

Supporting Information

RAFT Polymerization of Fatty Acid Containing Monomers: Controlled Synthesis of Polymers from Renewable Resources

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Table S1 Synthesis of various fatty acid based monomers.

Monomer	Yield (%)	Physical state	Actual mass [M + Na ⁺]	Mass found [M + Na ⁺]
CLAMA	75	solid	279.17	279.32
CRAMA	76	liquid	307.20	307.29
LAMA	80	liquid	335.23	335.27
MAMA	85	liquid	363.26	363.28
PAMA	77	solid	391.29	391.27
SAMA	74	liquid	419.32	419.28

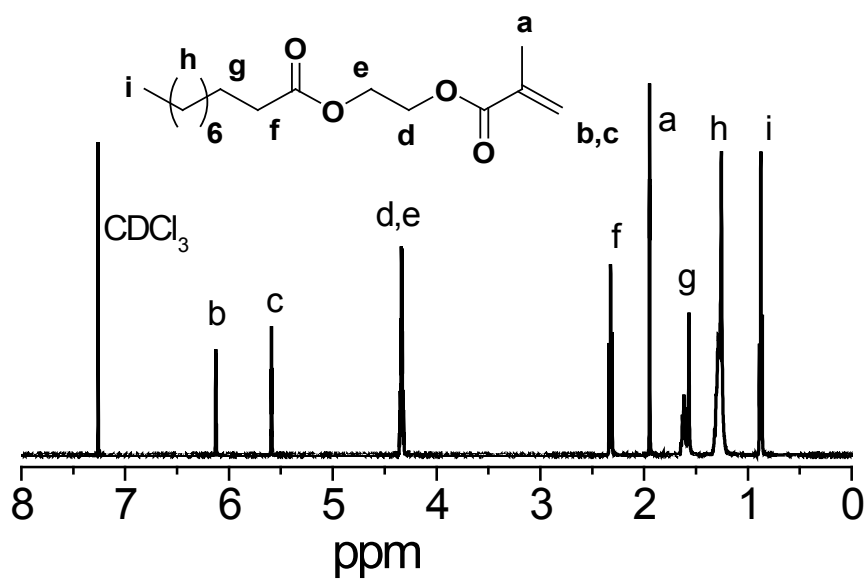


Fig. S3 ¹H NMR spectrum of CRAMA in CDCl₃.

