

Supplementary Information:

Separation and characterization of benzaldehyde-functional polyethylene glycols by liquid chromatography under critical conditions

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Table S1. Feed ratios of 4-carboxybenzaldehyde to MPEGOH 5k with the catalysts used and the average degrees of functionality of MPEGCHO 5k.

feed ratio of [COOH]: [OH] ^a	MPEGOH 5k/ [OH]	4- carboxybe nzaldehyd e/ [COOH]	DCC	DMAP	degree of functionality of MPEGCHO 5k mol % ^b
1:1	1.00 g/ 0.21 mmol	0.032 g, 0.21 mmol	0.052 g 0.25 mmol	0.065 g 0.53 mmol	44
2:1		0.063 g, 0.42 mmol	0.103 g 0.50 mmol	0.65 g 0.53 mmol	65
3:1		0.095 g, 0.63 mmol	0.157 g 0.76 mmol	0.065 g 0.53 mmol	97

^a[COOH]: 4-carboxybenzaldehyde; [OH]: MPEGOH 5k, $M_n=4677$

^b Determined by ¹H NMR.

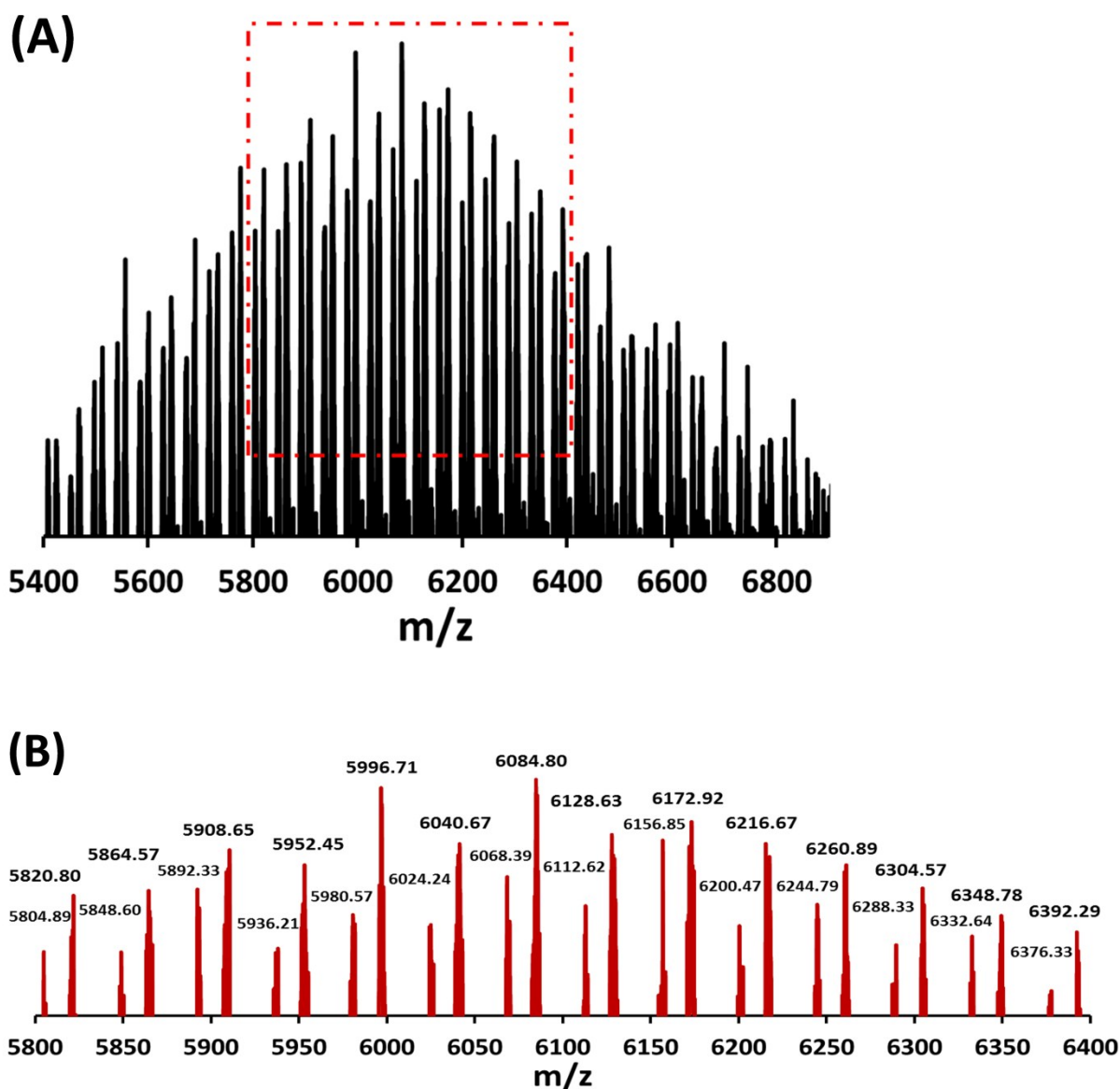


Fig. S1. MALDI-TOF mass spectrum for (A) bi-funtional fraction collected at 12.15-12.40 min of PEGDCHO 6k under LCCC on XB-Phenyl column at 30°C, (B) enlarged part from 5800 to 6400 m/z (the major series, $M_{\text{peak}} = n \times 44 (\text{CH}_2\text{CH}_2\text{O}^-) + 133 (-\text{CO}-\text{Ph}-\text{CHO}) + 149(-\text{COO}-\text{Ph}-\text{CHO}) + 39 (\text{K}^+)$; the minor series, $M_{\text{peak}} = n \times 44 (\text{CH}_2\text{CH}_2\text{O}^-) + 133 (-\text{CO}-\text{Ph}-\text{CHO}) + 149(-\text{COO}-\text{Ph}-\text{CHO}) + 23 (\text{Na}^+)$).

