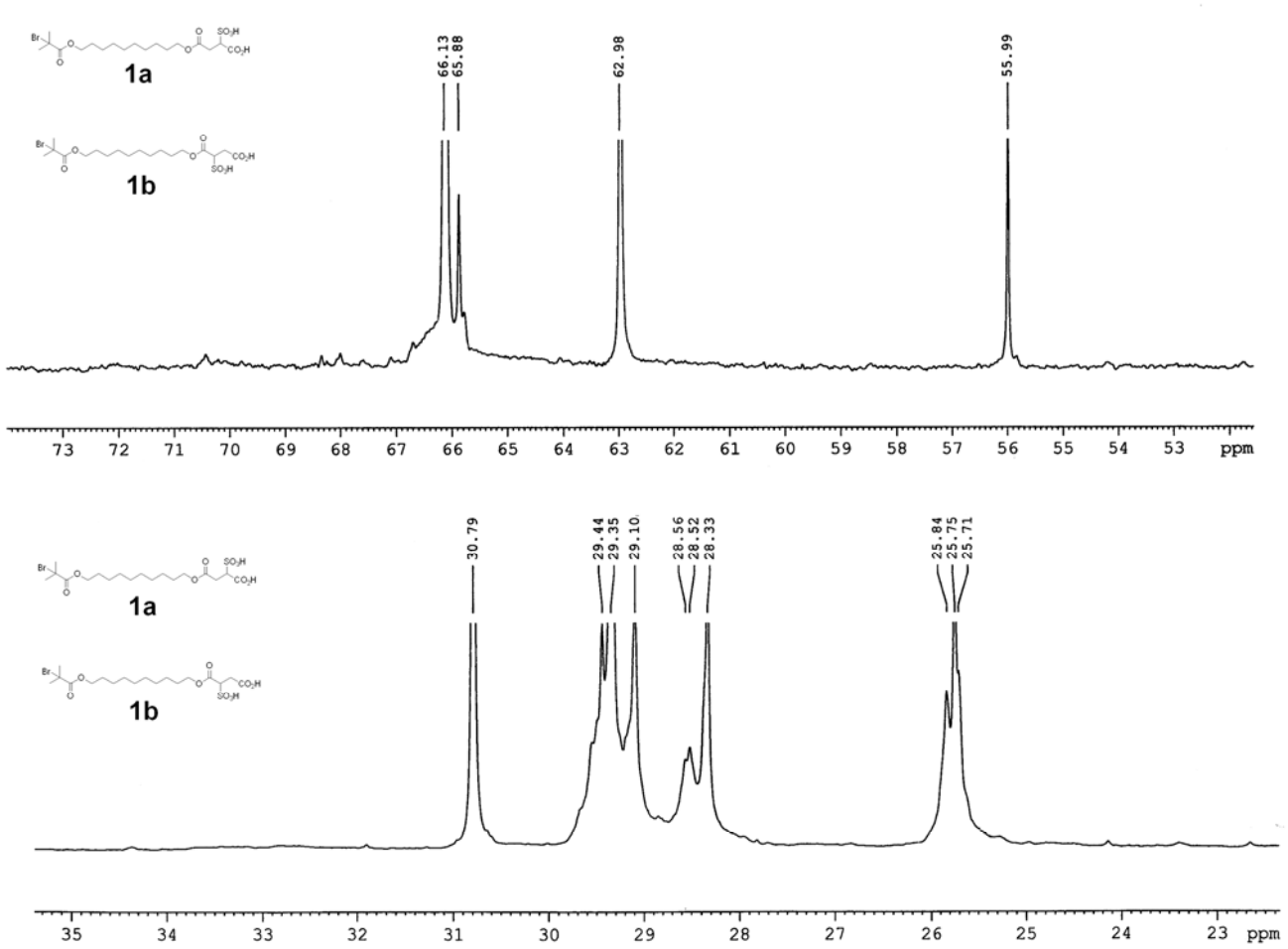
Compound **1**: ^{1}H NMR(400MHz, $CDCl_3$)



Compound **1**: ^{13}C NMR(100MHz, $CDCl_3$)



local amplification of ^{13}C NMR of **1**



The ^{1}H NMR of the product PMMA (Exp. A_4)