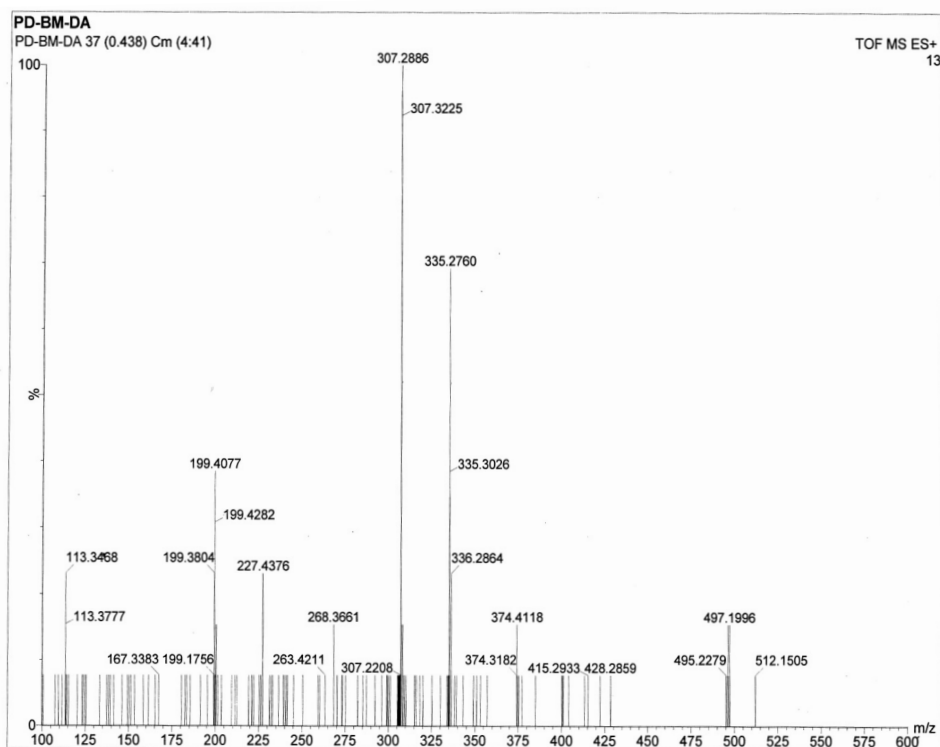


Fig. S4 ESI-MS spectrum of CRAMA (calculated m/z for $[M + Na^+]$: 307.20, observed: 307.29).

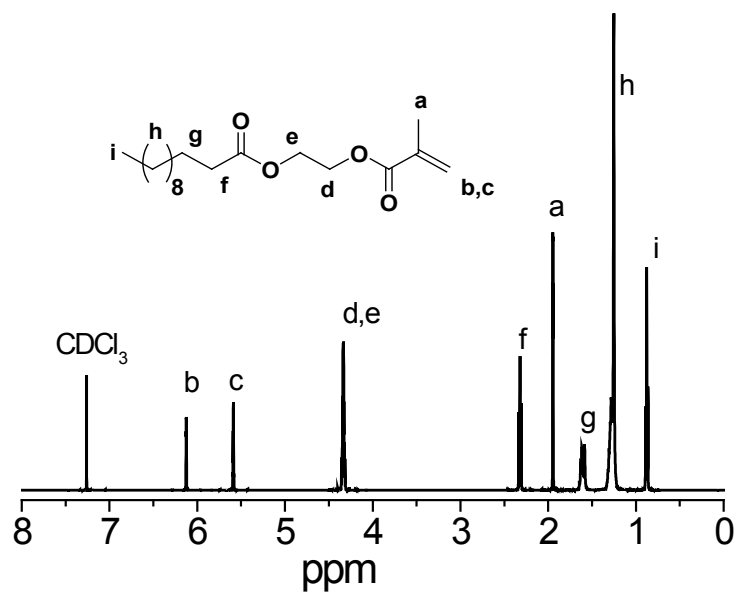


Fig. S5 ¹H NMR spectrum of LAMA in CDCl₃.