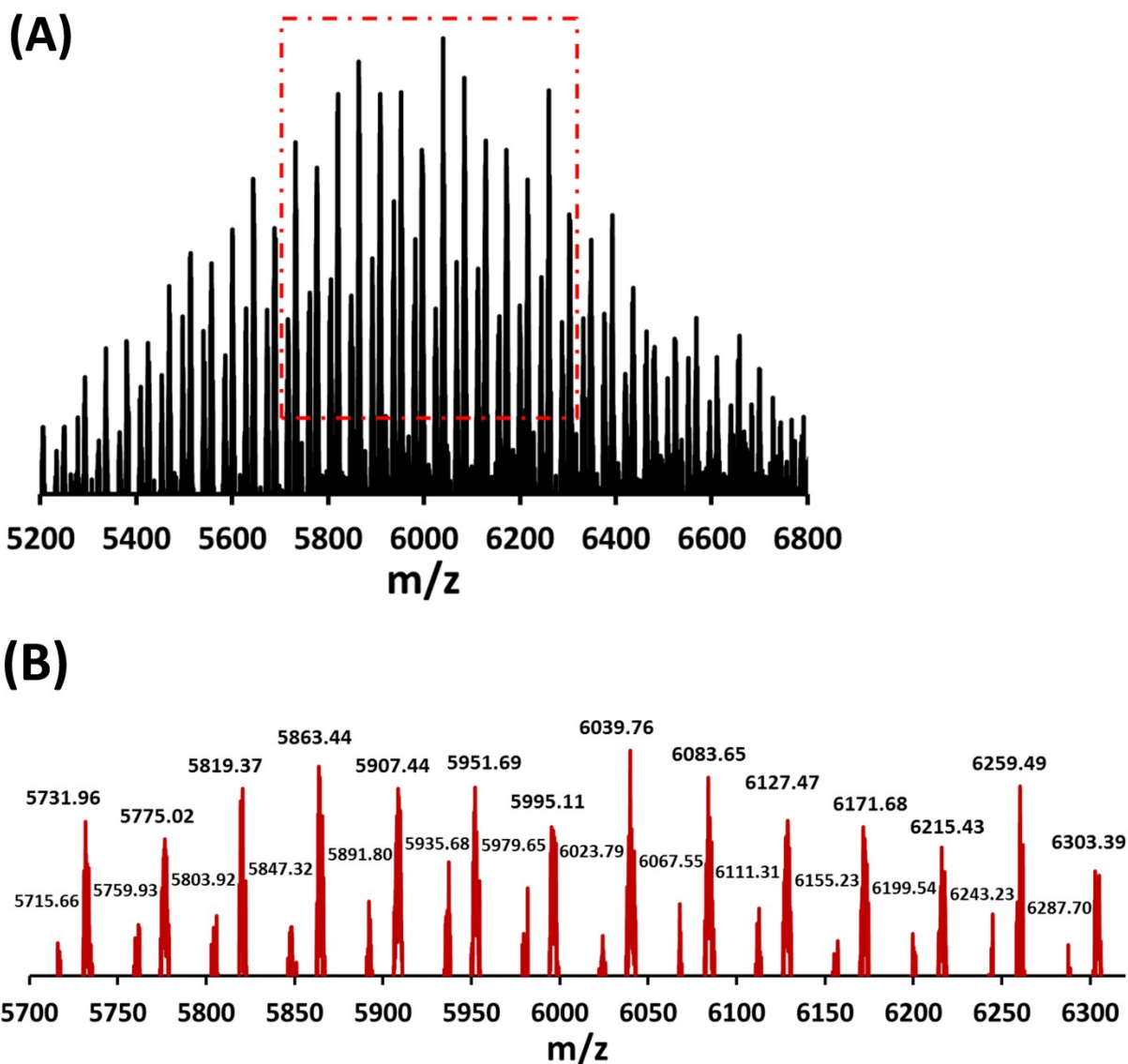


Fig. S2. MALDI-TOF mass spectrum for (A) mono-funtional fraction collected at 8.25-8.55 min of PEGCHO 6k under LCCC on XB-Phenyl column at 30°C, (B) enlarged part from 5700 to 6320 m/z (the major series, $M_{\text{peak}} = n \times 44 (\text{CH}_2\text{CH}_2\text{O}-) + 133 (-\text{CO}-\text{Ph}-\text{CHO}) + 17(-\text{OH}) + 39 (\text{K}^+)$; the minor series, $M_{\text{peak}} = n \times 44 (\text{CH}_2\text{CH}_2\text{O}-) + 133 (-\text{CO}-\text{Ph}-\text{CHO}) + 17(-\text{OH}) + 23 (\text{Na}^+)$).