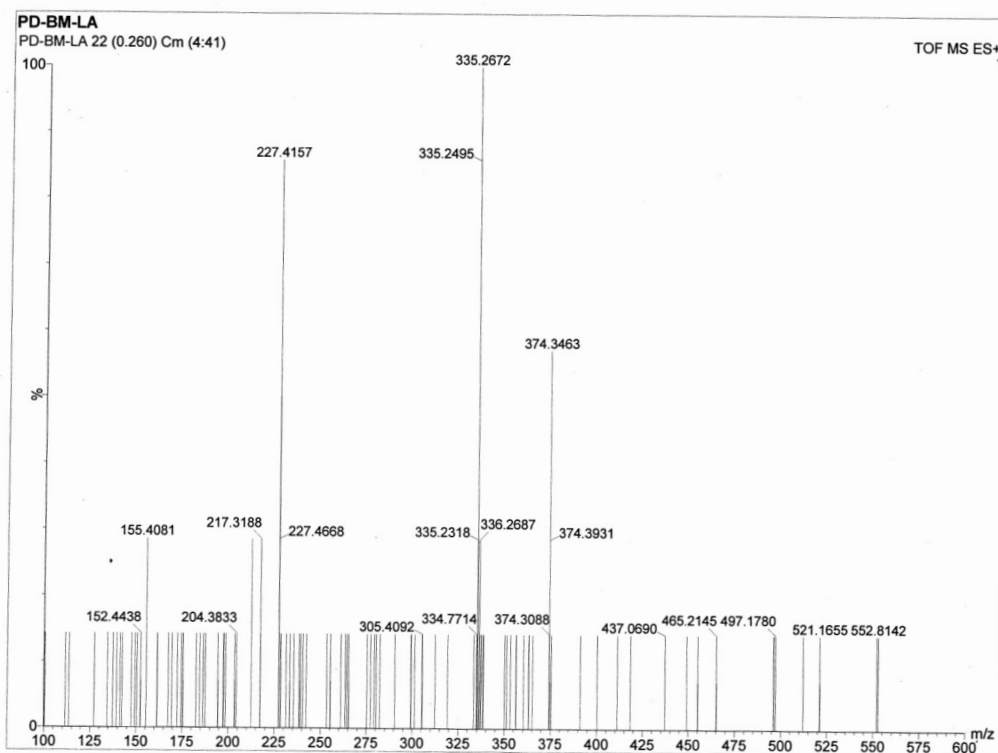


Fig. S6 ESI-MS spectrum of LAMA (calculated m/z for $[M + Na^+]$: 335.23, observed: 335.26).

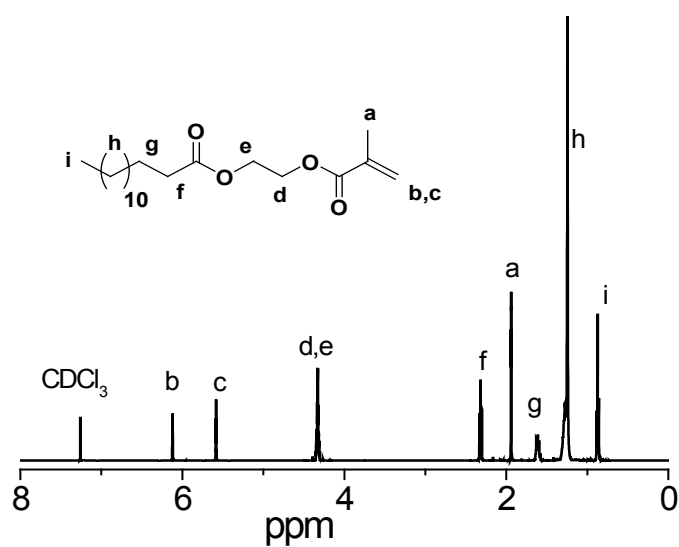


Fig. S7 ^1H NMR spectrum of MAMA in CDCl_3 .

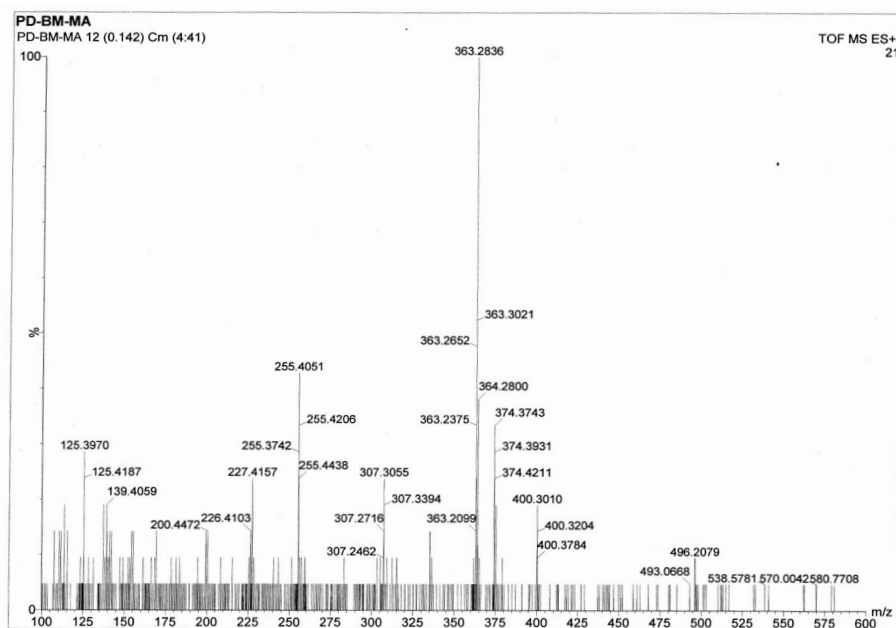


Fig. S8 ESI-MS spectrum of MAMA (calculated m/z for $[\text{M} + \text{Na}^+]$: 363.26, observed: 363.28).

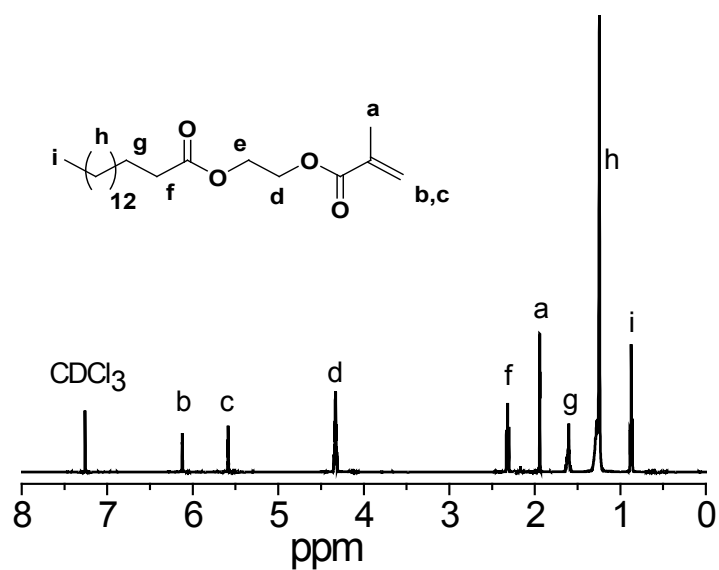


Fig. S9 ¹H NMR spectrum of PAMA in CDCl₃.

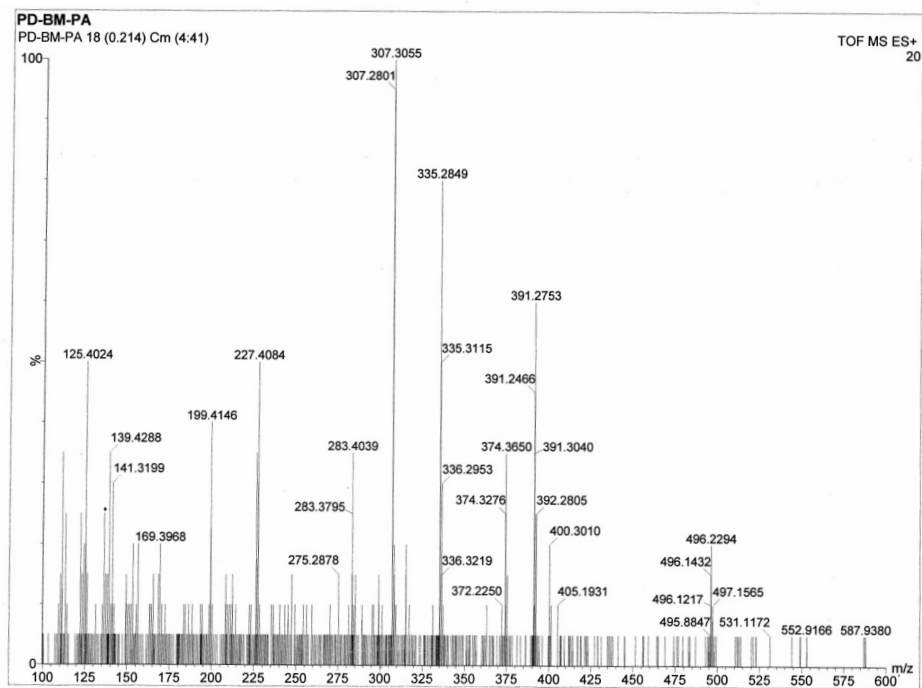


Fig. S10 ESI-MS spectrum of PAMA (calculated m/z for $[M + Na^+]$: 391.29, observed: 391.28).

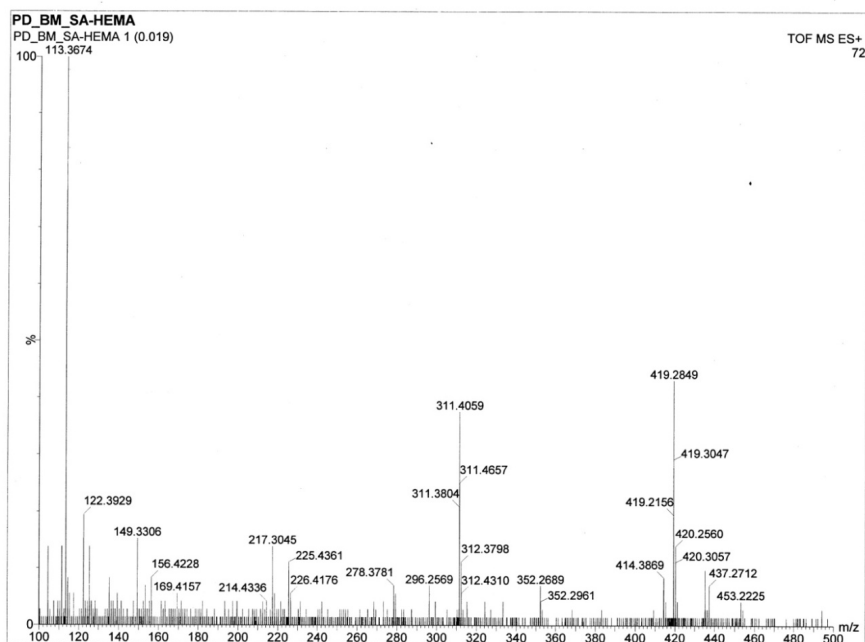


Fig. S11 ESI-MS spectrum of SAMA (calculated m/z for $[M + Na^+]$: 419.32, observed: 419.28).

Table S2 Solubility of fatty acid based monomer and polymer at room temperature.

Solvent	CLAMA	PCLAMA	SAMA	PSAMA
Water	-	-	-	-
Acetone	+	+	+	-
Chloroform	+	+	+	+
DCM	+	+	+	+
CCl ₄	+	+	+	+
Methanol	+	-	+	-
Ethanol	+	-	+	-
DMF	+	+	+	-
DMSO	+	+	+	-
THF	+	+	+	+
Pet ether	+	+	+	+
Diethyl ether	+	+	+	+
Ethyl acetate	+	+	+	+
Hexane	+	+	+	+
Benzene	+	+	+	+
Toluene	+	+	+	+
1,4-dioxane	+	+	+	+
Acetonitrile	+	-	+	-

The symbols (+) and (-) indicate soluble and insoluble, respectively.

Table S3 Polymerization of various FAMA's in DMF at 70 °C using CDP as CTA.^a

Monomer	Conv. ^b (%)	$M_{n,GPC}$ ^c (g/mol)	PDI ^c	$M_{n,theo}$ ^d (g/mol)
CLAMA	72	16300	1.06	9600
LAMA	75	15000	1.13	12100
PAMA	71	14700	1.09	13500
SAMA	35	15100	1.17	7600

^a [Monomer]/[CDP]/[AIBN] = 50/1/0.2; time = 4 h. ^b Determined by gravimetric analysis. ^c Measured by GPC using PMMA standards in THF. ^d Theoretical molecular weight ($M_{n,theo}$) = ([FAMA]/[CTA] × MW of FAMA × conversion) + (MW of CDP).

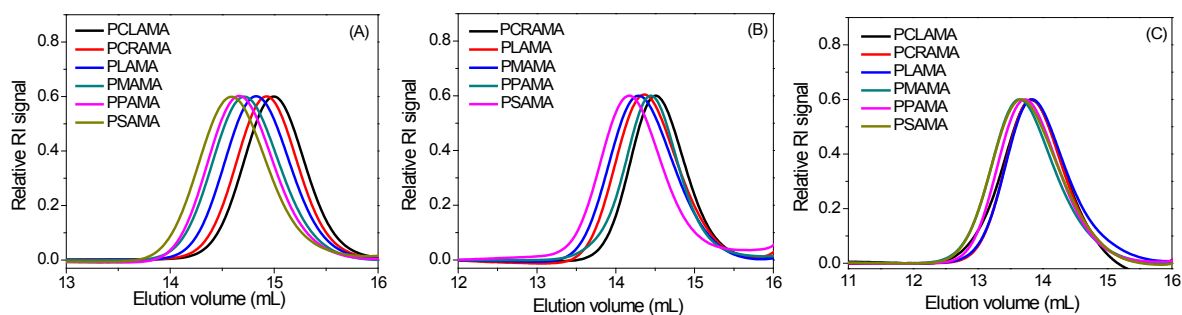


Fig. S12 GPC RI traces of various polymers obtained at different [M]/[CDP]/[AIBN] ratios; (A) 25:1:0.2, (B) 50:1:0.2 and (C) 100:1:0.2 for the RAFT polymerization of FAMA's in THF at 70 °C.

Table S4 Polymerization of various FAMA in THF at 70 °C using CDP as CTA.

Polymer	[M]/[CDP]/[AIBN]	Time (h)	Conv. ^a (%)	$M_{n,GPC}^b$ (g/mol)	PDI ^b	$M_{n,theo}^c$ (g/mol)
PCLAMA	25:1:0.2	6.5	78	7500	1.10	5400
PCLAMA	100:1:0.2	7.5	80	25300	1.28	20900
PLAMA	25:1:0.2	6.5	78	9600	1.11	6500
PLAMA	100:1:0.2	7.5	87	22400	1.30	27500
PMAMA	25:1:0.2	6.5	81	10700	1.11	7300
PMAMA	100:1:0.2	7.5	80	27400	1.34	27600
PPAMA	25:1:0.2	6.5	84	10900	1.12	8200
PPAMA	100:1:0.2	7.5	73	26100	1.28	27300

^aDetermined by gravimetric analysis. ^bMeasured by GPC using PMMA standards in THF.

^c $M_{n,theo} = ([FAMA]/[CDP] \times MW \text{ of FAMA} \times conv.) + MW \text{ of CDP}.$

Table S5 Polymerization of various FAMA in THF at 70 °C using CTP as CTA.^a

Monomer	Conv. ^b (%)	$M_{n,GPC}^c$ (g mol ⁻¹)	PDI ^c	$M_{n,NMR}^d$ (g mol ⁻¹)	$M_{n,theo}^e$ (g mol ⁻¹)
CLAMA	72	9000	1.09	9200	9500
CRAMA	78	15230	1.10	21000	11400
LAMA	75	15600	1.14	ND	12000
MAMA	81	16100	1.12	16000	14100
PAMA	79	19260	1.11	ND	14800
SAMA	83	19750	1.11	14980	17300

^a Molar ratio of [Monomer]/[CTP]/[AIBN] = 50/1/0.2, Time = 7 h; ^b Determined by gravimetric analysis. ^c Measured by GPC using PMMA standards in THF. ^d Calculated by ¹H NMR study. ^e $M_{n,theo} = ([FAMA]/[CTP] \times MW \text{ of FAMA} \times conversion) + MW \text{ of CTP}.$

Table S6 Block copolymerization with various PFAMA macro-CTAs at 70 °C in THF.^a

Block copolymers	macro CTA	Conv. ^b (%)	$M_{n,GPC}$ ^c (g/mol)	PDI ^c	$M_{n,theo}$ ^d (g/mol)	$M_{n,NMR}$ ^e (g/mol)
PCLAMA- <i>b</i> -PCLAMA	PCLAMA	64	14300	1.23	11600	ND ^f
PCLAMA- <i>b</i> -PMEO ₂ MA	PCLAMA	70	13500	1.15	12700	15700
PLAMA- <i>b</i> -PLAMA	PLAMA	90	14100	1.18	16600	16000
PLAMA- <i>b</i> -PMEO ₂ MA	PLAMA	52	13000	1.16	13500	10000
PPAMA- <i>b</i> -PPAMA	PPAMA	80	15900	1.16	18200	19900
PPAMA- <i>b</i> -PMEO ₂ MA	PPAMA	53	14200	1.15	14800	19400

^aMolar ratio of [Monomer]/[macro CTA]/[AIBN] = 25/1/0.2, time = 7 h. ^bDetermined by gravimetric analysis. ^cMeasured by GPC. ^dTheoretical M_n . ^eObtained from ¹H NMR chain end analysis. ^fNot determined.

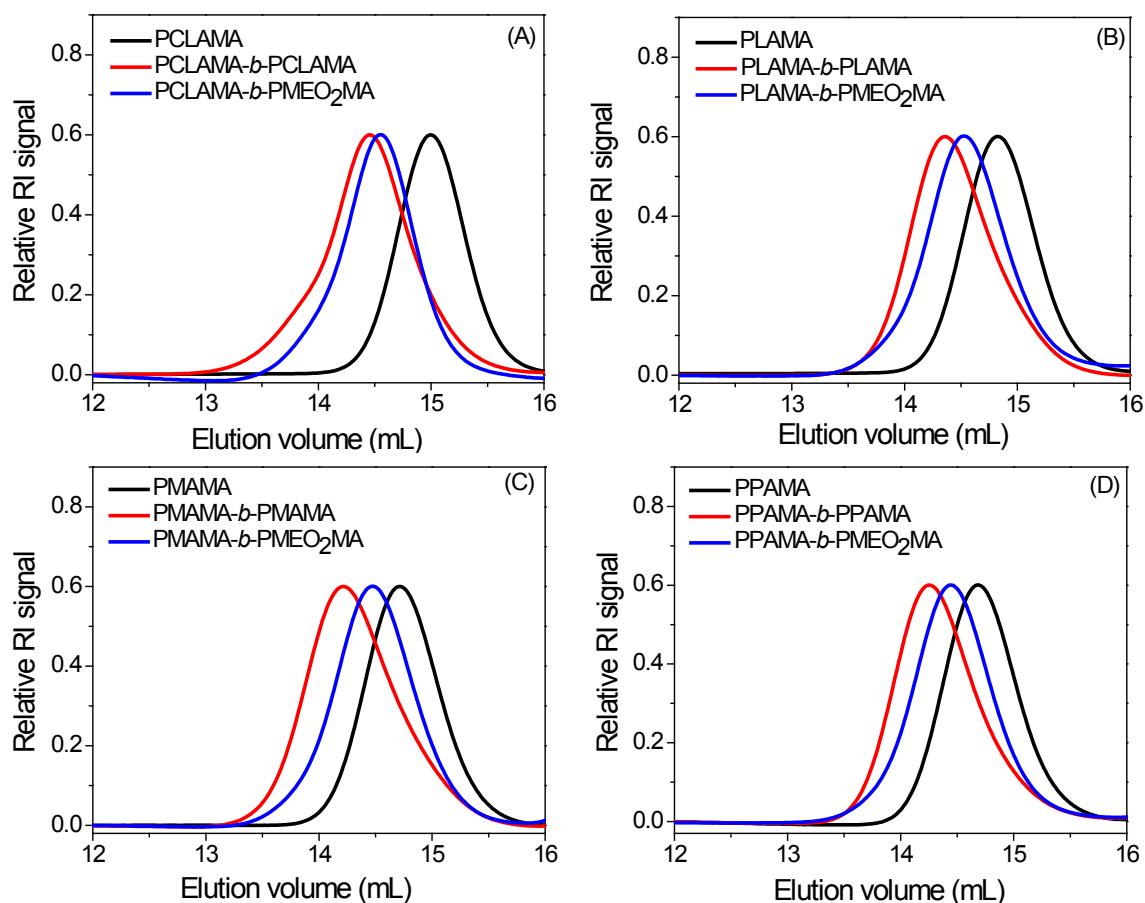


Fig. S13 GPC RI traces of the (A) PCLAMA-macroCTA, chain extended PCLAMA-*b*-PCLAMA and block copolymer PCLAMA-*b*-PMEO₂MA; (B) PLAMA-macroCTA, chain extended PLAMA-*b*-PLAMA and block copolymer PLAMA-*b*-PMEO₂MA; (C) PMAMA-macroCTA, chain extended PMAMA-*b*-PMAMA and block copolymer PMAMA-*b*-PMEO₂MA; and (D) PPAMA-macroCTA, chain extended PPAMA-*b*-PPAMA and block copolymer PPAMA-*b*-PMEO₂MA.